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Integrated Science Assessment for Oxides of Nitrogen and Sulfur – Environmental Criteria

(Second External Review Draft)

National Center for Environmental Assessment-RTP Division
Office of Research and Development
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Acronyms and Abbreviations

ACCENT	Atmospheric Composition Change: the European Network of excellence
AIRMoN	Atmospheric Integrated Research Monitoring Network
AIRS	Atmospheric Infrared Sounder (instrument)
Al	aluminum
Al^{3+}	aluminum ion
Al_i	inorganic aluminum
Al^{n+}	aluminum ion
Al_o	organic aluminum
$Al(OH)_3$	aluminum hydroxide
ALSC	Adirondack Lake Survey Corporation
ALTM	Adirondack Long Term Monitoring
AMD	acid mine drainage
ANC	acid neutralizing capacity
AOD	aerosol optical depth
AQCD	Air Quality Criteria Document
AQEG	Air Quality Expert Group
AQI	Air Quality Index
AQS	Air Quality System (database)
Ar	argon
ARP	Acid Rain Program
ARS	Agricultural Research Service
As	arsenic
ASI	Acid Stress Index
asl	above sea level
ATMOS	Atmospheric Trace Molecule Spectroscopy
ATTILA	type of Lagrangian model
AUSPEX	Atmospheric Utility Signatures, Predictions, and Experiments
AVIRIS	Airborne Visible and Infrared Imaging Spectrometer
Ba	barium
BBW	Bear Brook Watershed
BBWM	Bear Brook Watershed, Maine
BC	black carbon
BCS	base-cation surplus
BGC	BioGeoChemical (model)
B-IBI	benthic index of biological integrity
BMPs	best management practices
BNF	bacterial nitrogen fertilization
Br	bromine
Br^-	bromine ion
Br_2	molecular bromine
BrCl	bromine chloride

BrO	bromine oxide
BUV	Backscatter Ultraviolet Spectrometer
BUVD	Beneficial Use Values Database
C	carbon; concentration
^{12}C	carbon-12, stable isotope of carbon
^{13}C	carbon-13, stable isotope of carbon
C_a	ambient air concentration
Ca	calcium
Ca^{2+}	calcium ion
CAA	Clean Air Act
CAAA	Amendments to the Clean Air Act
CAAAC	Clean Air Act Advisory Committee
$CaCl_2$	calcium chloride
$CaCO_3$	calcium carbonate
CALIPSO	Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (satellite)
$Ca(NO_3)_2$	calcium nitrate
$Ca(OH)_2$	calcium hydroxide
CAPMoN	Canadian Air and Precipitation Monitoring Network
$CaSO_4{\cdot}2H_2O$	gypsum
CASTNet	Clean Air Status and Trends Network
CB4	Carbon Bond 4 (model)
Cd	cadmium
CEC	cation exchange capacity
CENTURY	model that simulates carbon, nitrogen, phosphorus, sulfur, and water dynamics in the soil-plant system at monthly intervals over time scales of centuries and millennia
CFCs	chlorinated fluorocarbons
CG	cloud-to-ground (lightning flash)
chl *a*	chlorophyll *a*
CH_4	methane
C_2H_4	ethene
C_2H_6	ethane
C_5H_8	isoprene
CH_3CHO	acetaldehyde
$CH_3C(O)$	acetyl radical
$CH_3C(O)OO$	acetyl peroxy radical
CH_2I_2	diiodomethane
CH_2O	formaldehyde
CH_3OOH	methyl hydroperoxide
CH_3-S-CH_3	dimethylsulfide, DMS
CH_3-S-H	methyl mercaptan
$(CH_3)_2SO$	dimethyl sulfoxide, DMSO
CH_3SO_3H	methanesulfonic acid
CH_3-S-S-CH_3	dimethyl disulfide, DMDS
C_i	interstitial air concentration

CL	critical load
Cl	chlorine
Cl^-	chlorine ion
Cl_2	molecular chlorine
CLaMS	type of Lagrangian model
CloudSat	NASA Earth observation satellite
$ClNO_2$	nitryl chloride
CMAQ	Community Multiscale Air Quality (modeling system)
CMSA	consolidated metropolitan statistical area
CO	carbon monoxide
CO_2	carbon dioxide
CO_3^-	carbonate
CONUS	continental United States
CPUE	catch per unit effort
CRREL	U.S. Army Cold Regions Research and Engineering Laboratory
CS	Consumer surplus
CS_2	carbon disulfide
CSS	coastal sage scrub (ecosystem)
CTM	chemical transport model
Cu	copper
CV	contingent valuation
CVM	contingent valuation method
Δ	difference; change
DayCent	model for daily biogeochemistry for forest, grassland, cropland, and savanna systems
DayCent-Chem	combination of DayCent-Chem and PHREEQC models
DC	dichotomous choice
DDRP	Direct Delayed Response Project
DDT	Damage Delay Time
DECOMP	decomposition model based on soil-plant system dynamics
DEP	Department of Environmental Protection
DIC	dissolved inorganic carbon
DIN	dissolved inorganic nitrogen
DMDS	dimethyl disulfide, CH_3-S-S-CH_3
DMS	dimethyl sulfide, CH_3-S-CH_3
DMSO	dimethylsulfoxide
DNDC	Denitrification-Decomposition (model)
DO	dissolved oxygen
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
EBB	East Bear Brook
EC	elemental carbon
EEAs	Essential Ecological Attributes
ELA	Experimental Lakes Area
ELS	Eastern Lakes Survey
EMAP	Environmental Monitoring and Assessment Program

EMEFS	Eulerian Model Evaluation Field Study
EMEP	Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe
EMF	ectomycorrhizal fungi
EOS	Earth Observation System
EPA	U.S. Environmental Protection Agency
EPT	Ephemeroptera-Plecoptera-Tricoptera (index)
ERP	Episodic Response Project
ESA	European Space Agency
EVRI	Environmental Valuation Reference Inventory
F	flux
F^-	fluorine ion
FAB	First-order Acidity Balance model
FACE	free-air CO_2 enrichment (studies)
Fe	iron
$FePO_4$	iron phosphate
FeS	iron sulfide
F-factor	fraction of the change in mineral acid anions that is neutralized by base cation release
FHM	Forest Health Monitoring
FIA	Forest Inventory and Analysis (program)
FISH	Fish in Sensitive Habitats (project)
FLEXPART	type of Lagrangian model
ForSAFE	three-component model using nitrogen, carbon cycling, and soil chemistry
FRM	Federal Reference Method
FTIR	Fourier Transform Infrared Spectroscopy
FW2	black carbon soot
F_x	flux
γN_2O_5	reaction potential coefficient for N_2O_5
GAW	Global Atmospheric Watch (program)
GCE	Goddard Cumulus Ensemble (model)
GDP	gross domestic product
GEOS	Goddard Earth Observing System
GEOS-Chem	Goddard Earth Observing System (with global chemical transport model)
GEOS-1DAS	Goddard Earth Observing System Data Assimilation System
GFED	Global Fire Emissions Database
GHG	greenhouse gas
GOES	Geostationary Operational Environmental Satellites
GOME	Global Ozone Monitoring Experiment
g_s	stomatal conductance
GtC	global ton carbon
Gton	global ton
GWP	global warming potential
H	hydrogen; hydrogen atom
^2H	hydrogen-2, deuterium, stable isotope of hydrogen

H^+	proton, hydrogen ion; relative acidity
ha	hectare
HAPs	hazardous air pollutants
HBEF	Hubbard Brook Experimental Forest
HBES	Hubbard Brook Ecosystem Study
HBN	Hydrologic Benchmark Network
HC	hydrocarbon
HCHO	formaldehyde
HCl	hydrochloric acid
Hg	mercury
HNO_2, HONO	nitrous acid
HNO_3, HOONO	nitric acid
HNO_4	pernitric acid
HO_2	hydroperoxyl radical
H_2O_2	hydrogen peroxide
HO_2NO_2	peroxynitric acid
HOBr	hypobromous acid
HOCl	hypochlorous acid
HOX	hypohalous acid
HP	hedonic pricing
HSO_3^-	bisulfate ion
HSO_4^-	sulfuric acid ion
H_2S	hydrogen sulfide
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
$h\nu$	photon with energy at wavelength ν
I	iodine
I_2	molecular iodine
IA	Integrated Assessment
IADN	Integrated Atmospheric Monitoring Deposition Network
IC	intracloud (lightning flash)
ICARTT	International Consortium for Atmospheric Research on Transport and Transformation
ILWAS	Integrated Lake-Watershed Acidification Study
IPC	International Cooperative Programme
IEc	Industrial Economics
IIASA	International Institute for Applied Systems Analysis
IMPROVE	Interagency Monitoring of Protected Visual Environments
ICARTT	International Consortium for Atmospheric Research on Transport and Transformation
INO_3	iodine nitrate
INTEX-NA	Intercontinental Chemical Transport Experiment - North America
IO	iodine oxide
IPCC	Intergovernmental Panel on Climate Change
IPCC-AR4	Intergovernmental Panel on Climate Change 4th Assessment Report
IPCC-TAR	Intergovernmental Panel on Climate Change 3rd Assessment Report

IQR	interquartile range
IR	infrared
ISA	Integrated Science Assessment
J	flux from a leaf
JPL	Jet Propulsion Laboratory
JRGCE	Jasper Ridge Global Climate Change Experiment
K	potassium
K^+	potassium ion
K_a	dissociation constant
K_b	dissociation constant
K_H	Henry's Law constant in M atm-1
KNO_3	potassium nitrate
K_w	ion product of water
LAF	Lake Acidification and Fisheries
LAR	leaf-area ratio
LB	laboratory bioassay
$LC_{0.01}$	lethal concentration at which 0.01% of exposed animals die
LD_{33}	lethal dose at which 33% of exposed animals die
LDH	lactic acid dehydrogenase
LIDAR	Light Detection and Ranging (remote sensing system)
LIF	laser-induced fluorescence
LIMS	Limb Infrared Monitor of the Stratosphere
LOD	limit of detection
LP	long-path
LRTAP	Long Range Transport of Air Pollution
LTER	Long-Term Ecological Research (program)
LTM	Long-Term Monitoring (project)
M	air molecule
MA	Millennium Ecosystem Assessment
MAGIC	Model of Acidification of Groundwater in Catchments (model)
MAHA	Mid-Atlantic Highlands Assessment of streams
MAQSIP	Multiscale Air Quality Simulation Platform (model)
MAT	moist acidic tundra
MAX-DOAS	multiple axis differential optical absorption spectroscopy
MBL	marine boundary layer
MDN	Mercury Deposition Network
MeHg	methylmercury
MEM	model ensemble mean
μeq	microequivalent
Mg	magnesium
Mg^{2+}	magnesium ion
MIMS	membrane inlet mass spectrometry
MM5	National Center for Atmospheric Research/Penn State Mesoscale Model, version 5
Mn	manganese
MOBILE6	Highway Vehicle Emission Factor Model

MODIS	Moderate Resolution Imaging Spectroradiometer
MOPITT	Measurement of Pollution in the Troposphere
MOZAIC	Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft
MOZART	Model for Ozone and Related Chemical Tracers
MPAN	peroxymethacrylic nitrate
MSA	metropolitan statistical area
Mt	million tons
N	nitrogen
N, n	number of observations
^{14}N	nitrogen-14, stable isotope of nitrogen
^{15}N	nitrogen-15, stable isotope of nitrogen
N_2	molecular nitrogen; nonreactive nitrogen
NA	not available; insufficient data
Na	sodium
Na^+	sodium ion
NAAQS	National Ambient Air Quality Standards
NaCl	sodium chloride
NADP	National Atmospheric Deposition Program
Na_2MoO_4	sodium molybdate
NAMS	National Air Monitoring Stations
NANI	Net anthropogenic nitrogen inputs
NAPAP	National Acid Precipitation Assessment Program
NASQAN	National Stream Quality Accounting Network
NARSTO	program formerly known as North American Regional Strategy for Atmospheric Ozone
NAS	National Academy of Sciences
NASA	National Aeronautics and Space Administration
Na_2SO_4	sodium sulfate
NASQAN	National Stream Quality Accounting Network
NATTS	National Air Toxics Trends (network)
NAWQA	National Water Quality Assessment (program)
NCore	National Core Monitoring Network
NEE	net ecosystem exchange
NEG/ECP	New England Governors and Eastern Canadian Premiers
NEI	National Emissions Inventory
NEON	National Ecological Observatory Network
NEP	net ecosystem productivity
NFI	net factor income
NH_3	ammonia
NH_2	amino (chemical group)
NH_4^+	ammonium ion
NH_4Cl	ammonium chloride
NH_4NO_3	ammonium nitrate
$(NH_4)_2SO_4$	ammonium sulfate
NH_X	category label for NH_3 plus NH_4^+
NH_Y	total reduced nitrogen

Ni	nickel
NILU	Norwegian Institute for Air Research
NITREX	NITRogen saturation EXperiments
nitro-PAH	nitro-polycyclic aromatic hydrocarbon
NLCD	National Land Cover Data
NMOC	nonmethane organic compound
NO	nitric oxide
NO_2	nitrogen dioxide
NO_2^-	nitrite
NO_3^-	nitrate
N_2O	nitrous oxide
N_2O_5	dinitrogen pentoxide
NOAA	U.S. National Oceanic and Atmospheric Administration
NOAA-ARL	U.S. National Oceanic and Atmospheric Administration Air Resources Laboratory
NOAEL	no-observed-adverse-effect level
NOEC	no-observed-effect concentration
NO_X	sum of NO and NO_2
NO_Y	sum of NO_X and NO_Z; odd nitrogen species; total oxidized nitrogen
NO_Z	sum of all inorganic and organic reaction products of NO_X (HONO, HNO_3, HNO_4, organic nitrates, particulate nitrate, nitro-PAHs, etc.)
NPOESS	National Polar-orbiting Operational Environmental Satellite System
NPP	net primary production
NPS	National Park Service
N_r	reactive nitrogen
NRC	National Research Council
NS	nonsignificant
NSF	National Science Foundation
NSS	National Stream Survey
nss	non-sea salt
NSTC	National Science and Technology Council
NSWS	National Surface Water Survey
NTN	National Trends Network
NuCM	nutrient cycling model
O_2	molecular oxygen
O_3	ozone
^{16}O	oxygen-16, stable isotope of oxygen
^{18}O	oxygen-18, stable isotope of oxygen
^{19}O	oxygen-19, radioactive isotope of oxygen
OC	organic carbon
OCO	Orbiting Carbon Observatory
OCS	carbonyl sulfide
$O(^1D)$	electronically excited oxygen atom
OH	hydroxyl radical
OMI	Ozone Monitoring Instrument
$O(^3P)$	ground-state oxygen atom

P	phosphorus
P, p	probability value
P_1	1st percentile
P_5	5th percentile
P_{95}	95th percentile
P_{99}	99th percentile
PAHs	polycyclic aromatic hydrocarbons
PAMS	Photochemical Assessment Monitoring Stations
PAN	peroxyacetyl nitrate
PANs	peroxyacyl nitrates
PARASOL	Polarization and Anisotropy of Reflectances for Atmospheric Sciences coupled with Observations from a Lidar (satellite)
Pb	lead
PBL	planetary boundary layer
PC	payment card
PCBs	polychlorinated biphenyl compounds
pH	relative acidity
$P(HNO_3)$	production of nitric acid
PHREEQC	model for soil and water geochemical equilibrium
PIRLA	Paleocological Investigation of Recent Lake Acidification (projects)
pK_a	dissociation constant
PM	particulate matter
$PM_{2.5}$	particulate matter with aerodynamic diameter of #2.5 µm
PM_{10}	particulate matter with aerodynamic diameter #10 µm
$PM_{10\text{-}2.5}$	particulate matter with aerodynamic diameter between 10 and 2.5 µm
PM-CAMx	Comprehensive Air Quality Model with extensions and with particulate matter chemistry
PnET	Photosynthesis and EvapoTranspiration (model)
PnET-BGC	Photosynthesis and EvapoTranspiration-BioGeoChemical (model)
PnET-CN	Photosynthesis and EvapoTranspiration model of C, water, and N balances
PnET-N-DNDC	Photosynthesis and EvapoTranspiration-Denitrification-Decomposition (model)
pNO_3^-	particulate nitrate
$P(O_3)$	production of O_3
PO_4^-, PO_4^{3-}	phosphate
POPs	persistent organic pollutants
ppb	parts per billion
PPN	peroxypropionyl nitrate
ppt	parts per trillion
PRB	policy relevant background
PRE-STORM	Preliminary Regional Experiment for STORM
PROFILE	model using soil mineralogy as input
PS	producer surplus
pSO_4^{2-}	particulate sulfate
$P(SO_4^{2-})$	production of sulfate

Q	flow rate; discharge
Q_{10}	temperature coefficient
QAPP	Quality Assurance Project Plan
R	generic organic group attached to a molecule
R^2	coefficient of determination
r^2	correlation coefficient
R_a	aerodynamic resistance
R_b	boundary layer resistance
R_c	internal resistance
RADM	Regional Acid Deposition Model
RAMS	Regional Atmospheric Modeling System
RAPS	Regional Air Pollution Study
RCOO-s	strongly acidic organic anions
RC(O)OO	organic peroxy radical
RDT	Recovery Delay Time
REMAP	Regional Environmental Monitoring and Assessment Program
RH	relative humidity
RLTM	Regional Long-Term Monitoring
RMCC	Research and Monitoring Coordinating Committee
RMSE	root mean squared error
RO_2	organic peroxyl; organic peroxy
$RONO_2$	organic nitrate
RO_2NO_2	peroxynitrate
RP	revealed preferences
RR_X	lognormal-transformed response ratio
RuBisCO	ribulose-1,5-bisphosphate carboxylase/oxygenase
S	sulfur
^{32}S	sulfur-32, stable isotope of sulfur
^{34}S	sulfur-34, stable isotope of sulfur
^{35}S	sulfur-35, radioactive isotope of sulfur
SAA	sum of mineral acid anion concentrations
SAFE	Soil Acidification in Forest Ecosystems (model)
SAMAB	Southern Appalachian Man and the Biosphere (program)
SAMI	Southern Appalachian Mountains Initiative
SAO	Smithsonian Astrophysical Observatory
SAPRAC	Statewide Air Pollution Research Center
SBC	sum of base cation concentrations
SBUV	Solar Backscatter Ultraviolet Spectrometer
SC	safe concentration
SCAQS	Southern California Air Quality Study
SCIAMACHY	Scanning Imaging Absorption Spectrometer for Atmospheric Chartography
Se	selenium; standard error
SEARCH	Southeastern Aerosol Research and Characterization Study (monitoring program)
Si	silicon

SIP	State Implementation Plan
SJAQS	San Joaquin Valley Air Quality Study
SLA	specific leaf area
SLAMS	State and Local Air Monitoring Stations
SMART	Simulation Model for Acidification's Regional Trends (model)
SMB	Simple Mass Balance (model)
SO	sulfur monoxide
SO_2	sulfur dioxide
SO_3	sulfur trioxide
SO_3^{2-}	sulfite
SO_4^{2-}	sulfate ion
S_2O	disulfur monoxide
SONEX	Subsonics Assessment Ozone and Nitrogen Oxides Experiment
SOS	Southern Oxidant Study
SOS/T	State of Science/Technology (report)
SO_X	sulfur oxides
SP	stated preferences
SPARROW	SPAtially Referenced Regressions on Watershed Attributes (model)
Sr	strontium
^{86}Sr	strontium-86, stable isotope of strontium
^{87}Sr	strontium-87, stable isotope of strontium
SRB	sulfate-reducing bacteria
SRP	soluble reactive phosphorus
SSWC	Steady State Water Chemistry (model)
STE	stratospheric-tropospheric exchange
STN	Speciation Trends Network
SUM06	seasonal sum of all hourly average concentrations ∃ 0.06 ppm
SVOC	semivolatile organic compound
SWAS	Shenandoah Watershed Study
τ	atmospheric lifetime
T	time; duration of exposure
TAF	Tracking and Analysis Framework (model)
T_{air}	air temperature
TAMM	Timber Assessment Market Model
TAR	Third Assessment Report
TC	total carbon; travel cost
TCM	travel cost method
TDLAS	Tunable Diode Laser Absorption Spectrometer
Tg	teragram
TIME	Temporally Integrated Monitoring of Ecosystems (program)
TN	total nitrogen
TOMS	Total Ozone Mapping Spectrometer
TOR	tropospheric ozone residual
TP	total phosphorus
TRACE-P	Transport and Chemical Evolution over the Pacific
TSI	timber-stand improvement

TSS	total suspended solids
T_{water}	water temperature
UMD-CTM	University of Maryland Chemical Transport Model
UNECE	United Nations Economic Commission for Europe
USDA	U.S. Department of Agriculture
USFS	U.S. Forest Service
USGS	U.S. Geological Survey
UV	ultraviolet
UV-A	ultraviolet radiation of wavelengths from 320 to 400 nm
UV-B	ultraviolet radiation of wavelengths from 280 to 320 nm
V_d	deposition rate
VOC	volatile organic compound
VSD	Very Simple Dynamic (soil acidification model)
VTSSS	Virginia Trout Stream Sensitivity Study
WARMS	Waterfowl Acidification Response Modeling System
WATERSN	Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen
WBB	West Bear Brook
WEBB	Water, Energy, and Biogeochemical Budgets
WFPS	water-filled pore space
WGE	Working Group on Effects
WLS	Western Lakes Survey
WMO	World Meteorological Organization
WMP	Watershed Manipulation Project
WSA	Wadeable Stream Assessment (survey)
wt %	percent by weight
WTA	willingness-to-accept
WTP	willingness-to-pay
XNO_3	nitrate halogen-X salt
XO	halogen-X oxide
Zn	zinc
ZnO	zinc oxide

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Oxides of Nitrogen and Sulfur

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EXECUTIVE SUMMARY

Introduction

This draft Integrated Science Assessment (ISA) is a concise synthesis and evaluation of the most policy-relevant science to help form the scientific foundation for the review of the secondary (welfare-based) national ambient air quality standards (NAAQS) for oxides of nitrogen (NO_X) and sulfur oxides (SO_X). The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on man-made materials, economic values, and personal comfort and well-being. The current secondary NAAQS for SO_X, set in 1973, is a 3-hour average of 0.5 ppm sulfur dioxide (SO_2), not to be exceeded more than once per year. The secondary NAAQS for NOX is identical to the primary standard set in 1971: an annual average of 0.053 ppm nitrogen dioxide (NO_2), not to be exceeded. The current secondary NAAQS were set to protect against direct damage to vegetation by exposure to gas-phase NO_X or SO_X.

Scope

This draft ISA is focused on ecological effects resulting from deposition of N- and S-containing compounds at current levels. Both N and S contribute to acidifying deposition and subsequent effects on ecosystems. Deposition of Nitrogen contributes to N-nutrient enrichment and eutrophication. An assessment of the complex ecological effects of atmospheric N deposition requires consideration of many different chemical forms of Nr; for this reason, the ISA includes evaluation of data on the most common reduced inorganic forms of N, ammonia (NH_3) and ammonium (NH_4^+); on oxidized inorganic forms including NO and NO2, nitrate (NO3), HNO_3, and nitrous oxide (N_2O), and organic N compounds including PAN

Other welfare effects addressed in the ISA include S-deposition effects on mercury methylation, along with recent evidence related to direct exposure to gas-phase NO_X and SO_X. The key conclusions of the draft ISA follow.

Current concentrations and deposition in the US

Ambient annual NOX and SOx concentrations have decreased significantly. NOx decreased ~35% in the period 1990–2005, to current annual average concentrations of ~15 ppb. Emissions of SOX have been significantly reduced in recent years: ambient annual SOX concentrations have decreased ~50% in the period 1990–2005 and now stand at ~ 4 ppb for both aggregate annual and 24 h average concentrations nation-wide.

Deposition is spatially heterogeneous across the U.S. In the years 2004–2006, mean S deposition in the United States was greatest east of the Mississippi River with the highest reported deposition, 21 kg/ha/yr, in the Ohio River valley where most recording stations reported three-year averages for this period of more than10 kg/ha$^/$yr. Numerous other stations in the eastern United States reported S deposition greater than 5 kg/ha/yr. Data are sparse for the central United States between the 100th meridian and the Mississippi River; but, where available, deposition values there were lower than in most of the eastern United States, ranging from 4 to over 5 kg/ha/yr. Total S deposition in the United States west of the 100th meridian is lower than in the East or upper Mid-west, owing to lower densities of high-emitting sources there. In the years 2004—2006, all recording stations in the West reported less than 2 kg/ha/yr and many reported less than 1 kg/ha/yr. S was primarily deposited in the form of wet sulfate (SO_4^{2-}), followed by a smaller proportion of dry SO_2, and a much smaller proportion of dry SO_4^{2-}.

Expanding urbanization, agricultural intensity, and industrial production during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the United States and comprises ~50 to 75% of total N atmospheric deposition. This wet and dry atmospheric N deposition is spatially heterogeneous owing to precipitation patterns and land use.

For 2004–2006, routine national monitoring networks reported the highest mean N deposition totals in the Ohio River valley, specifically in the states of Indiana and Ohio, with values greater than 9 kg/ha/yr. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central United States the highest N deposition totals were on the order of 6 to 7 kg/ha/yr. Measured concentrations and inferred deposition totals were dominated by wet NO_3^- and NH_4^+ species, followed by dry HNO_3, dry NH_4^+, and dry NO_3^-. Significantly, NH_3 is not yet measured routinely in any national networks; however, smaller-scale intensive monitoring and numerical modeling both indicate that it may account for more than 80% of the dry reduced N deposition total. Although deposition in most areas of the United States occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

The thin coverage of monitoring sites in many areas, especially in the rural West, means that no data exist on deposition totals in a significant number of potentially sensitive places. Numerical modeling experiments can help fill-in these data gaps and suggest that local and even regional areas of high concentration and deposition exist where no data exist. Model-predicted values for N deposition in some regions of the Adirondacks in New York are greater than 20 kg/ha/yr; other model estimates as high as 32 kg/ha/yr have been made for a region of southern California, with more than half of that total predicted to come from NO and NO2. Because adverse biological outcomes have been measured in these areas of model-predicted locally high N deposition, the ISA concludes that the national-scale networks routinely monitoring N deposition are inadequate to characterize either the full range of reduced and oxidized forms of N deposition or the significant regional heterogeneity across the landscape of the U.S.

Ecological effects of acidification

The available evidence is *sufficient to infer a causal relationship* between acidifying deposition at current levels and effects on the following aspects of ecosystem structure and function:
(1) biogeochemistry related to terrestrial and aquatic ecosystems;
(2) biota in terrestrial and aquatic ecosystems.

Both N and S can acidify ecosystems. Sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is predominantly governed by surficial geology. Other factors contributing to the sensitivity of soils and surface waters to acidifying deposition include topography, vegetation, soil chemistry, land use, and hydrologic flowpath. Soil acidification is a natural process, but is often accelerated by acidifying deposition, which can decrease concentrations of exchangeable base cations in soils. Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum toxicity and decreased ability of plant roots to take up base cations. Forests in the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians are among the areas most sensitive to terrestrial acidification effects from acidifying deposition.

In aquatic systems, consistent and coherent evidence from multiple studies of many species shows that acidification can cause the loss of acid-sensitive species, and that more species are lost with greater acidification. These effects are linked to changes in surface water chemistry, including concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and Ca, surface water pH, sum of base cations, acid neutralizing capacity (ANC), and base cation surplus. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in zooplankton, macroinvertebrates, and fish species richness. Although both N and S deposition can cause terrestrial and aquatic acidification, S deposition is the primary cause of chronic acidification. Following decreases in S deposition in the 1980’s and 1990’s, one quarter to one third of the chronically acidic lakes and streams in the U.S. were no longer acidic in the year 2000. A number of lakes and streams, however, remain acidic even though wet SO_4^{2-} deposition has fallen by 19 to more than 30 % since 1989. N deposition, which has also fallen in the years since 1990 in most places in the U.S. with routine monitoring, is the primary cause of episodic acidification which, despite its short duration, has been shown to cause long-term biological effects.

Many surface waters most sensitive to acidification in the U.S. are found in the Northeast and mountainous West. In the West, acidic surface waters are rare and the extent of chronic surface water acidification that has occurred to date has been limited. However, episodic acidification does occur. In both the mountainous West and the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. The ISA highlights evidence from two well-studied areas to provide more detail on how acidification affects ecosystems: The Adirondacks (NY) and Shenandoah National Park (VA). In the Adirondacks, the current rates of N and S deposition exceed the amount that would allow recovery of the most acid sensitive lakes. In the Shenandoah, past SO_4^{2-} has accumulated in the soil and is slowly released from the soil into stream water where it causes acidification and makes parts of this region sensitive to current loading. Numeric models specifically calibrated to these locations and conditions suggest that the number of acidic streams will increase under the current deposition rates.

Ecological effects of N deposition

The available evidence is sufficient to infer a *causal relationship* between N deposition at current levels and the alteration of the following aspects of ecosystem structure and function:
(1) biogeochemical cycling of N and C in terrestrial, wetland, freshwater aquatic, and coastal marine ecosystems;
(2) biogenic flux of methane (CH_4), and N_2O in terrestrial and wetland ecosystems;
(3) species richness, species composition, and biodiversity in terrestrial, wetland, freshwater aquatic and coastal marine ecosystems

The contribution of N deposition to total N load varies among ecosystems. Atmospheric N deposition is the main source of new N to most terrestrial ecosystems, high elevation lakes and low-order streams. Atmospheric N deposition contributes to the total N load of some wetland and aquatic ecosystems that receive N through multiple pathways (i.e. agricultural land runoff and waste water effluent).

In terrestrial ecosystems, there are multiple chemical indicators of N deposition effects on biogeochemical cycling. NO_3^- leaching is one of the best documented and indicates that an ecosystem is receiving more N that it uses; the onset of leaching is calculated to be between 5.6 and 10 kg N/ha/yr for Eastern forests.

N deposition often increases primary productivity. This does not necessarily increase C sequestration. C budgets are complicated by numerous factors that influence carbon exchange (e.g. climate). However alteration of primary productivity can alter competitive interactions among plant species. The increase in growth is greater for some species than others, leading to shifts in population dynamics, species composition, community structure and, in extreme instances, ecosystem type.

Lichen are the most sensitive terrestrial taxa to N deposition, with documented adverse effects occurring at 3 kg N/ha/yr (Pacific NW and S. California), 5 kg N/ha/yr correlates to the onset of declining biodiversity within grasslands (Minnesota and the E.U.), and at 10 kg N/ha/yr causes community composition of Alpine ecosystems and forest encroachment into temperate grasslands.

N deposition alters the biogenic sources and sinks of CH_4 and N_2O in terrestrial and wetland ecosystems resulting in more GHG flux to the atmosphere. Non-flooded upland soil uptakes about 6% of atmospheric CH_4 and is the largest biological sink. N addition significantly reduced CH_4 uptake in coniferous and deciduous forests, with a reduction of 28% and 45%, respectively. In wetlands, N addition increases CH_4 production, but has no significant effect on CH_4 uptake. Terrestrial soil is the largest source of N_2O, accounting for 60% of global emissions. Nr deposition increases the biogenic emission of N_2O in coniferous forest, deciduous forests, grasslands and wetlands.

In aquatic ecosystems, N deposition alters primary productivity, leading to changes in community composition and eutrophication. In the western U.S., deposition loads of approximately 1.5-2 kg N/ha/yr are reported to alter species composition in the diatom communities in some freshwater lakes, an indicator of impaired water quality.

In estuarine ecosystems, additional N from atmospheric and non-atmospheric sources contributes to increased phytoplankton and algal productivity leading to eutrophication. Estuary eutrophication is an ecological problem indicated by water quality deterioration, resulting in numerous adverse effects including hypoxic zones, species mortality, and harmful algal blooms. The contribution of atmospheric deposition to total N loads can be greater than 72% in estuaries. The Chesapeake Bay is an example of a large, well-studied and severely eutrophic estuary that receives 21-30% of its total N load from the atmosphere.

Other welfare effects

The available evidence is *sufficient to infer a causal relationship* between S deposition at current levels and increased Hg methylation in aquatic environments; this effect occurs only where other factors are present at levels within a range to allow methylation.

Hg is a highly neurotoxic contaminant, which is primarily taken up by organisms in the methylated form. Methyl-mercury (MeHg) is then concentrated in higher trophic levels, including fish eaten by humans. The production of meaningful amounts of MeHg requires the presence of SO_4^{2-} and Hg, but the amount of MeHg produced varies with oxygen content, temperature, pH, and supply of labile organic carbon. Watersheds with conditions known to be conducive to Hg methylation can be found in the northeastern United States and southeastern Canada, but studies in other regions with significant Hg accumulation in biota have not been as extensive.

The available evidence is sufficient to infer a causal relationship between exposure to SO_2, NO, NO_2, PAN, and HNO_3 and injury to vegetation.

Acute and chronic exposures to SO_2 have phytotoxic effects on vegetation which include foliar injury, decreased photosynthesis, and decreased growth. Exposures to NO_2, nitric oxide (NO), peroxyacetyl nitrate (PAN), and nitric acid (HNO_3) cause similar forms of plant foliar injury and decreased growth. In addition, current atmospheric concentrations of these gas-phase nitrogen (N) oxides may contribute to N saturation in some areas of the U.S. Overall, little new evidence exists for phytotoxic effects from direct exposures of vegetation to gas-phase sulfur (S) or N oxides at current concentrations in the US.

Conclusion

The three main effects presented in the ISA are acidification, nitrogen enrichment and mercury methylation. Acidification is driven by the deposition resulting from NOX and SOX pollution. It causes a cascade of effects that harm terrestrial and aquatic ecosystems, including slower growth and injury to forests, and localized extinction of fishes and other aquatic species. In addition to acidification, deposition resulting from NOx, along with other sources of reactive nitrogen (e.g., fertilizers, wastewater, and atmospheric ammonia deposition), causes a suite of ecological problems including biodiversity losses, disease, eutrophication, and harmful algal blooms. Particulate sulfate can interact with methanogenic bacteria to produce methylmercury, a powerful toxin that can bioaccumulate to toxic amounts in higher trophic levels (e.g. otters, and kingfishers).

Chapter 1. Introduction

This draft Integrated Science Assessment (ISA) is a concise synthesis and evaluation of the most policy-relevant science used to help form the scientific foundation for review of the secondary (welfare-based) National Ambient Air Quality Standards (NAAQS) for oxides of nitrogen (NO_X) and sulfur oxides (SO_X). The Clean Air Act definition of welfare effects includes, but is not limited to, effects on soils, water, wildlife, vegetation, visibility, weather, and climate, as well as effects on materials, economic values, and personal comfort and well-being.

The intent of the ISA, according to the Clean Air Act, is to "accurately reflect the latest scientific knowledge expected from the presence of [a] pollutant in ambient air" (U.S. Code\, 2003). It includes scientific research from atmospheric sciences, exposure and deposition, biogeochemistry, hydrology, soil science, marine science, plant physiology, animal physiology, and ecology conducted at multiple scales (e.g., population, community, ecosystem, landscape levels). Key information and judgments formerly found in the Air Quality Criteria Documents (AQCDs) for NO_X and SO_X are included; Annexes provide a more detailed discussion of the most pertinent scientific literature. Together, the ISA and Annexes serve to update and revise the last NO_X and SO_X AQCDs which were published in 1993 and 1982, respectively.

As discussed in the *Draft Integrated Plan for the Review of the Secondary NAAQS for Nitrogen Dioxide (NO_2) and Sulfur Dioxide (SO_2)* (EPA, 2007), a series of policy-relevant questions frames this review of the scientific evidence used to provide a scientific basis for evaluation of the secondary NAAQS for NO_2 (0.053 parts per million [ppm], annual average) and SO_2 (0.5 ppm, 3–h average). The framing questions considered are:

1. What are the known or anticipated welfare effects influenced by ambient NO_X and SO_X? For which effects is there sufficient information available to be useful as a basis for considering distinct secondary standards?
2. What is the nature and magnitude of ecosystem responses to NO_X and SO_X that are understood to have known or anticipated adverse effects? What is the variability associated with these responses, (including ecosystem type, climatic conditions, environmental effects, and interactions with other environmental factors and pollutants)?
3. To what extent do the current standards provide the requisite protection for the public welfare effects associated with NO_X and SO_X?
4. Which biotic species are most vulnerable to the adverse effects of NO_X and SO_X air pollution? How is adversity defined?
5. What ecosystems are most sensitive to NO_X and SO_X pollution?

6. How does NO_X and SO_X pollution impact ecosystem services?
7. What are the most appropriate spatial and temporal scales to evaluate impacts on ecosystems?
8. What is the relationship between ecological vulnerability to NO_X and SO_X pollution and variations in current meteorology or gradients in climate?

1.1. Scope

NO_X and SO_X are being considered jointly due to the joint role they play in acidification and their effects on ecosystems. The scope of this document includes:

1. Effects related to the deposition of nitrogen (N)- and sulfur (S)-containing compounds. Ecological effects from acidification and N-nutrient enrichment and eutrophication are the two types of effects studied most extensively in the ecological literature. An assessment of the complex ecological effects of N deposition requires consideration of multiple forms of N; thus, this assessment includes evaluation of data on inorganic reduced forms of N (e.g., ammonia (NH_3) and ammonium ion [NH_4^+]), inorganic oxidized forms (e.g., NO_X, nitric acid [HNO_3], nitrous oxide [N_2O], nitrate (NO_3), and organic N compounds (e.g., urea, amines, proteins, nucleic acids). In addition to acidification and N-nutrient enrichment, other welfare effects related to deposition of N- and S-containing compounds are discussed, such as SO_X interactions with mercury (Hg) methylation.
2. Evidence related to direct ecological effects of gas-phase NO_X and SO_X. The direct effects of gas-phase SO_X on vegetation formed a primary basis for the initial establishment of the secondary NAAQS for SO_2. The contribution of gas-phase NO_X as greenhouse gas (GHG), particularly N_2O, is considered, chiefly in the response of soils to reactive nitrogen (N_r) enrichment.

NO_X and SO_X alter numerous linked biogeochemical cycles. A simplified diagram of the combined NO_X and SO_X cycle is presented in Figure 1-1. Figures with these elements presented in more detail are found throughout the ISA. These figures include atmospheric cycling, interactions between the N cycle and carbon (C), the N cycle and phosphorous (P), and the S cycle and Hg.

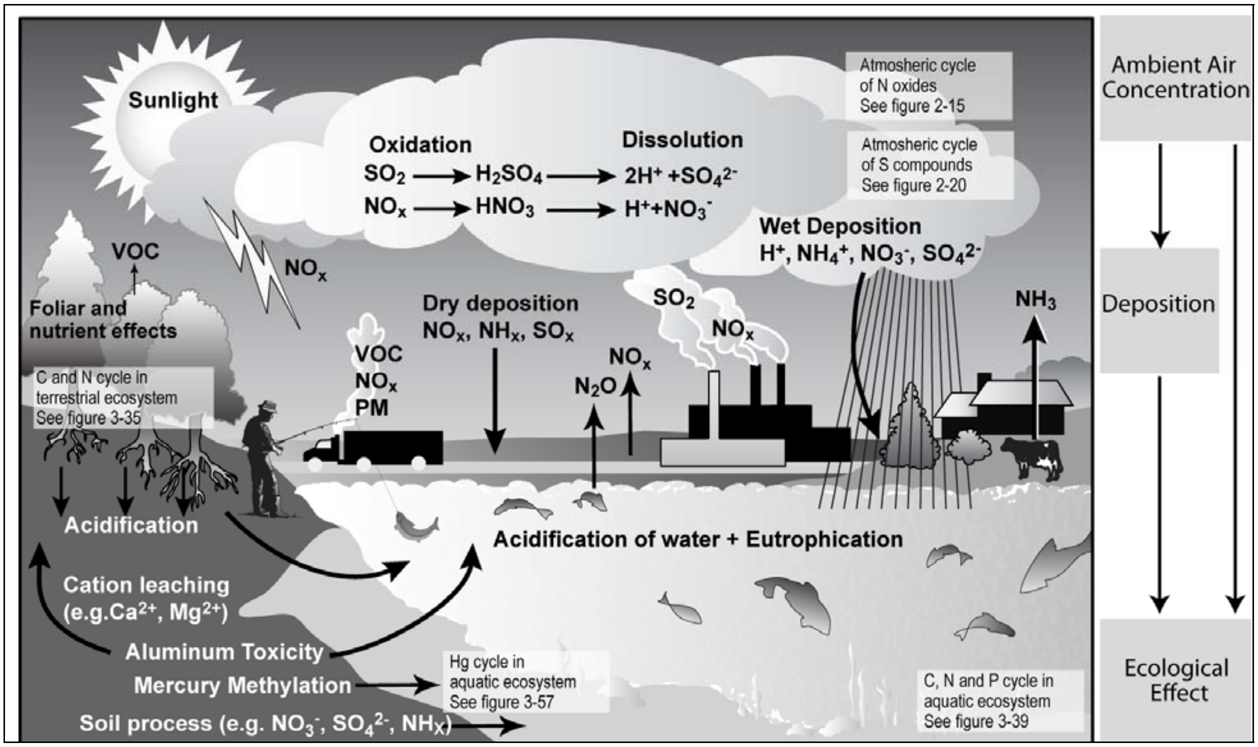

Figure 1-1. Biogeochemical cycles of NO_X and SO_X.

Recent data on direct welfare effects of particulate-phase NO_X and SO_X in the ambient air — primarily visibility impairment and positive and negative climate interactions — will be evaluated in the particulate matter (PM) NAAQS review, currently underway. (For more information, see http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_index.html.)

1.2. History of the NO_X Review

In 1971, EPA promulgated identical primary and secondary NAAQS for NO_2: 0.053 ppm as an annual average (36 FR 8186). The scientific and technical bases for these NAAQS are provided in the AQCD for NO_X (EPA, 1971).

In 1984, EPA proposed to retain these standards (49 FR 6866), and after the public commentary period, finalized that decision in 1985 (50 FR 25532); the scientific bases for this review was provided by the 1982 AQCD for NO_X (EPA, 1982).

In 1991, EPA released an updated draft AQCD for the Clean Air Scientific Advisory Committee (CASAC) and public review and comment (56 FR 59285). CASAC reviewed the document and concluded it "provides a scientifically balanced and defensible summary of current knowledge of the effects of this pollutant and provides an adequate basis for EPA to make a decision as to the appropriate

NAAQS for NO_2" (Wolff, 1993). The EPA also prepared a draft Staff Paper that summarized and integrated the key studies and scientific evidence contained in the revised AQCD and identified the critical elements to be considered in the review of the NO_2 NAAQS. In September 1995, EPA finalized the Staff Paper, *Review of the National Ambient Air Quality Standards for Nitrogen Dioxide: Assessment of Scientific and Technical Information*, (EPA, 1995). The Administrator made a final determination that revisions to the primary and secondary NAAQS for NO_2 were appropriate at that time (61 FR 52852, October 8, 1996). The level for both the existing primary and secondary NAAQS for NO_2 remains 0.053 ppm (equivalent to 100 micrograms per cubic meter of air [$\mu g/m^3$]) in annual arithmetic average, calculated as the arithmetic mean of the 1–h NO_2 concentrations.

1.3. History of the SO_X Review

Based on the 1970 SO_X AQCD (U.S. Department of Health, 1970), EPA promulgated primary and secondary NAAQS for SO_2, under section 109 of the Clean Air Act on April 30, 1971 (36 FR 8186). The secondary standard had been set at 0.02 ppm in an annual arithmetic mean and a 3–h average of 0.5 ppm, not to be exceeded more than once per year. These standards were established solely on the basis of vegetation effects evidence. In 1973, revisions made to Chapter 5 "Effects of Sulfur Oxide in the Atmosphere on Vegetation" of the SO_X AQCD (EPA, 1973), indicated that it could not properly be concluded that the reported vegetation injury resulted from the average SO_2 exposure over the growing season, rather than from short-term peak concentrations. EPA, therefore, proposed (38 FR 11355) and then finalized a revocation of the annual mean secondary standard (38 FR 25678).

In 1979, EPA announced that it was revising the SO_X AQCD concurrently with the PM review, and would produce a combined PM-SO_X AQCD. Following its review of a draft revised criteria document in August 1980, CASAC concluded that acidic deposition was a topic of extreme scientific complexity because of the difficulty in establishing firm quantitative relationships among (a) emissions of relevant pollutants (e.g., SO_2 and NO_X), (b) formation of acidic wet and dry deposition products, and (c) effects on terrestrial and aquatic ecosystems. CASAC also noted that acidic deposition involves, at a minimum, several different criteria pollutants (i.e., SO_X, NO_X, and the fine particulate fraction of suspended particles). The Committee felt that any document on this subject should address both wet and dry deposition, since dry deposition was believed to account for at least half of the total acid deposition problem.

For these reasons, CASAC recommended that a separate, comprehensive document on acidic deposition be prepared prior to any regulatory consideration for the control of acidic deposition. CASAC also suggested that a discussion of acidic deposition be included in the AQCDs for both NO_X and PM-SO_X. Following CASAC closure on the criteria document for SO_2 in 1981, EPA's Office of Air Quality

Planning and Standards (OAQPS) published a Staff Paper (EPA, 1982); it did not, however directly address this issue. EPA followed CASAC guidance and subsequently prepared the following documents: *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Review Papers, Volumes I and II* (EPA, 1984; EPA, 1984), and *The Acidic Deposition Phenomenon and Its Effects: Critical Assessment Document* (EPA, 1984). These documents, though they were not considered criteria documents and did not undergo CASAC review, represented the most comprehensive summary of relevant scientific information completed by the EPA up until that point.

On April 26, 1988 (53 FR 14926), EPA proposed not to revise the existing primary and secondary standards. Regarding the secondary SO_2 NAAQS, the EPA Administrator concluded that (1) based upon then-current scientific understanding of the acidic deposition problem, it would be premature and unwise to prescribe any regulatory control program at that time, and (2) when the fundamental scientific uncertainties had been reduced through ongoing research efforts, EPA would draft and support an appropriate set of control measures. On May 22, 1996, EPA's final decision, that revisions of the NAAQS for SO_X were not appropriate at that time, was announced in the Federal Register (61 FR 25566).

1.4. History of the Current Review

EPA's National Center for Environmental Assessment in Research Triangle Park, NC announced the official initiation of the current periodic review of air quality criteria for NO_X on December 9, 2005 (70 FR 73236), and for SO_X on May 15, 2006 (71 FR 28023) with a call for information. A workshop addressing the separate, joint review of the secondary standards for these two pollutants was announced in the Federal Register on June 20, 2007 (72 FR 11960). The review of the secondary NAAQS for NO_2 and SO_2 is under a court-ordered schedule; it includes a deadline for completion of the final ISA of December 12, 2008. The first external review draft of the ISA was published in December, 2007 (72 FR 72719) and reviewed by CASAC at a public meeting on April 2–3, 2008. Comments received have been addressed in this second external review draft.

1.5. Development of the ISA

Publications were identified through an extensive literature search process; additional publications were identified by EPA scientists in a variety of disciplines. In addition to peer-reviewed literature, previous EPA reports and materials obtained from scouring reference lists were examined. The focus of this ISA is on literature published since the 1993 NO_X AQCD and the 1982 SO_X AQCD. Key findings and conclusions from the 1993 and 1982 reviews are discussed in conjunction with recent studies. In addition, analyses of air quality and emissions data, and studies on atmospheric chemistry, transport, and fate of these emissions were scrutinized. Further information was acquired from consultation with content and area experts, CASAC and the public.

Emphasis has been placed on studies that evaluate effects near ambient levels and studies that consider NO_X and SO_X as components of a complex mixture of air pollutants. Studies conducted in any country that contribute significantly to the knowledge base have been considered for inclusion, but emphasis has been placed on findings from studies conducted in the U.S. and Canada where differences in emissions and the air pollutant mixture are important. In assessing the relative scientific quality of studies reviewed here and to assist in interpreting their findings, the following considerations were taken into account:

1. To what extent are the aerometric data/exposure metrics of adequate quality and sufficiently representative to serve as credible exposure indicators?
2. Were the study populations well defined and adequately selected so as to allow for meaningful comparisons between study groups?
3. Were the ecological assessment endpoints reliable and policy relevant?
4. Were the statistical analyses used appropriate and properly performed and interpreted?
5. Were likely important covariates (e.g., potential confounders or effect modifiers) adequately controlled or taken into account in the study design and statistical analyses?
6. Were the reported findings consistent, biologically plausible, and coherent in terms of consistency with other known facts?

These guidelines provide benchmarks for evaluating various studies and for focusing on the highest quality studies in assessing the body of environmental effects evidence. Detailed critical analysis of all NO_X and SO_X environmental effects studies, especially in relation to the above considerations, is beyond the scope of the ISA and its Annexes. Of most relevance for evaluation of studies is whether they provide useful qualitative or quantitative information on exposure effect or exposure response relationships for the environmental effects associated with current ambient air concentrations of NO_X and SO_X or deposition levels likely to be encountered in the U.S.

1.6. Causality Framework

EPA uses a two-step approach to evaluate the scientific evidence on welfare effects of criteria pollutants, similar to the approach it uses for health effects. The steps address two general policy–relevant questions:

1. Given the total body of evidence, what, if any, are the welfare effects of NO_X and SO_X?
2. Can levels of exposure at which welfare effects of concern occur be defined?

The first step determines the weight of evidence in support of causation, and characterizes the strength of any resulting causal classification. The second step includes further evaluation of the quantitative evidence with respect to concentration-response relationships and the levels, duration, and pattern of exposures at which effects are observed.

The most widely cited aspects of causality in public health were articulated by Sir Austin Bradford Hill (1965), and have been widely used (IARC, 2006; Samet, 2008). Several adaptations of the Hill aspects have been used in aiding causality judgments in the ecological sciences (Adams, 2003; Buck, 2000; Collier, 2003; Fox, 1991; Gerritsen, 1998). Based on these adaptations, EPA uses eight aspects in judging causality (see Table 1-1). The broad national scale of this assessment differs from the site-specific scale of ecological assessment for which applications of the Hill aspects have been published. The following were developed to meet the scope of this ISA:

Table 1-1. Aspects to aid in judging causality.

CONSISTENCY of the observed association. The inference of causality is strengthened when the same association between agent and effect is observed across similar, independent studies. The reproducibility of findings constitutes one of the strongest arguments for causality. If there are discordant results among comparable investigations, possible reasons such as differences in exposure, confounding factors, and the power of the study are considered.

STRENGTH of the observed association. The finding of large, well demarcated effects increases confidence that the association is causal. However, given a truly causal agent, a small magnitude in the effect could follow from a lower level of exposure, a lower potency, or the prevalence of other agents causing similar effects. While large effects support causality, modest effects therefore do not preclude it.

SPECIFICITY of the observed association. The effect is only observed after exposure to that agent, and the agent produces only that effect. Hill (1965), and subsequent authors, consider specificity a weak aspect. At the scale of ecosystems, as in epidemiology, complexity is such that single agents causing single effects, and single effects following single causes, are extremely unlikely. The absence of specificity cannot be used to exclude causality, especially at those scales. However, if specificity can be demonstrated, as in some laboratory or other experimental studies, it does add strong support to causality.

TEMPORALITY of the observed association. Evidence of a temporal sequence between the introduction of an agent, and appearance of the effect, constitutes another argument in favor of causality.

GRADIENT. A clear exposure-response relationship (e.g., increasing effects associated with greater exposure) strongly suggests cause and effect.

PLAUSIBILITY. A credible ecological basis for the observed association adds strength to an inference of causality. A proposed mechanistic linking between an effect, and exposure to the agent, is an important source of support for causality, especially when data establishing the existence and functioning of those mechanistic links are available. A lack of biological understanding, however, is not sufficient reason to reject causality.

EXPERIMENTAL evidence. Controlled exposure to the stressors provides results that support the proposed causal relationship. The practical limits on control, as the number of potential interacting factors increases, are such that the most compelling experiments can only be conducted at the scale of a laboratory, growth chamber, or at most, mesocosm. Therefore, since a judgment of causality derived from experimental evidence often cannot be extended very far beyond the scale at which the experiment was conducted, experimental evidence is generally only one element of the information that comes to bear in determining causality at the ecosystem, regional, or greater scales.

COHERENCE. Given the scale and complexity of the environment and of ecosystems, determinations of causality are usually based on many lines of evidence, considered jointly. Evidence may be drawn from a variety of experimental approaches (e.g., greenhouse, laboratory, and field) and subdisciplines of ecology (e.g., community ecology, biogeochemistry and paleological/historical reconstructions). The coherence of the available sources is a critical aspect of assessing the strength of a causal association. The coherence of evidence from various fields, and at various scales, greatly adds to the strength of an inference of causality.

While these aspects provide a framework for assessing the evidence, they are not simple formulas or fixed rules of evidence leading to conclusions about causality (Hill, 1965). The principles in Table 1-1 cannot be used as a strict checklist, but rather to determine the weight of the evidence for inferring causality. In particular, the absence of one or more of the aspects does not automatically exclude a study from consideration (e.g., see discussion in, Department of Health and Human Services, 2004). For example, one cannot simply count the number of studies reporting statistically significant or non-significant results, and reach credible conclusions about the relative weight of the evidence and the likelihood of causality. Rather, the aspects are an important part of the assessment, whose goal is to produce an objective appraisal of the evidence, and is informed by peer and public comment and advice, including weighing of alternative views on controversial issues.

1.6.1. First Step: Determination of Causality

In this ISA, EPA assesses results of recent publications available since the previous NAAQS review. This evaluation builds upon evidence available and conclusions drawn in the previous review in order to draw conclusions on the causal relationships between relevant pollutant exposures and welfare outcomes. A five-level hierarchy is used to classify the weight of evidence for causation, as assessed by the reviewing group with input from peers, CASAC, and the public. Through integration of the evidence from all relevant lines, such as laboratory studies, ecosystem experiments, simulation models and regional observations, the weight of evidence in support of causality is expressed using one of the five descriptors (see Table 1-2).

Table 1-2. Descriptors for weight of evidence for use in causal determination.

SUFFICIENT TO INFER A CAUSAL RELATIONSHIP Evidence is sufficient to conclude that there is a causal relationship between relevant pollutant exposure and the outcome. Causality is supported when an association has been observed between the pollutant and the outcome in studies in which chance, bias, and confounding could be ruled out with reasonable confidence. Controlled exposure (laboratory or small- to medium-scale field studies) provides the strongest evidence for causality, but the scope of inference may be limited. Generally, determination is based on multiple studies conducted by multiple research groups, and evidence that is considered sufficient to infer a causal relationship is usually obtained from the joint consideration of many lines of evidence that reinforce each other.

SUFFICIENT TO INFER A LIKELY CAUSAL RELATIONSHIP Evidence is sufficient to conclude that there is a likely causal association between relevant pollutant exposures and the outcome. That is, an association has been observed between the pollutant and the outcome in studies in which chance, bias and confounding are minimized, but uncertainties remain. For example, field studies show a relationship, but suspected interacting factors cannot be controlled, and other lines of evidence are limited or inconsistent. Generally, determination is based on multiple studies in multiple research groups.

SUGGESTIVE, BUT NOT SUFFICIENT TO INFER A CAUSAL RELATIONSHIP Evidence is suggestive of an association between relevant pollutant exposures and the outcome, but chance, bias and confounding cannot be ruled out. For example, at least one high-quality study shows an association, but the results of other studies are inconsistent.

INADEQUATE TO INFER THE PRESENCE OR ABSENCE OF A CAUSAL RELATIONSHIP The available studies are of insufficient quality, consistency or statistical power to permit a conclusion regarding the presence or absence of an association between relevant pollutant exposure and the outcome.

SUGGESTIVE OF NO CAUSAL RELATIONSHIP Several adequate studies, examining relationships between relevant exposures and outcomes, are consistent in failing to show an association between exposure and the outcome at any level of exposure.

1.6.2. Second Step: Evaluation of Ecological Response

Beyond judgments regarding causality are questions relevant to characterizing exposure and risk to ecosystems (e.g., the levels and loads of pollution at which ecological effects occur). Such questions include:

1. What elements of the ecosystem (e.g., types, regions, taxonomic groups, populations, functions, etc.) appear to be affected, or are more susceptible to effects?

2. Under what exposure conditions (amount or concentration, duration and pattern) are effects seen?
3. What is the shape of the concentration-response or exposure-response relationship?

Causal and likely causal claims typically characterize how the probability of ecological effects changes in response to exposure. The ecological scale at which those quantitative considerations are valid is an overriding concern. Initially, responses are evaluated within the range of observation, but ecological data for concentration-response analyses are often not available at the national or even regional scale. They are therefore typically presented site by site. Where greenhouse or animal ecotoxicological studies are available, they may be used to aid in characterizing concentration-response relations, particularly relative to mechanisms of action, and characteristics of sensitive biota.

1.7. Organization of the ISA

This ISA includes four chapters. Chapter 1 provides background information on the purpose of the document, explains how policy-relevant scientific studies are identified and selected for inclusion in the ISA, and introduces the causality framework used in EPA's assessments. Chapter 2 presents fundamental and applied atmospheric science data to support assessing the environmental exposures and effects associated with N and S oxides. Information relevant to the review of the welfare effects of NO_X and SO_X is integrated and evaluated in Chapter 3. Findings are organized into three categories: ecological effects of acidification, ecological effects of N nutrient pollution, and other welfare effects, which address several minor welfare effects, including gas phase foliar toxicity and the role of S in Hg methylation. Finally, summary and conclusions are found in Chapter 4. The ISA is supplemented by Annexes, which provide additional details.

Chapter 2. Source to Dose

This chapter provides fundamental and applied atmospheric science data to support assessing the environmental exposures and effects associated with N and S oxides. More specifically, these data relate to N and S emissions sources and rates, atmospheric transformation and transport, total atmospheric loadings, measurement and modeling techniques, and deposition issues relevant to this review of the NAAQS. These data are prologue for the detailed descriptions of the evidence of environmental effects from N and S oxides that follow in Chapter 3, and as a source of information to help interpret those effects when integrated with these data on atmospheric concentrations and biological exposures.

2.1. Introduction

As noted in Chapter 1, the definition of "nitrogen oxides" appearing in the NAAQS enabling legislation differs from the one used by atmospheric scientists and air quality control experts. The atmospheric sciences community defines NO_X as the sum of NO and NO_2. However, in the Federal Register Notice (FRN) for the most recently published (October 8, 1996) AQCD for NO_2 (61 FR 52852,), the term "nitrogen oxides" was used to "describe the sum of NO, NO_2, and other oxides of nitrogen." This ISA uses the legal, rather than the technical definition; hence the terms "oxides of nitrogen" and "nitrogen oxides" here refer to all forms of oxidized N compounds, including NO, NO_2, and all other oxidized N-containing compounds transformed from NO and NO_2.[1] Additionally, because some of the constituent members of the NO_X family of chemical species interact with particulate-phase chemical species and change phase themselves, the chemistry, concentrations, and deposition of particulate N compounds are also considered in this assessment.

SO_X is defined here to include sulfur monoxide (SO), sulfur dioxide (SO_2)—the largest component of SO_X and the EPA Criteria Air Pollutant—sulfur trioxide (SO_3), and disulfur monoxide (S_2O). Of these, only SO_2 is present in the lower troposphere at concentrations relevant for environmental considerations. Moreover, some gas-phase sulfur oxides interact with particles and change phase themselves, just as do some constituent members of the N family of gas-phase chemical species; hence, particulate-phase S compounds are also assessed here.

NH_3 is included in this ISA both because its oxidation can be a minor source of NO_X and because it is the precursor for ammonium ion (NH_4^+), which plays a key role in neutralizing acidity in ambient

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[1] This follows usage in the Clean Air Act, Section 108(c): "Such criteria [for oxides of nitrogen] shall include a discussion of nitric and nitrous acids, nitrites, nitrates, nitrosamines, and other carcinogenic and potentially carcinogenic derivatives of oxides of nitrogen." The category label used by the air pollution research and control community for the sum of all oxidized N compounds, including those listed in Section 108(c), is NO_Y.

particles produced from NO_2 and SO_2 and in cloud, fog, and rain water. (NH_3 and NH_4^+ are conventionally grouped together under the category label NH_X.) Excess NH_3 is also an actor in nitrification of aqueous and terrestrial ecosystems, participating alone and together with NO_X in the N cascade (Galloway, 2003). Additionally, NH_3 is involved in the ternary nucleation of new particles and reacts with gas-phase HNO_3 to form ammonium nitrate (NH_4NO_3), a major component of N deposition in many areas of the contiguous U.S. (CONUS).

2.2. Sources and Emissions of Troposphere NO_X

Troposphere NO_X emissions sources can be anthropogenic, resulting from human activity, or biogenic, resulting from the activity of non-human organisms, though sometimes with the addition of human activities, as with production from livestock or agriculture. However, anthropogenic sources contribute substantially more mass than biogenic ones. The anthropogenic and biogenic sources of NO_X are described in detail and their emissions totals are provided just below.

2.2.1. Major Anthropogenic Sources

Anthropogenic NO_X emissions are dominated by fossil fuel combustion sources which release NO_X predominantly in the form of NO with variable amounts of NO_2. In 2002, anthropogenic NO_X emissions in the U.S. totaled 23.19 Tg/year. Table 2-1 lists fractions and totals from anthropogenic NO_X sources collected for the 2002 National Emissions Inventory (NEI) (EPA, 2006).

Table 2-1. Emissions of NO_X, NH_3, and SO_2 in the U.S. by source and category, 2002.

2002 Emissions (Tg/yr)	NO_X[1]	NH_3[2]	SO_2
Total All Sources	**23.19**	**4.08**	**16.87**
Fuel Combustion Total	**9.11**	**0.02**	**14.47**
Fuel Combustion Electrical Utilities	5.16	< 0.01	11.31
Coal	4.50	< 0.01	10.70
Bituminous	2.90		8.04
Subbituminous	1.42		2.14
Anthracite & Lignite	0.18		0.51
Other	< 0.01		
Oil	0.14	< 0.01	0.38
Residual	0.13		0.36
Distillate	0.01		0.01
Gas	0.30	< 0.01	0.01
Natural	0.29		
Process	0.01		
Other	0.05	< 0.01	0.21
Internal Combustion	0.17	< 0.01	0.01
Fuel Combustion Industrial	3.15	< 0.01	2.53
Coal	0.49	< 0.01	1.26
Bituminous	0.25		0.70
Subbituminous	0.07		0.10
Anthracite & Lignite	0.04		0.13
Other	0.13		0.33
Oil	0.19	< 0.01	0.59
Residual	0.09		0.40
Distillate	0.09		0.16
Other	0.01		0.02
Gas	1.16	< 0.01	0.52
Natural	0.92		
Process	0.24		
Other	< 0.01		
Other	0.16	< 0.01	0.15
Wood/Bark Waste	0.11		
Liquid Waste	0.01		
Other	0.04		
Internal Combustion	1.15	< 0.01	0.01
Fuel Combustion Other	0.80	< 0.01	0.63
Commercial/Institutional Coal	0.04	< 0.01	0.16
Commercial/Institutional Oil	0.08	< 0.01	0.28
Commercial/Institutional Gas	0.25	< 0.01	0.02

2002 Emissions (Tg/yr)	NO_X[1]	NH_3[2]	SO_2
Misc. Fuel Combustion (Exc. Residential)	0.03	< 0.01	0.01
Residential Wood	0.03		< 0.01
Residential Other	0.36		0.16
Distillate Oil	0.06		0.15
Bituminous/Subbituminous	0.26		< 0.01
Other	0.04		< 0.01
Industrial Process Total	**1.10**	**0.21**	**1.54**
Chemical & Allied Product Mfg	0.12	0.02	0.36
Organic Chemical Mfg	0.02	< 0.01	0.01
Inorganic Chemical Mfg	0.01	< 0.01	0.18
Sulfur Compounds			0.17
Other			0.02
Polymer & Resin Mfg	< 0.01	< 0.01	< 0.01
Agricultural Chemical Mfg	0.05	0.02	0.05
Ammonium Nitrate/Urea Mfg.		< 0.01	
Other		0.02	
Paint, Varnish, Lacquer, Enamel Mfg	0.00		0.00
Pharmaceutical Mfg	0.00		0.00
Other Chemical Mfg	0.03	< 0.01	0.12
Metals Processing	0.09	< 0.01	0.30
Non-Ferrous Metals Processing	0.01	< 0.01	0.17
Copper			0.04
Lead			0.07
Zinc			0.01
Other			< 0.01
Ferrous Metals Processing	0.07	< 0.01	0.11
Metals Processing	0.01	< 0.01	0.02
Petroleum & Related Industries	0.16	< 0.01	.38
Oil & Gas Production	0.07	< 0.01	0.11
Natural Gas			0.11
Other			0.01
Petroleum Refineries & Related Industries	0.05	< 0.01	0.26
Fluid Catalytic Cracking Units		< 0.01	0.16
Other		< 0.01	0.07
Asphalt Manufacturing	0.04		0.01
Other Industrial Processes	0.54	0.05	0.46
Agriculture, Food, & Kindred Products	0.01	< 0.01	0.01
Textiles, Leather, & Apparel Products	< 0.01	< 0.01	< 0.01
Wood, Pulp & Paper, & Publishing Products	0.09	< 0.01	0.10
Rubber & Miscellaneous Plastic Products	< 0.01	< 0.01	< 0.01
Mineral Products	0.42	< 0.01	0.33
Cement Mfg	0.24		0.19
Glass Mfg	0.01		
Other	0.10		0.09
Machinery Products	< 0.01	< 0.01	< 0.01
Electronic Equipment	< 0.01	< 0.01	< 0.01
Transportation Equipment	< 0.01		< 0.01
Miscellaneous Industrial Processes	0.01	0.05	0.02
Solvent Utilization	0.01	< 0.01	< 0.01
Degreasing	< 0.01	< 0.01	< 0.01
Graphic Arts	< 0.01	< 0.01	< 0.01
Dry Cleaning	< 0.01	< 0.01	< 0.01
Surface Coating	< 0.01	< 0.01	< 0.01
Other Industrial	< 0.01	< 0.01	< 0.01
Nonindustrial	< 0.01		
Solvent Utilization Nec	< 0.01		
Storage & Transport	< 0.01	< 0.01	0.01
Bulk Terminals & Plants	< 0.01	< 0.01	< 0.01
Petroleum & Petroleum Product Storage	< 0.01	< 0.01	< 0.01
Petroleum & Petroleum Product Transport	< 0.01	< 0.01	< 0.01
Service Stations: Stage II	< 0.01		< 0.01
Organic Chemical Storage	< 0.01	< 0.01	< 0.01
Organic Chemical Transport	0.01		< 0.01
Inorganic Chemical Storage	< 0.01	< 0.01	< 0.01
Inorganic Chemical Transport	< 0.01		< 0.01
Bulk Materials Storage	0.01	< 0.01	< 0.01
Waste Disposal & Recycling	0.17	0.14	0.03
Incineration	0.06	< 0.01	0.02
Industrial			
Other			< 0.01
Open Burning	0.10	< 0.01	< 0.01
Industrial			< 0.01
Land Clearing Debris			
Other			< 0.01
Public Operating Treatment Works	< 0.01	0.14	< 0.01
Industrial Waste Water	< 0.01	< 0.01	< 0.01
Treatment, Storage, And Disposal Facility	< 0.01	< 0.01	< 0.01
Landfills	< 0.01	< 0.01	< 0.01
Industrial			< 0.01
Other			< 0.01
Other	< 0.01	< 0.01	< 0.01
Transportation Total	**12.58**	**0.32**	**0.76**
Highway Vehicles	8.09	0.32	0.30
Light-Duty Gas Vehicles & Motorcycles	2.38	0.20	0.10
Light-Duty Gas Vehicles	2.36		0.10
Motorcycles	0.02		0.00
Light-Duty Gas Trucks	1.54	0.10	0.07
Light-Duty Gas Trucks 1	1.07		0.05
Light-Duty Gas Trucks 2	0.47		0.02
Heavy-Duty Gas Vehicles	0.44	< 0.01	0.01
Diesels	3.73	< 0.01	0.12
Heavy-Duty Diesel Vehicles	3.71		
Light-Duty Diesel Trucks	0.01		
Light-Duty Diesel Vehicles	0.01		
Off-Highway	4.49	< 0.01	0.46
Non-Road Gasoline	0.23	< 0.01	0.01
Recreational	0.01		
Construction	0.01		
Industrial	0.01		
Lawn & Garden	0.10		
Farm	0.01		
Light Commercial	0.04		
Logging	< 0.01		
Airport Service	< 0.01		
Railway Maintenance	< 0.01		
Recreational Marine Vessels	0.05		
Non-Road Diesel	1.76	< 0.01	0.22
Recreational	0.00		
Construction	0.84		
Industrial	0.15		
Lawn & Garden	0.05		
Farm	0.57		
Light Commercial	0.08		
Logging	0.02		
Airport Service	0.01		
Railway Maintenance	< 0.01		
Recreational Marine Vessels	0.03		
Aircraft	0.09		0.01
Marine Vessels	1.11		0.18
Diesel	1.11		
Residual Oil			
Other			
Railroads	0.98		0.05
Other	0.32	< 0.01	0.00
Liquefied Petroleum Gas	0.29		
Compressed Natural Gas	0.04		
Miscellaneous	0.39	3.53	0.10
Agriculture & Forestry	< 0.01	3.45	< 0.01
Agricultural Crops		< 0.01	
Agricultural Livestock		2.66	
Other Combustion		0.08	0.10
Health Services			
Cooling Towers			
Fugitive Dust			
Other			
Natural Sources	3.10	0.03	

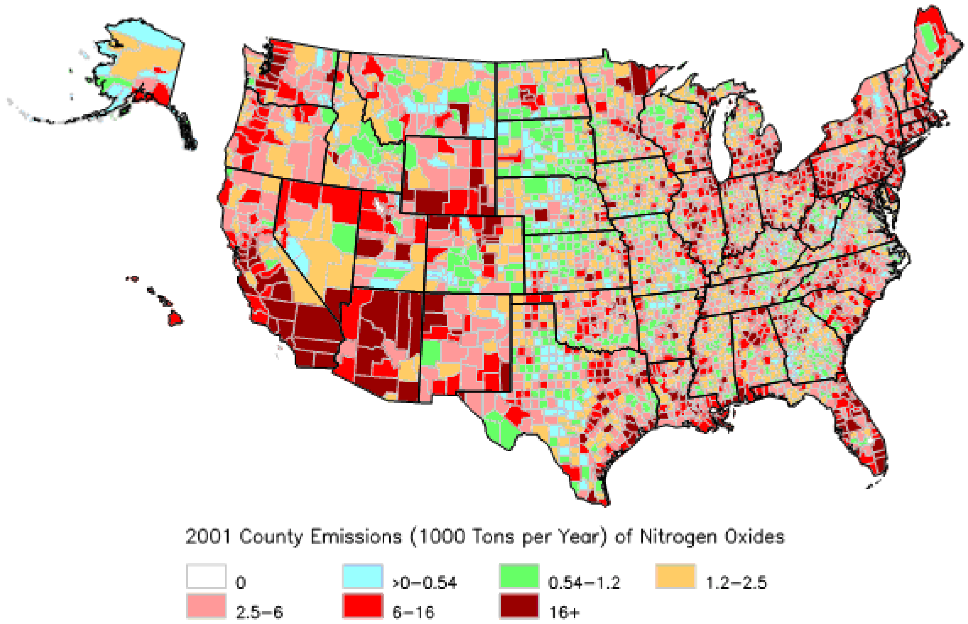
[1] Emissions are expressed in terms of NO_2.

[2] Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides

Source: (EPA, 2006)

Of this total, emissions from all types of transportation accounted for ~56% of NO_X, or 12.58 Tg, with on-road highway vehicles representing the major mobile source component, 8.09 Tg. Roughly one-half of these on-road emissions have diesel engine sources and one-half have gasoline engine sources. (Sawyer et al. (2000) reviewed the in detail factors associated with NO_X emissions by mobile sources.) The next largest source category, electric-generating utilities (EGUs), accounted for ~22%, or 5.16 Tg of total NO_X in 2002. Stationary engines, non-road vehicles, and industrial facilities also emit NO_X, but because they are fewer in number or burn less fuel, their mass contributions to total NO_X are less than transportation and EGUs.

The values in Table 2-1 are U.S. national averages; thus, they may not reflect differences in the relative contributions of NO_X sources to ambient mass loadings at any particular location; hence, these values are not likely to be useful predictors of any particular localized exposures to NO_X. As a partial refinement of scale, county-level NO_X emissions are depicted in Figure 2-1[1]. A further refinement appears in Figure 2-2, where the same 2001 NO_X emissions data are plotted as area-normalized intensities: tons per square mile. This normalized emissions intensity base is also used to show the separate contributions from EGUs and on-road mobile sources in Figure 2-3 and Figure 2-4, respectively.



Source: U.S. EPA (2006)

Figure 2-1. 2001 county-level total U.S. NO and NO_2 emissions.

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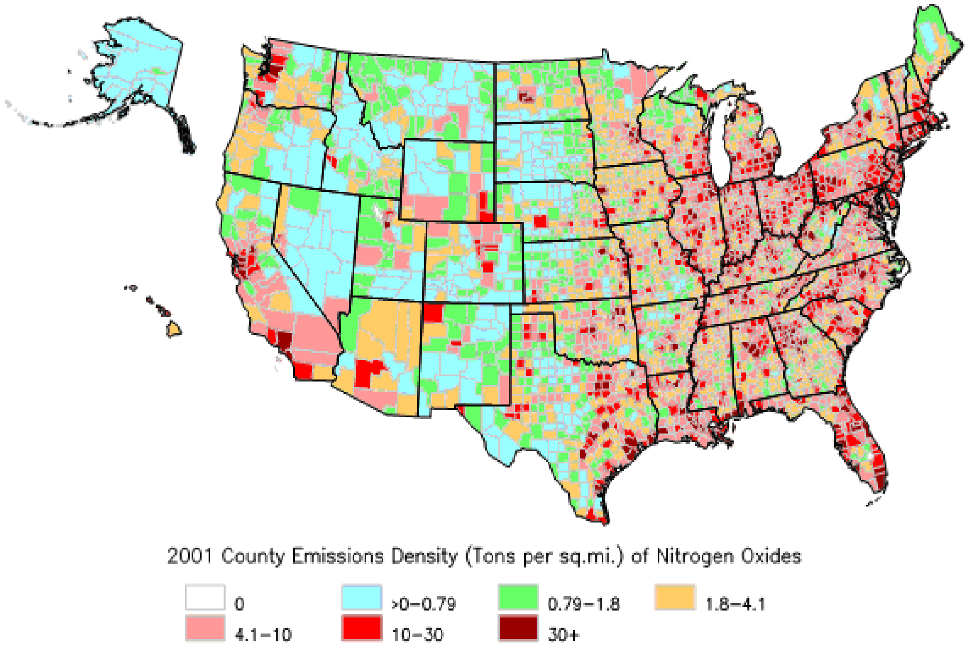
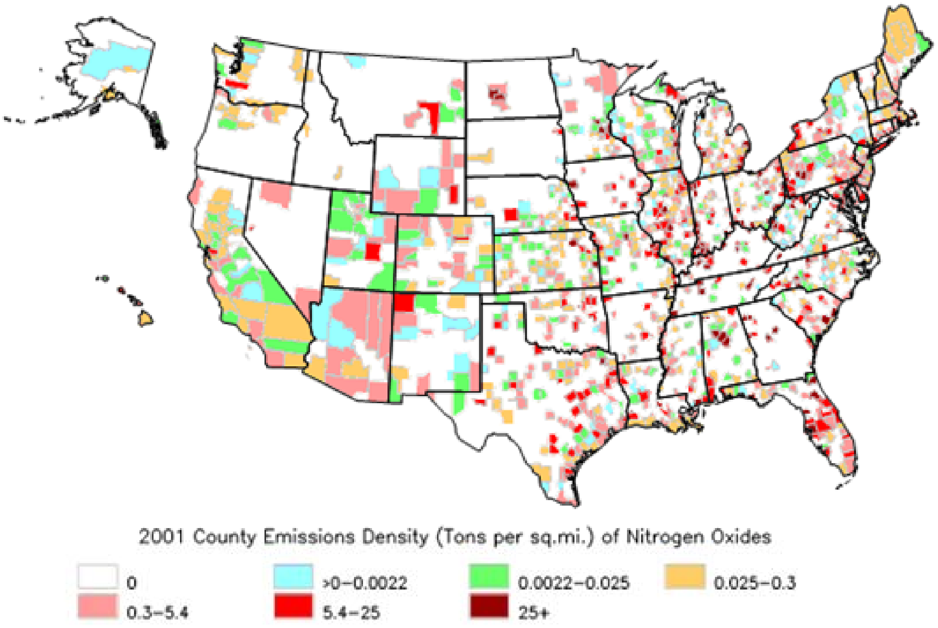
[1] The maps in Figures 2-1 through 2-9 and 2-13 through 2-15 all use this scale for their range values: white, 0 or no reported value; cyan, from the smallest non-zero to the 10th percentile value; green, from above the 10th to the 25th percentile; gold, from above the 25th to the 50th percentile; rose, from above the 50th to the 75th percentile; red, from above the 75th to the 90th percentile; brown, from above the 90th percentile to the highest reported value.



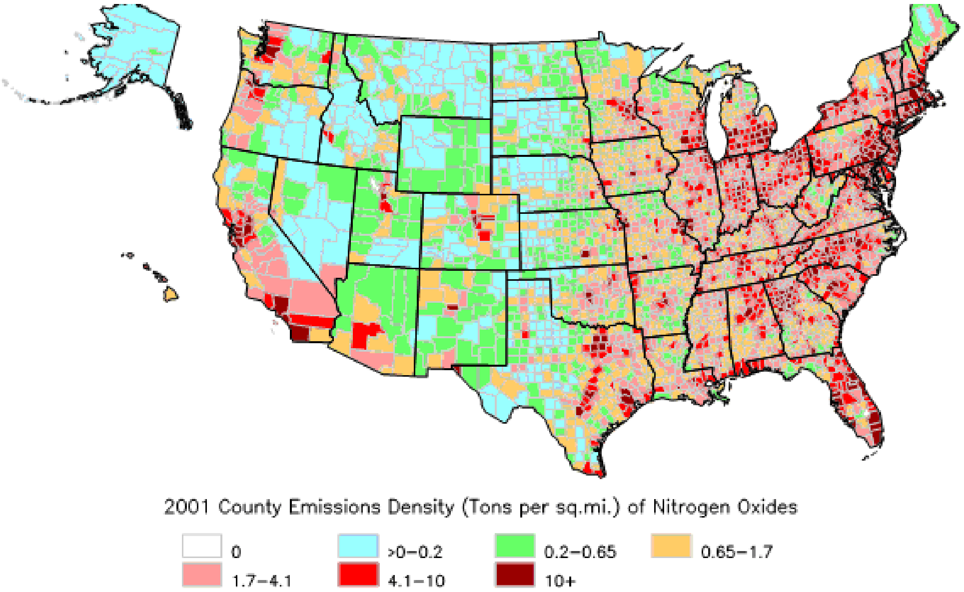
Source: U.S. EPA (2006)

Figure 2-2. 2001 county-level total U.S. NO and NO$_2$ emissions densities (tons per square mile).



Source: U.S. EPA (2006)

Figure 2-3. 2001 county-level total U.S. NO and NO$_2$ emissions densities (tons per square mile) from EGUs.



Source: U.S. EPA (2006)

Figure 2-4. 2001 county-level total U.S. NO and NO_2 emissions densities (tons per square mile) from on-road mobile sources.

Emissions of NO_X from combustion are derived from both fuel N and atmospheric N. Combustion-zone temperatures > ~1300 K are required to fix atmospheric N_2 by the reaction

$$N_2 + O_2 \rightarrow 2NO$$

Reaction 1

Below this temperature NO can be formed from fuel N by the reaction

$$C_aH_bO_cN_d + O_2 \rightarrow xCO_2 + yH_2O + zNO$$

Reaction 2

Both Reaction 1 and Reaction 2 have temperature dependencies and vary with concentrations of hydroxyl radical (OH), hydroperoxy radical (HO_2), and O_2.

The N content in fossil fuels and its specific chemical form vary strongly with source type, fuel, engine emissions controls, and running conditions. N content in fuel stocks ranges from 0.05% by weight (wt %) in light distillates such as diesel fuel, to 1.5 wt % in heavy fuel oils, and from 0.5 to 2.0 wt % in coal, as surveyed by the United Kingdom Air Quality Expert Group (2004).

On-road mobile source emissions constitute the largest type of emissions from all transportation sources. Significant variability attaches to these emissions. For example, the ratio of NO_2 to total NO_X in exhaust gases in primary emissions ranges from 1 to 3% from gasoline engines tested on dynamometers

(Heeb, 2008; Hilliard, 1979). On the other hand, some European studies have reported NO_2 to NO_X ratios ≥ 15% from gasoline vehicles based on integrated measurements from Tedlar bags (Lenner, 1987; Soltic, 2003). However, subsequent studies suggesting that NO-to-NO_2 conversion will occur within a bag sample of diluted exhaust if not properly handled have led groups performing these measurement to revise their measurement techniques to avoid use of Tedlar bag samples (Alvarez, 2008). As a result, dynamometer-based measurements generally indicate that in the absence of post-tailpipe transformation, NO_2 comprises, at most, only a few percent of the total NO_X in current-generation gasoline engine exhaust.

The emissions ratio ranges between 5 and 12% from heavy-duty diesel truck engines, although some emission control devices used for diesel engines in Europe increase the fraction of exhaust NO_X emitted as NO_2 to > 20% (Carslaw, 2005; Carslaw, 2005; Carslaw, 2007; Kessler, 2006). In the U.S., on-road experiments with diesel engines propelling heavy buses in congested urban areas like New York City have shown that engines equipped with emissions control devices similar to those in the European studies increased the NO_2 to NO_X ratio from ~10% before addition of the new controls to ~30% after controls were added (Shorter, 2005). In a second type of experiment in a different setting, Kittelson et al. (Kittelson, 2006) used an on-road laboratory to sample exhaust plumes of a truck equipped with the European-style emissions control device under highway cruise conditions and found the NO_2-to-NO_X ratios for this exhaust under highway cruise conditions ranged from 59 to 70%. The wide range revealed by comparing these two studies illustrates the significant differences in NO_X exhaust under different conditions of engine load and ambient temperature.

As for other combustion sources, NO_2-to-NO_X emissions ratios for compressed natural gas engines range between 5 and 10%, and between 5 and 10% from most stationary sources. The NO_2-to-NO_X ratios in emissions from turbine jet engines are as high as 35% during taxi and takeoff (U.S. Environmental Protection Agency, 1996).

In addition to NO and NO_2, mobile sources emit other forms of oxidized N including nitrous acid (HNO_2); measured ratios of HNO_2 to NO_X range from a low of 0.3% in the Caldecott Tunnel, San Francisco, CA (Kirchstetter, 1996), up to as much as 0.5 and 1.0% in studies in the United Kingdom (U.K. Air Quality Expert Group, 2004).

Marine transport represents an additional source of NO_X in the U.S., especially for coastal cities with large ports, but constitutes a larger source in Europe where it is expected to represent more than 60% of land-based NO_X sources (U.K. Air Quality Expert Group, 2004).

The anthropogenic sources of NO_X are distributed with height such that some, like on-road mobile sources, are nearer to ground level than others, like the emissions stacks from EGUs and some industrial emitters. Emissions height is an important consideration because the prevailing winds aloft are generally stronger than those at the surface. The result is that emissions from elevated sources can be distributed over a wider area than those emitted at the surface and hence can be diluted to lower mixing ratios than those emitted nearer their sources.

2.2.2. Major Biogenic Sources

2.2.2.1. Soils

Nitrification and denitrification processes in soils produce two gas-phase intermediates, NO and N_2O, which can evolve from soil microbes before reaching their reaction endpoint, N_2. N_2O is not among the nitrogen oxides important for urban and regional air quality either for human health concerns or environmental effects because its reaction potential on these spatio-temporal scales in the troposphere is insignificant. As a result, NO from soil metabolism is the prime, but not exclusive, form of atmospheric NO_X from the biosphere relevant to this ISA.

Biogenic NO_X emissions are predominately the result of incomplete bacterial denitrification and nitrification processes, as described above. Denitrification is a reduction process performed by particular groups of heterotrophic bacteria having the ability to use nitrate ion (NO_3^-) as an electron acceptor during anaerobic respiration, thereby converting NO_3^- in soils and water to gas-phase forms (Firestone, 1989). At low O_2 concentrations, these microbial communities may use NO_3^-, nitrite (NO_2^-), or N_2O as alternative electron acceptors to O_2 (Davidson, 1995).

The basic outlines of these reaction pathways are known, but uncertainty remains concerning the conditions favoring production of the various products of the NO_3 transformations. Groups of aerobic bacteria use most NH_4^+ in soils as an energy source, oxidizing it to NO_2 and then NO_3. Oxidized N products from nitrification may undergo denitrification and thus also drive production of NO_X. Some bacteria are known to be nitrifiers and denitrifiers and can change depending on environmental conditions, including high loadings of exogenous N.

Soil emissions of NO_X can be increased by agricultural practices and activities, including the use of synthetic and organic fertilizers, production of N-fixing crops, cultivation of soils with high organic content, and the application of livestock manure to croplands and pasture. All of these practices directly add exogenous N to soils, of which a portion will then be converted to NO or N_2O on the pathway to full conversion to N_2. Additionally, indirect additions of N to soils can also result in NO_X emissions from agricultural and non-agricultural systems. Indirect additions include processes by which atmospheric NO_X is deposited directly to a region or N from applied fertilizer or manure volatilizes to NH_3 and is oxidized to NO_X and then is ultimately re-deposited onto soils as NH_4NO_3, HNO_3, or NO_X (EPA, 2006).

N metabolism in soils is strongly dependent on soil substrate concentrations and physical conditions. Where N is limiting, it is efficiently retained and little gas-phase N is released; where N is in excess of demand, N emissions increase. As a consequence, soil NO emissions are highest from fertilized agricultural lands and tropical soils (Davidson, 1997; Williams, 1992). In addition, temperature, soil moisture, and O_2 concentrations control both the rates of reaction and the partitioning between NO and N_2O. In flooded soils where O_2 concentrations are low, N_2O is the dominant soil N gas; as soils dry, more O_2 diffuses in and NO emissions increase. In very dry soils, microbial activity is inhibited and emissions of both N_2O and NO decrease.

Emission rates of NO from cultivated soils depend largely on fertilization levels and soil temperature. Production of NO from agriculture results from the oxidation of NH_3 emitted both by livestock and by soils after fertilization with NH_4NO_3. Estimates of biogenic N emissions are far less certain than those of anthropogenic emissions sources. Uncertainty on the order of a factor of 3 or more is introduced by the variation within biomes to which fertilizer is applied, such as between shortgrass and tallgrass prairie for example (Davidson, 1997; Williams, 1992; Yienger, 1995). The contribution of soil emissions to the global NO_X budget is approximately 10% (Finlayson-Pitts, 2000; Van Aardenne, 2001; Seinfeld, 1998), but NO_X emissions from fertilized fields are highly variable. Soil NO emissions can be estimated from the fraction of the applied fertilizer N emitted as NO_X, for example, but the flux depends strongly on land use type and temperature. Estimates of globally averaged fractional-applied N lost as NO varies from a low of 0.3% (Skiba, 1997) up to 2.5% (Yienger, 1995).

The spatial scales of these N fluxes are also significant. Local contributions to soil NO_X can be much greater than the global average, particularly in summer, and especially where corn is grown extensively. Approximately 60% of total NO_X emitted by soils in the U.S. occurs in the U.S. central corn belt. Nitrification of fertilizer NH_3 to NO_3 in aerobic soils appears to be the dominant pathway to soil NO_X emissions, but the mass and chemical form of N applied to soils, the vegetative cover, the temperature and soil moisture characteristics, and the agricultural practices such as tillage all influence the amount of fertilizer N converted and released as NO_X. On sub-national scales these emissions can be large and highly variable. Williams et al. (1992) estimated that NO_X from soils in Illinois was ~1/4 as large as the total NO_X emissions from industrial and commercial processes in that state. In Iowa, Kansas, Minnesota, Nebraska, and South Dakota—states with smaller human populations than Illinois—soil emissions may, in fact, dominate the NO_X budget.

Emissions of NO_X from soils often peak in summer when ozone (O_3) formation is also at a maximum. The significance of agricultural emission sources of NO and NH_3 among other air pollutants was described in detail in a recent National Research Council report (NRC, 2002). That report recommended immediate implementation of best management practices to control these emissions, and called for additional research to quantify the magnitude of emissions and the effects of agriculture on air quality. The effects of such changes in management practice can be dramatic: Civerolo and Dickerson

(1998) reported that the use of no-till cultivation techniques on a fertilized cornfield in Maryland reduced NO emissions by a factor of 7.

2.2.2.2. Live Vegetation

Extensive work on N inputs from the atmosphere to forests was conducted in the 1980s as part of the Integrated Forest Study, summarized by Johnson and Lindberg (1992). As noted below and in Chapter 3, our understanding of NO_2 exchange with vegetation suggests that NO_2 should be emitted from foliage when ambient concentrations are below the compensation point of ~1 ppb. However, Lerdau et al. (2000) noted that current understanding of the global distribution of NO_X is not consistent with the large source that would be expected in remote forests if NO_2 emissions were significant when atmospheric concentrations were below the 1 ppb compensation point.

2.2.2.3. Biomass Burning

During biomass burning, N is derived mainly from fuel N and not from atmospheric N_2, since temperatures required to fix atmospheric N_2 are likely to be found only in the flaming crowns of the most intense boreal forest fires. N is present in plants mostly as amine (NH_2) groups in amino acids. During combustion, N is released in many forms, mostly unidentified and presumably as N_2, leaving very little N remaining in the fuel ash. Emissions of NO_X are estimated to be ~0.2 to 0.3% of the total biomass burned (e.g., Radke, 1991; Andreae, 1991). The most abundant NO_X species in biomass burning plumes is NO, emissions of which account for ~10 to 20% of the total fuel N loadings (Lobert, 1991); other N-containing species such as NO_2, nitriles, and NH_3 together account for a similar amount. Westerling et al. (2006) noted that the frequency and intensity of wildfires in the western U.S. increased substantially since 1970, lending added importance to consideration of all NO_X emissions from this sector.

2.2.2.4. Lightning

Annual global production of NO by lightning is the most uncertain source of atmospheric N. In the last decade, literature values of the global average production rate ranged from 2 to 20 Tg N/yr. Most recent estimates, however, are in the range of 3 to 8 Tg N/yr. This large and persistent uncertainty stems from several factors: (1) a wide range of as much as 2 orders of magnitude in NO production rates per meter of flash length; 2) uncertainty over whether cloud-to-ground (CG) and intracloud (IC) flashes produce substantially different NO levels; 3) the global average flash rate; and (4) the ratio of the number of IC to CG flashes.

Estimates of the NO concentration produced per flash have been made from theoretical considerations (e.g.,, Price, 1997), laboratory experiments (e.g.,, Wang, 1998), and field experiments (e.g., Huntrieser, 2002; Huntrieser, 2007, 93018; Stith, 1999), and with a hybrid method of cloud-resolving model simulations, observed lightning flash rates, and measurements of NO concentrations in cloud anvils (e.g., DeCaria, 2000; 2005; Ott, 2007). A series of midlatitude and subtropical thunderstorm events were simulated with the model of DeCaria et al. (2005) and the derived NO production per CG flash was, on avg, 500 moles/flash, while production per IC flash was 425 moles/flash on avg (Ott, 2006). The hybrid method had earlier been used by Pickering et al. (1998) who showed that only ~5 to 20% of the total NO produced by lightning in a given storm exists in the planetary boundary layer (PBL) at the end of a thunderstorm event, thereby reducing its importance as a direct emissions source to the urban and regional troposphere.

2.2.3. Anthropogenic and Biogenic Sources of N_2O

N_2O has an atmospheric lifetime (τ) of ~114 years, resulting from its having effectively no chemistry in the lower troposphere on urban and regional scales. The chief N_2O loss pathway (with a quantum yield of ~1) is the photodissociation process

$$N_2O \rightarrow N_2 + O(^1D)$$

Reaction 3

driven by the short wavelength UV present only in the stratosphere.

However, N_2O is also a GHG with a global warming potential (GWP) on the conventional 100–year time horizon of ~296; i.e., 1 molecule of N_2O is nearly 300 times more effective at trapping heat in the atmosphere than 1 molecule of carbon dioxide (CO_2) over a 100–year period (EPA, 2002) (Houghton, 2001). The high GWP of N_2O results from its combination of direct and indirect radiative forcing climate effects in the stratosphere. By comparison, the primary climate effects of NO and NO_2 are indirect and result from their role in promoting the production of O_3 ($P(O_3)$) in the troposphere and, to a lesser degree, in the lower stratosphere where NO_X has positive radiative forcing effects. Additional complications for calculating NO_X GWPs arise because NO_X emissions from high-altitude aircraft are also likely to decrease methane (CH_4) concentrations, a negative radiative forcing effect (Houghton, 1996), and because pNO_3 transformed from NO_X also have negative radiative forcing effects. The EPA does not calculate GWPs for total NO_X or SO_X or for the other atmospheric constituents for which no agreed-upon method exists to estimate the contributions from these gases that are short-lived in the atmosphere, have strong spatial variability, or have only indirect effects on radiative forcing.

Thus, because there are no tropospheric reactions or effects to consider, N_2O is not a significant component of NO_X for the purposes of this ISA. However, the role of N_2O as an intermediate product along with NO from the complex soil metabolism described in Section 2.2.2.1 means that a brief description of its emissions strengths and its component part of the total budget of U.S. GHGs will be useful, and so appears just below.

N_2O is a contributor to the total U.S. GHG budget, with 6.5% of total GHG on a Tg CO_2 equivalents basis (CO_2e) in 2005 (EPA, 2007). CO_2, by comparison, accounted for 83.9% in that same year, and CH_4 for 7.4% (EPA, 2007). Although atmospheric concentrations of N_2O have increased globally by ~18% to a current value of ~315 ppb due to Western industrialization since 1750 C.E. (Hofmann, 2004), there is considerable interannual variation in N_2O emissions which remains largely unexplained (Houghton, 2001). N_2O emissions in the U.S., for example, decreased by 2.8%, or 13.4 Tg CO_2e, between 1990 and 2005 (EPA, 2007).

N_2O is produced by biological processes occurring in the soil and water and by a variety of anthropogenic activities in the agricultural, energy, industrial, and waste management sectors. The chief anthropogenic activities producing N_2O in the U.S. are agricultural soil management, fuel combustion in motor vehicles, manure management, production of adipic acid (nylon) and HNO_3, wastewater treatment, and stationary fuel combustion.

N_2O emissions from anthropogenic activities in the U.S. were 386.7 Tg CO_2e/yr between 1990 and 2004 (EPA, 2007). These emissions resulted from the fuel combustion, industrial practices, and stimulation of biogenic sources through agricultural practices enumerated above. In 2005, N_2O emissions from mobile sources were 38.0 Tg CO_2e, or ~8% of the U.S. N_2O emissions total (EPA, 2007). In the period between 1990 and 1998, control technologies on mobile sources reduced on-road vehicle NO and NO_2 emissions at the expense of increasing N_2O emissions by 10%. The overall reduction in N_2O mobile source emissions between 1998 and 2005 (when totals were last available), however, has been 13% owing to more efficient controls used after 1998.

Biogenic production of N_2O stimulated through soil management accounted for > 75% of all U.S. N_2O emissions in 2005 (EPA, 2007). N_2O emissions from these sources have shown no significant long-term trend, because the biogenic emitters are highly sensitive to the concentrations and forms of N applied to soils, and these applications have been largely constant (EPA, 2007).

Aquatic sources of N_2O may also be stimulated by environmental conditions. In some ocean areas, large areas of surface water can become depleted in O_2, allowing active denitrification in open water, and potentially increasing N_2O emissions as described in Section 2.2.2. In addition, oceanic N_2O can also arise from denitrification in marine sediments, particularly in nutrient rich areas such as those of estuaries.

2.3. Sources and Emissions of Tropospheric SO_X

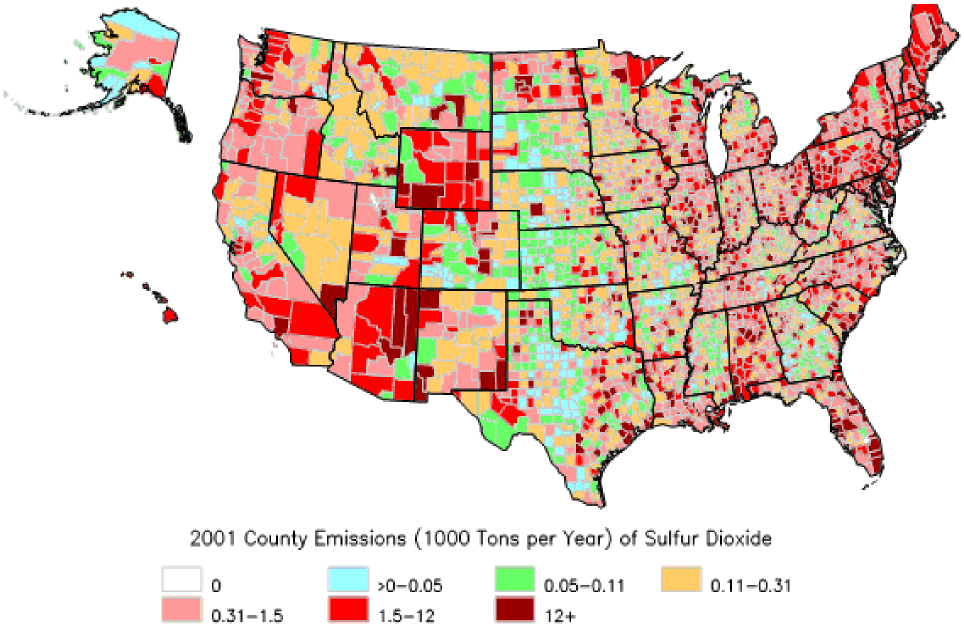
Emissions of SO_2, the chief component of SO_X, are due mostly to combustion of fossil fuels by EGUs and industrial processes with transportation-related sources making smaller but significant contributions.

2.3.1. Major Anthropogenic Sources

Table 2-1 shows that for 2002, fossil fuel combustion at EGUs accounted for ~66% of total SO_2 emissions in the U.S., or 11.31 Tg of the total 16.87 Tg. All transportation sources accounted for ~5% of the total U.S. SO_2 emissions in 2002, or 0.76 Tg. On-road vehicles produced ~40% of the transportation-related total SO_2 emissions in 2002, with off-road diesel and marine traffic together accounting for the remainder. Thus, most SO_2 emissions originate from point sources having well-known locations and identifiable fuel streams.

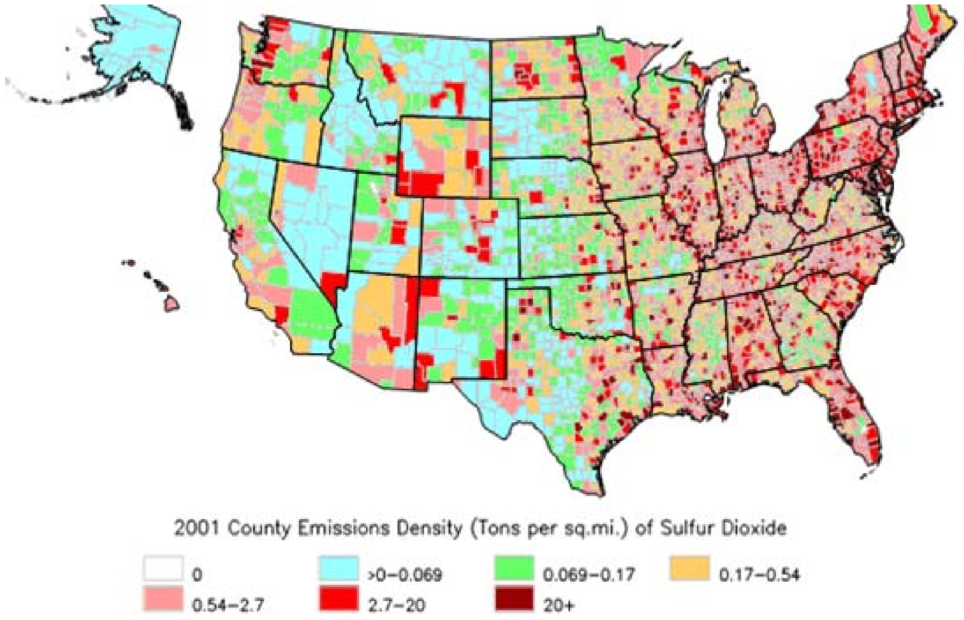
Since nearly all S in fuels is released in volatile components, either SO_2 or SO_3, during combustion, total S emissions from these point sources can be computed from the known S content in fuel stocks with greater accuracy than can total NO_X emissions from point sources. However, just as for the NO_X emissions totals described above, total SO_X emissions estimates are national-scale averages and so can not accurately reflect the contribution of local sources to selected environmental exposures to SO_X at specific locations and times. To refine those national estimates, county-level average SO_2 emissions for 2001 are shown in Figure 2-5; normalized emissions intensities per square mile like those shown above for NO_X are shown for SO_2 in Figure 2-6.

Figure 2-6 illustrates the west-to-east increasing gradient in SO_2 emissions densities, with most counties east of the Mississippi River in warmer colors (greater emissions densities) than most counties in the West. The upper end of the SO_2 emissions density distribution represented includes many counties in the eastern U.S.—primarily in the Ohio River Valley—with 2001 SO_2 emissions densities significantly greater than 20. Examples of these high densities (in tons per square mile) are: Hillsborough County, FL, 80; Grant County, WV, 156; Indiana County, PA, 190; Washington County, OH, 273; and Armstrong County, PA, 292. In these counties, SO_2 emissions were due mostly to EGU fuel combustion, as shown in Table 2-2. For the EGU emissions densities in Figure 2-7, and the total SO_2 densities in Figure 2-6, the upper end of the density distribution compresses a wide range (see Table 2-2). Thus, for the five counties considered above, non-EGU emissions were < 5% of total SO_2 emissions in Washington County, OH, and < 1% in Indiana County, PA, Armstrong County, PA, and Grant County, WV. Hillsborough County, FL, is an exception, where 17% of the 2001 SO_2 emissions density came from non-EGU sources, the largest of which was chemical and allied product manufacturing.



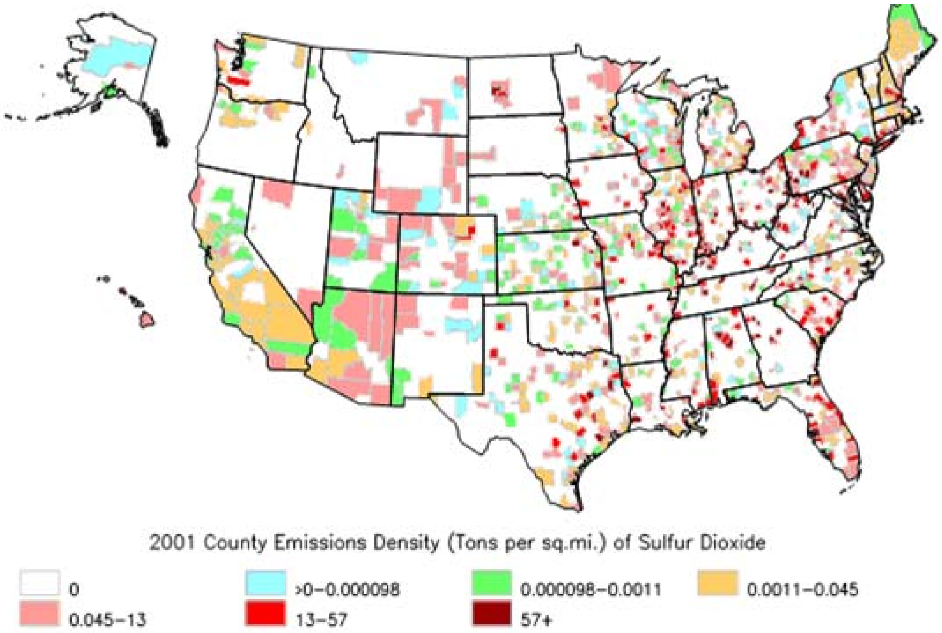
Source: U.S. EPA (2006)

Figure 2-5. 2001 county-level total U.S. SO_2 emissions.



Source: U.S. EPA (2006)

Figure 2-6. 2001 county-level total U.S. SO_2 emissions densities (tons per square mile).



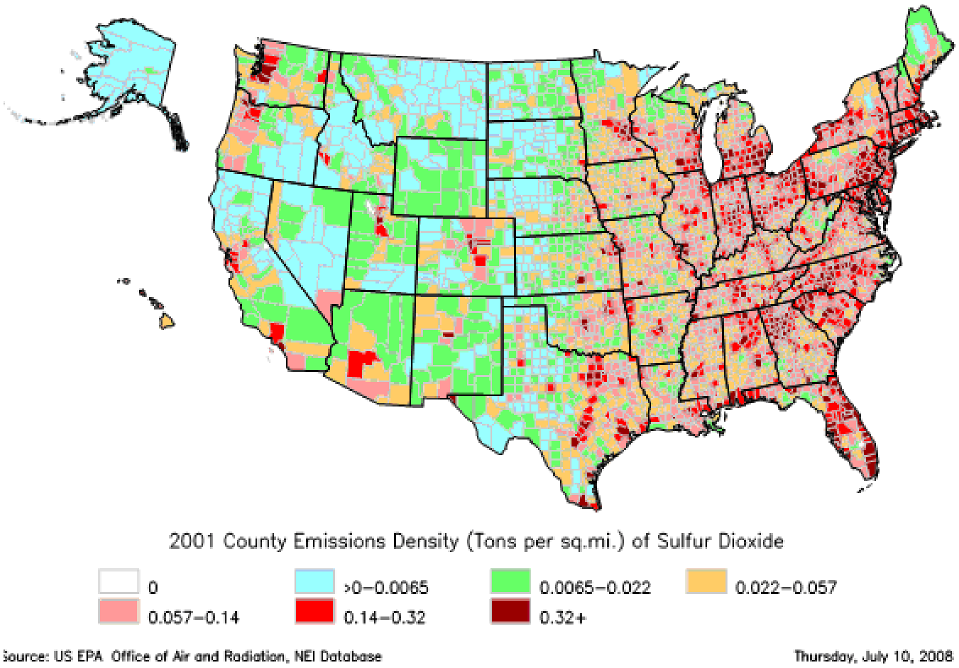
Source: U.S. EPA (2006)

Figure 2-7. 2001 county-level SO_2 emissions densities (tons per square mile) from EGUs.

Table 2-2. Total and non-EGU SO_2 emissions densities for selected U.S. counties, 2001.

County	SO_2 Emissions Density (tons/mi²)	Non-EGU Emissions Density Fraction (%)
Hillsborough, FL	80	17
Grant, WV	156	< 1
Indiana, PA	190	< 1
Washington, OH	273	< 5
Armstrong, PA	292	< 1

Although on-road mobile sources in 2001 contributed < 5% to SO_2 emissions totals on the national scale, their fraction of county-level emissions densities varies widely. Generally, however, on-road mobile source SO_2 emissions reflect the west-to-east increasing gradient in the densities of both total SO_2 emissions and U.S. population, as shown in Figure 2-8. In areas such as Wayne County, MI, and Bronx County, NY, for example, 2001 SO_2 emissions densities from on-road mobile sources were 3 and 8.8 tons per square mile out of totals of 98 and 160 tons per square mile, respectively, total SO_2. In other areas like Dallas County, TX, and DeKalb County, GA, however, the on-road fraction of total SO_2 emissions densities in 2001 was substantially greater: 1.5 out of the total 4.1 tons per square mile in Dallas County, and 3.5 out of the total 6.5 tons per square mile in DeKalb County.

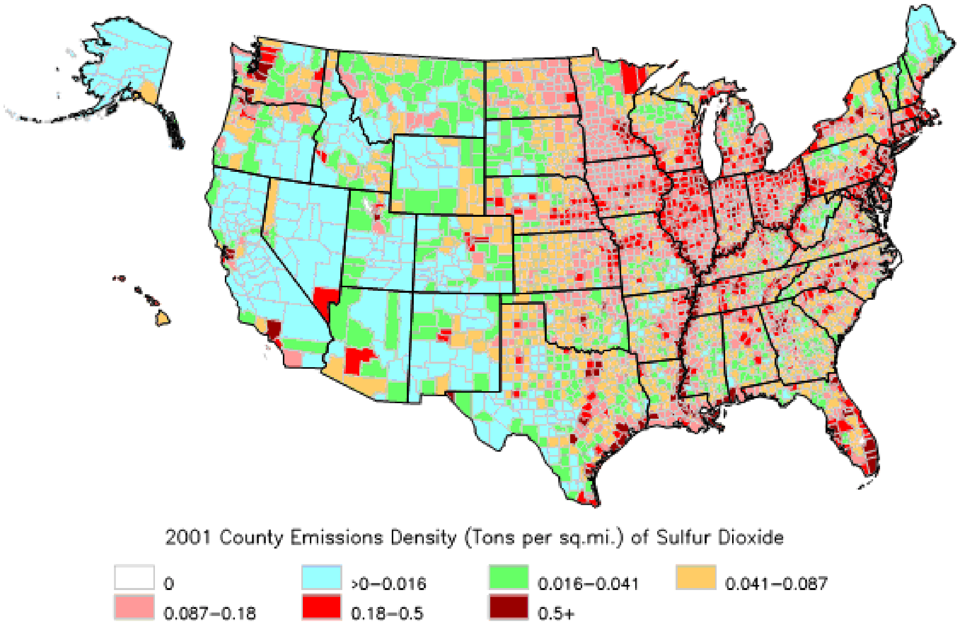

2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

Source: US EPA Office of Air and Radiation, NEI Database

Thursday, July 10, 2008

Source: U.S. EPA (2006)

Figure 2-8. 2001 county-level SO_2 emissions densities (tons per square mile) from on-road mobile sources.


2001 County Emissions Density (Tons per sq.mi.) of Sulfur Dioxide

Source: U.S. EPA (2006)

Figure 2-9. 2001 county-level SO_2 emissions densities (tons per square mile) from off-road mobile and other transportation sources.

An additional source of SO_2 emissions of concern in particular locations not immediately obvious from national-scale averages and totals are transit and in-port activities in areas with substantial shipping traffic (Wang, 2007). Because of the importance of these SO_2 emissions, the ports of Long Beach and Los Angeles, CA, for example, are part of a Sulfur Emissions Control Area in which S contents of fuels are not to exceed 1.5%. Figure 2-9 shows SO_2 emissions densities combined for all non-road transportation-related emitters in which coastal areas with ports and shipping routes, such as the Mississippi River, are easily discerned. In Los Angeles County, CA, for example, off-road transportation including shipping and port traffic contributed 1.4 of the total 4.1 tons of SO_2 per square mile in 2001; in King County (including the city of Seattle), WA, the off-road transportation fraction was 42% of the total SO_2 emissions density, or 1.2 of the total 2.8 tons per square mile. Emissions density data at finer scales more specific to the ports are not available in the routine emissions inventories and some confusion attends estimates of the actual SO_2 loads from these sources. Modeling studies by Vutukuru (2008) for southern California ports, for example, have shown that ships contribute >1 ppb to the 24-h avg SO_2 concentration in Long Beach, CA, with < 10% of that, or ~100s of ppt farther inland.

2.3.2. Major Biogenic Sources

The major biogenic sources of SO_2 are volcanoes, biomass burning, and dimethylsulfide (DMS) oxidation over the oceans. Although SO_2 constitutes a relatively minor fraction of 0.005% by volume of total volcanic emissions (Holland, 1978), concentrations in volcanic plumes can be in the range of several to tens of ppm. The ratio of hydrogen sulfide (H_2S) to SO_2 is highly variable in volcanic gases, typically < 1, as in the Mount St. Helens eruption in the Washington Cascade Range (46.20 N, 122.18 W, summit 2549 m asl) (Turco, 1983). However, in addition to being degassed from magma, H_2S can be produced if ground waters, especially those containing organic matter, come into contact with volcanic gases. In this case, the ratio of H_2S to SO_2 can be > 1. H_2S produced this way would more likely be emitted through side vents than through eruption columns (Pinto, 1989). Primary particulate sulfate (pSO_4) is a component of marine aerosol and is also produced by wind erosion of surface soils.

Since 1980, the Mount St. Helens volcano has been a variable source of SO_2. Its major effects came in the explosive eruptions of 1980, which primarily affected the northern part of the mountainous western half of the U.S. The Augustine volcano near the mouth of the Cook Inlet in southwestern Alaska (59.363 N, 153.43 W, summit 1252 m asl) has had variable SO_2 emissions since its last major eruptions in 1986. Volcanoes in the Kamchatka peninsula of the eastern region of Siberian Russia do not significantly affect surface SO_2 concentrations in northwestern North America. The most serious effects from volcanic SO_2 in the U.S. occur on the island of Hawaii. Nearly continuous venting of SO_2 from Mauna Loa and Kilauea produces SO_2 in such large amounts that > 100 km downwind of the island, levels of SO_2 can exceed 30 ppb (Thornton, 1993).

Emissions of SO_2 from burning vegetation are generally in the range of 1 to 2% of the biomass burned (e.g.,, Levine, 1999). S is bound in amino acids in vegetation, and ~50% of this organically-bound S is released during combustion, leaving the remainder in the ash (Delmas, 1982). Gas-phase emissions are mainly in the form of SO_2, with much smaller amounts of H_2S and carbonyl sulfide (OCS). The ratio of reduced S species such as H_2S to more oxidized forms like SO_2 increases as the fire conditions change from flaming to smoldering phases of combustion because emissions of reduced species are favored by the lower temperatures and decreased O_2 availability.

SO_2 is also produced by the photochemical oxidation of reduced S compounds such as dimethylsulfide ($CH_3{-}S{-}CH_3$, or DMS), H_2S, carbon disulfide (CS_2), OCS, methyl mercaptan ($CH_3{-}S{-}H$), and DMS ($CH_3{-}S{-}S{-}CH_3$). The sources for these compounds are mainly biogenic (see Table 2-1). Emissions of reduced S species are associated typically with marine organisms living either in pelagic or coastal zones and with anaerobic bacteria in marshes and estuaries. Emissions of DMS from marine plankton represent the largest single source of reduced S species to the atmosphere (Berresheim, 1995). Other sources such as wetlands and terrestrial plants and soils account for < 5% of the DMS global flux, with most of this coming from wetlands.

Other than OCS, which is lost mainly by photolysis with a τ of ~6 months, SO_X species are lost mainly by reaction with OH^- and NO_3^-, and are relatively short-lived, with τ ranging from a few hours to a few days. Reaction with NO_3^- at night most likely represents the major loss process for DMS and methyl mercaptan. Although the mechanisms for the oxidation of DMS are not known with certainty, excess SO_4^{2-} in marine aerosol appears related mainly to production of SO_2 from the oxidation of DMS. Emissions of SO_X from natural sources are small compared to industrial emissions within the U.S. (see Table 2-1). However, important exceptions occur locally as the result of volcanic activity, wildfires, and in certain coastal zones as described above.

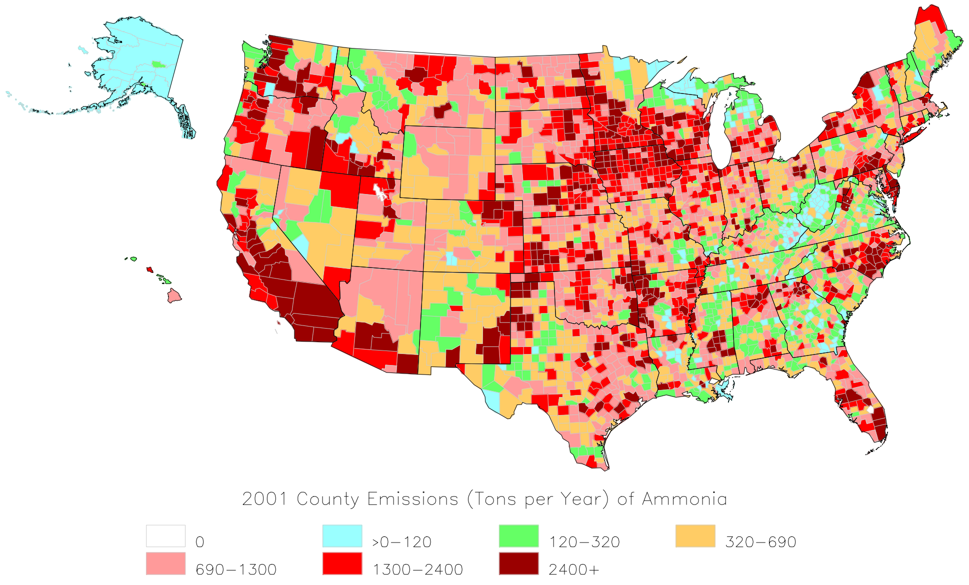
Because OCS is relatively long-lived, it can survive oxidation in the troposphere and be transported upward into the stratosphere. Crutzen (1976) proposed that its oxidation to SO_4^{2-} in the stratosphere serves as the major source of the stratospheric aerosol layer. However, Myhre et al. (2004) proposed that SO_2 transported upward from the troposphere by deep convection is the most likely source, since the flux of OCS is too small to account for current atmospheric loadings. In addition, in situ measurements of the isotopic composition of S in stratospheric SO_4^{2-} do not match those of OCS (Leung, 2002). Thus, in addition to biogenic OCS, anthropogenic SO_2 emissions could be important precursors to the formation of the stratospheric aerosol layer.

The coastal and wetland sources of DMS have a dormant period in the fall and winter from plant senescence. Marshes die back in fall and winter, so DMS emissions from them are lower, and lower light levels in winter at mid-to-high latitudes lessen phytoplankton growth also tend to lower DMS emissions. Western coasts at mid-to-high latitudes have lower actinic flux to drive photochemical production and oxidation of DMS. Freezing at mid and high latitudes affects the release of biogenic S gases, particularly in the nutrient-rich regions around Alaska. Transport of SO_2 from regions of biomass burning seems to be limited by heterogeneous losses that accompany convective processes that ventilate the surface layer and the lower boundary layer (Thornton, 1996).

Reduced S species are also produced by several anthropogenic industrial sources: DMS is used in petroleum refining and in petrochemical production processes to control the formation of coke and CO; and it is used to control dusting in steel mills, and in a range of organic syntheses; as a food flavoring component; and can also be oxidized by natural or artificial means to dimethyl sulfoxide, a widely-used industrial solvent.

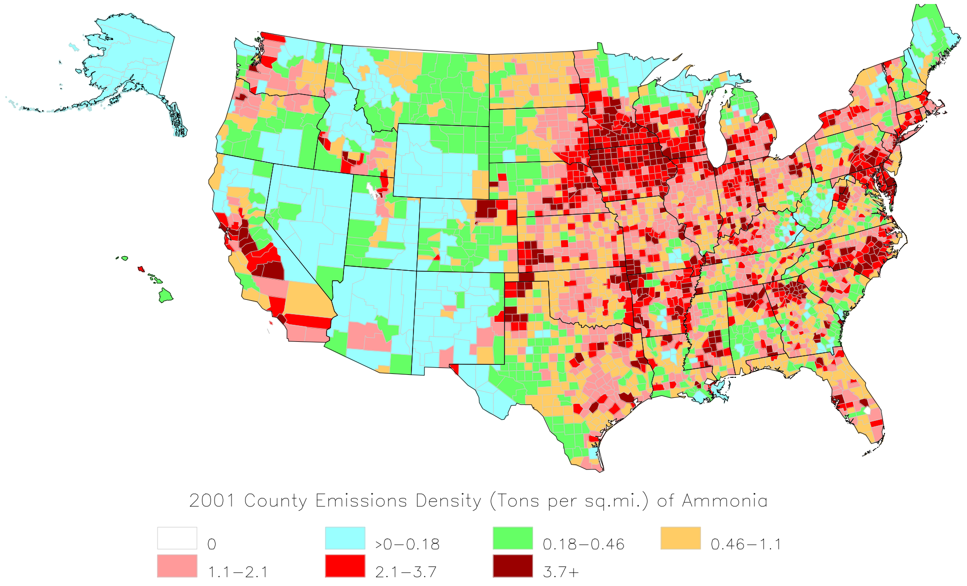
2.4. NH_X Emissions

NH_3 can be emitted from or deposited to soils, water, or vegetation depending on the ratio of atmospheric NH_3 concentration to the compensation point of the underlying surface. The compensation point, χ, generally is governed by the form, concentration, and acidity of N at the surface of exchange, and hence changes over time as these variables change. For most of the year, large areas of the U.S. are very near the nominal χ of 1 ug/m^3, with the result that the NH_3 air-surface flux is very often highly dynamic. Figure 2-10 and Figure 2-11 show county-level annual total NH_3 emissions for 2001 in tons, and the spatially normalized county-level emissions in tons per square mile, respectively.



Source: U.S. EPA (2006)

Figure 2-10. 2001 county-level total U.S. NH_3 emissions.

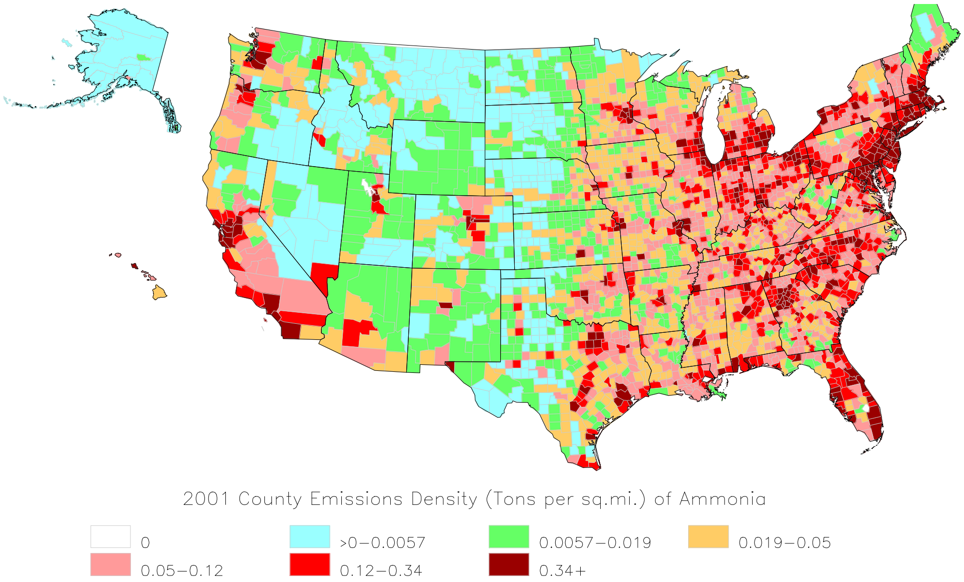


Source: U.S. EPA (2006)

Figure 2-11. 2001 county-level total U.S. NH_3 emissions densities.

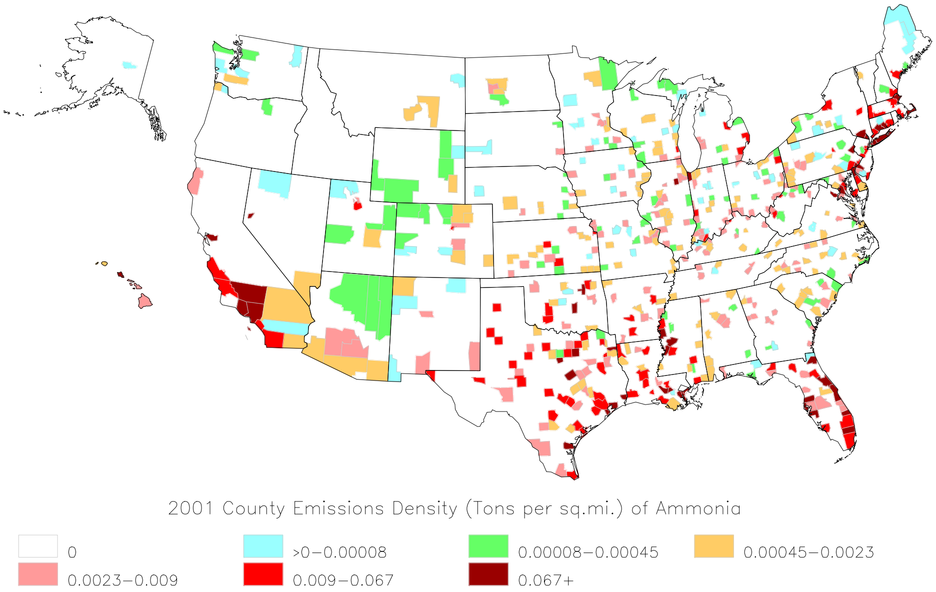
Total emissions of NH_3 on a national scale show a strikingly different pattern from those of NO_X or SO_2 as comparison of these figures to their NO_X and SO_X analogs above illustrates. Anthropogenic NH_3 emissions from mobile sources are small since the three-way catalysts used in motor vehicles emit only small amounts of NH_3 as a byproduct during the reduction of NO_X; in 2002, this totaled ~8% of the national NH_3 total of ~3.7m short tons. Stationary combustion sources including EGUs make even smaller contributions to emissions of NH_3 because their efficient combustion favors NO_X formation and NH_3 is produced during combustion largely by inefficient, low-temperature burning. In 2002, the total from all stationary source fuel combustion processes amounted to < 2% of total NH_3 emissions and chemical production added only ~0.7% more. For these reasons, NH_3 emissions totals are dominated by biogenic production from agriculture, chiefly from livestock management and fertilizer applications to soils. In 2002, these sources accounted for ~86% of U.S. total emissions.

As with NO_X and SO_X emissions, however, these national-scale emissions totals obscure important variability at finer scales. To illustrate this point, Figures 2-13 through 2-15 show county-level NH_3 emissions densities separately for emissions from on-road mobile sources, EGUs, and miscellaneous and biogenics, respectively.



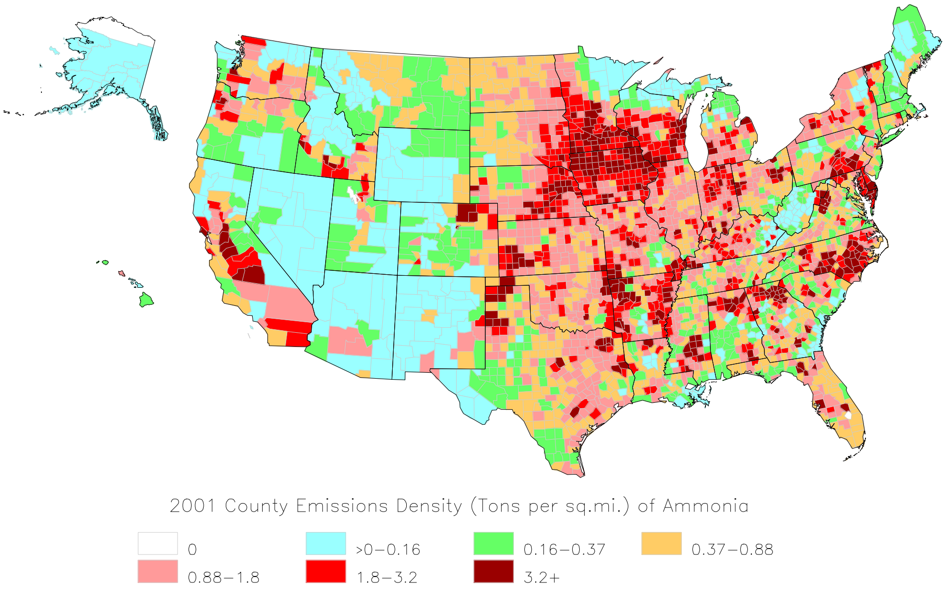
Source: U.S. EPA (2006)

Figure 2-12. 2001 county-level NH_3 emissions densities from on-road mobile sources.



Source: U.S. EPA (2006)

Figure 2-13. 2001 county-level NH_3 emissions densities from EGUs.



Source: U.S. EPA (2006)

Figure 2-14. 2001 county-level NH_3 emissions densities from miscellaneous and biogenic sources

2.5. Evaluating Emissions Inventories

Emissions inventories are very complex and highly changeable conjoined forms built from measurements and production and transfer rates, some of which are measured directly, others indirectly, and others merely assumed, and with model predictions. National-scale emissions inventories like the ones illustrated in county-level maps have uncertainties embedded in them owing to unknown emission factors, unknown and varying emission rates, generalized or depleted profiles, and the like. Substantial effort is applied at national, state, and local scales to test these terms in the final product emissions totals, and to assure their quality.

One means for evaluating emissions inventories has been to compare predictions in the inventories to measured long-term trends, or to ratios of pollutants in ambient air. Comparisons of emissions model predictions with observations have been performed in a number of environments. Very often emissions inventories for NO_X and SO_X are evaluated in relation to CO emissions because the low reactivity of CO on urban and regional scales means it can be treated as largely conserved on these scales. Using the distinction between mobile sources which emit NO_X and CO but little SO_2, and power plants which emit NO_X and SO_2 but little CO, Stehr et al. (2000) evaluated emissions estimates for the eastern U.S. Results indicated that coal combustion contributes 25 to 35% of the total area NO_X emissions in rough agreement with the U.S. EPA NEI (EPA, 1997). Studies using ratios of CO concentrations to NO_X concentrations, and concentrations of nonmethane organic compounds (NMOC) to NO_X carried out in the early 1990s in tunnels and ambient air indicated that emissions of CO and NMOC were systematically underestimated in emissions inventories at that time. More details are available in the *Air Quality Criteria for Carbon Monoxide* (EPA, 2000).

These reconciliation studies depend on the assumption that NO_X emissions are predicted correctly by emissions factor models which are merely mean and aggregate descriptions of the highly variable U.S. mobile source fleet. Roadside remote sensing data have indicated that > 50% of non-methane hydrocarbons (NMHC) and CO emissions are produced by less than 10% of vehicles (Stedman, 1991), typically the poorly maintained "super-emitters."

Parrish et al. (1998) and Parrish and Fehsenfeld (2000) proposed methods to derive emission rates by examining measured ambient ratios among individual volatile organic compounds (VOCs), NO_X, and NO_Y. Typically, strong correlations exist among measured values for these species because emission sources are geographically collocated, even when individual sources are different. Correlations can be used to derive emissions ratios between species, including adjustments for the effect of photochemical aging. Examples of this type include using correlations between CO and NO_Y (e.g.,, Parrish, 1991), between individual VOC species and NO_Y (Arnold, 2007; Goldan, 1995, 2005) and among various VOC species (McKeen, 1993, 1996). Many of these studies were summarized in Trainer et al. (2000), Parrish et al. (1998), and Parrish and Fehsenfeld (2000).

Other methods for emissions evaluation exist. Buhr et al. (1992) derived emission estimates from principal component analysis (PCA) and other statistical methods. Goldstein and Schade (2000) also used species correlations to identify the relative effects of anthropogenic and biogenic emissions. Chang et al. (1996; , 1997) and Mendoza-Dominguez and Russell (2000) used inverse modeling to derive emission rates in conjunction with results from chemical-transport models (CTMs).

A decadal field study of ambient CO at a rural site in the eastern U.S. (Hallock-Waters, 1999) indicated a downward trend consistent with the downward trend in estimated emissions over the period 1988 to 1999 (EPA, 2000), even when the global downward trend was taken into account. Measurements at two urban areas in the U.S. confirmed the decrease in CO emissions (Parrish, 2002). That study also indicated that the ratio of CO to NO_X emissions decreased by approximately a factor of 3 over 12 years. NEI estimates (EPA, 1997) indicated a much smaller decrease in this ratio, suggesting that NO_X emissions from mobile sources may have been underestimated or increasing or both. Parrish et al. (2002) concluded that O_3 photochemistry in U.S. urban areas may have become more NO_X-limited over the past decade. (See Section 2.6.2.1 for a discussion of NO_X and its role in enhancing and limiting O_3 formation.)

Results from some of these recent emissions evaluation studies have been mixed, with some studies showing agreement to within ±50% (EPA, 2000). However, Pokharel et al. (2002) employed remotely sensed emissions from on-road vehicles and fuel use data to estimate emissions in Denver. Their calculations indicated a continual decrease in CO, hydrocarbons (HC), and NO emissions from mobile sources over the 6–year study period, 1996 through 2001. Inventories based on the ambient data were 30 to 70% lower for CO, 40% higher for HC, and 40 to 80% lower for NO than those predicted by the MOBILE6 on-road mobile source emissions model (see http://www.epa.gov/otaq/m6.htm for information on MOBILE6).

Satellite data also have proved useful for optimizing estimates of emissions of NO_2 (Leue, 2001; Martin, 2003; Jaeglé, 2005). Satellite-borne instruments such as the Global Ozone Monitoring Experiment (GOME) (see Martin, 2003 and references therein) and the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) (see Bovensmann, 1999) retrieve tropospheric columns of NO_2 that can then be combined with model-derived τ of NO_X to yield emissions of NO_X.

Top-down inference of NO_X emission inventories from the satellite observations of NO_2 concentrations columns by mass balance requires at minimum three pieces of information: (1) the retrieved tropospheric NO_2 column; 2) the ratio of tropospheric NO_X to NO_2 in the columns; and (3) the NO_X τ against reaction losses to stable chemical reservoirs. (See the discussion of these chemical reservoirs in Section 2.6). A photochemical model has been used to provide information on the latter two pieces of information. The method is most often applied to land surface emissions, excluding lightning. Tropospheric NO_2 columns are largely insensitive to lightning NO_X emissions since most of the lightning NO_X in the upper troposphere is present as NO at the time of the satellite measurements (Ridley, 1996), owing to the slower reactions of NO with O_3 at the altitude where lightning production is most prevalent.

Using satellite data, Bertram et al. (2005) found clear signals in the SCIAMACHY observations of short, intense NO_X pulses following springtime fertilizer application and subsequent precipitation over agricultural regions of the western U.S. For the agricultural region in north-central Montana, they calculated an annual SCIAMACHY top-down estimate that is 60% greater than a commonly-used model of soil NO_X emissions by Yienger and Levy (1995).

Jaeglé et al. (2005) applied additional information on the spatial distribution of emissions and fire activity to partition NO_X emissions into sources from fossil fuel combustion, soils, and biomass burning. Global a posteriori estimates of soil NO_X emissions were 68% larger than the a priori estimates. Large increases were found for the agricultural region of the western U. S. during summer, increasing total U.S. soil NO_X emissions by a factor of 2.

Martin et al. (2006) retrieved tropospheric NO_2 columns for May 2004 to April 2005 from the SCIAMACHY satellite instrument to derive top-down NO_X emissions estimates via inverse modeling with the GEOS-Chemistry global chemical transport model (see http://www.as.harvard.edu/ctm/geos/ for more information on GEOS-Chem). The top-down emissions were combined with a priori information from a bottom-up emission inventory with error weighting to achieve an improved a posteriori estimate of the global distribution of surface NO_X emissions. Their *a posteriori* inventory improved GEOS-Chem simulations of NO_X, peroxyacetyl nitrate (PAN), and HNO_3 as compared against airborne in situ measurements over and downwind of New York City. Their a posteriori inventory showed lower NO_X emissions from the Ohio River Valley in summer than winter, reflecting recent controls on NO_X emissions from electric utilities there. Their *a posteriori* global inventory was highly consistent with the NEI 99 (R^2 = 0.82, bias = 3%); however, it was 68% greater than a recent inventory by Streets et al. (2003) for East Asia for the year 2000.

Significant uncertainties attach to estimates of the magnitude and spatial and temporal variability of NH_3 emissions. A strong seasonal pattern should be evident in NH_3 emissions profiles to correspond with the overwhelmingly agricultural sources of NH_3 and strong seasonal temperature differences in NH_3 volatility, for example, but this pattern has not appeared in previous emissions factors and inventories. The magnitude of these temporal differences is large: Heber et al. (2001) showed that NH_3 flux from two swine finishing buildings were ~70% higher in June than in fall and winter months, and Aneja et al. (2000) found fluxes from hog waste lagoons ~80 to 90% higher in summer as compared to winter.

The value of inverse modeling techniques using large-scale Eulerian air quality models (AQMs) has been successfully demonstrated for several aspects of emissions inventories; see, for example, Mendoza-Dominguez and Russell (2000; , 2001; Mendoza-Dominguez, 2001), Gilliland et al. (2001; , 2001; , 2003) and Pinder et al. (2006) have worked extensively with Kalman filter inverse modeling and the U.S. EPA Community Multiscale Air Quality (CMAQ) modeling system (Byun, 1999) to reduce uncertainties specifically in NH_3 emissions. NH_3 is an especially good case for emissions estimate evaluation with inverse modeling techniques because the modeled response in NH_4^+ wet deposition is strongly linear with changes in NH_3 emissions. Correcting the NH_3 emissions estimates was also shown to be an essential step for reasonable model-prediction of other N compounds (Gilliland, 2003). Results can be highly significant. For example: the *a posteriori* R value of CMAQ predictions against measured west NH_4^+ concentrations from the National Atmospheric Deposition Program (NADP) cites in the U.S. was 0.98, increased from the a priori value of 0.12. Pinder et al. (2004) provided the first farm-level model for NH_3 emissions from dairy cattle, and this has been coupled with the seasonally varying fertilizer inventory for NH_3 from Goebes et al. (2003) and with the inverse modeling results of Gilliland et al. (2003) to correct the NEI NH_3 emissions totals. The estimate of Gilliland et al. (2003) was that the annual NEI NH_3 was ~37% too high to optimize modeled wet NH_4^+ concentration. Following earlier work by Gilliland and others in this vein, U.S. EPA (EPA, 2002), in fact, reported its intention to decrease total NH_3 emissions in the NEI by 23% by altering emissions factors for nondairy cows and swine.

Holland et al. (2005) estimated wet and dry deposition of NH_X based on measurements over the CONUS and reported that NH_3 emissions in the 1999 NEI (http://www.epa.gov/ttn/chief/net/1999inventory.html) were underestimated by a factor of ~2 or 3.

Possible reasons for this error included under-representation of deposition monitoring sites in populated areas and the neglect of off-shore transport in the NEI. The use of fixed deposition velocities (V_d) not reflective of local conditions at the time of measurement introduces additional uncertainty into estimates of dry deposition to which NH_3 is particularly sensitive.

2.6. NO_X-SO_X-NH_X Chemistry in the Troposphere

2.6.1. Introduction

NO_X, VOCs, and CO are precursors in the formation of O_3 and other elements of photochemical smog and PM. The role of NO_X in $P(O_3)$, mechanisms for transporting the NO_X and VOC O_3 precursors, factors controlling $P(O_3)$ efficiency, methods for calculating O_3 from its NO_X and VOC precursors, and methods for measuring and estimating NO_Y were all reviewed in Chapter 2, Section 2.2 of the *Air Quality Criteria Document for Ozone and Related Photochemical Oxidants* (O_3 AQCD) (EPA, 2006) and are available in numerous texts (Seinfeld, 1998; Jacob, 2000; Jacobson, 2002). Hence, these are only briefly recounted here with special reference to the secondary NO_X and SO_X NAAQS.

Important compounds, reactions, and cycles are schematized in Figure 2-15. Figure 2-15 also illustrates that NO_2, itself an oxidant, can react to form other photochemical oxidants including organic nitrates ($RONO_2$) like the PANs shown in Figure 2-15, and can react with toxic compounds like the polycyclic aromatic hydrocarbons (PAHs) to form nitro-PAHs, some of which demonstrate greater toxicity than either reactant alone. NO_2 can also be further oxidized to HNO_3 and can contribute in that form to the acidity of cloud, fog, and rain water and can form ambient pNO_3.

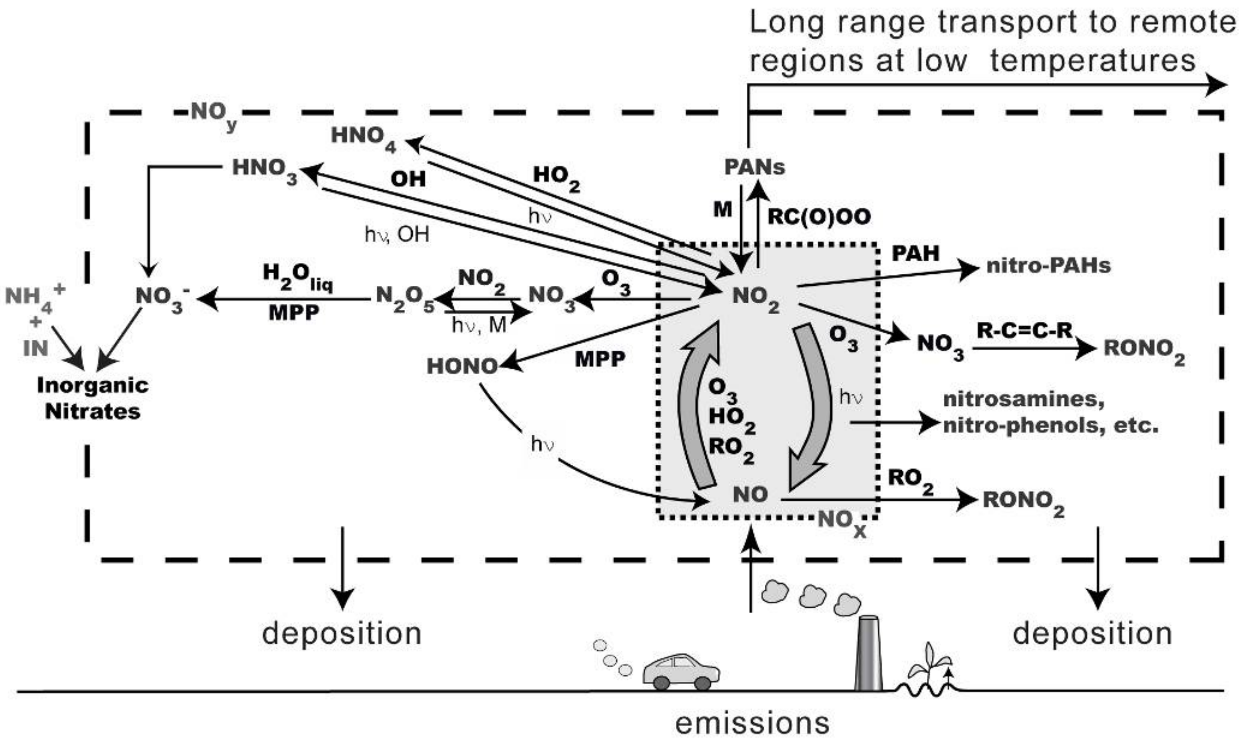
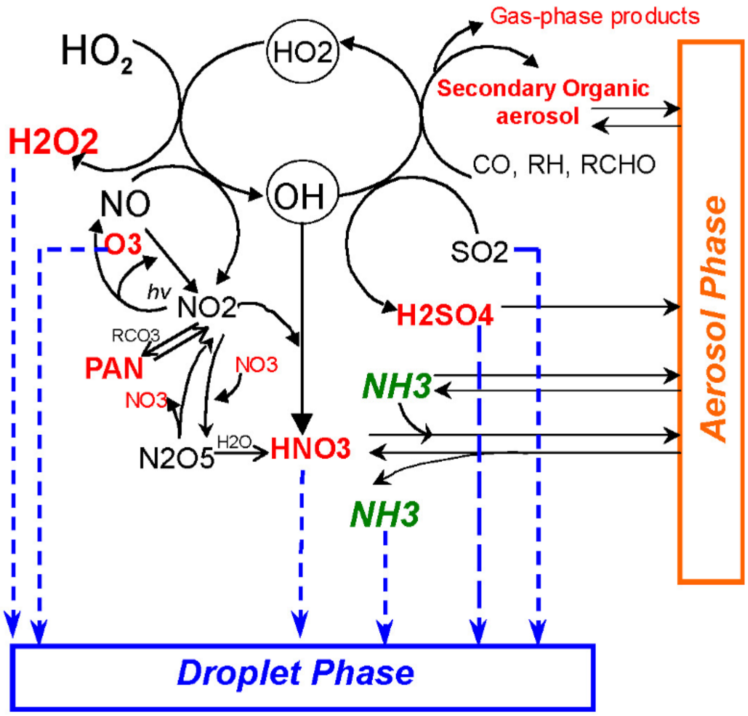


Figure 2-15. Schematic diagram of the cycle of reactive oxidized N species in the atmosphere. NO_Y refers to all the species shown within the inner and outer box; NO_X to NO and NO_2 (in the inner box); to all the species outside of the inner box. IN refers to inorganic particulate species (e.g., sodium (Na+), calcium (Ca++)), MPP to multiphase processes, hv to a solar photon and R to an organic radical. Particle-phase $RONO_2$ are formed from the species shown on the right side. For the purposes of this EPA document, "NO_X" is defined as the group of all N-containing compounds inside the large dashed-line box, the same group generally termed "NO_Y" by atmospheric scientists.

The only gas-phase forms of SO_X of interest in tropospheric chemistry are SO_2 and SO_3. SO_3 can be emitted from the stacks of power plants and factories; however, it reacts extremely rapidly with H_2O in the stacks or immediately after release into the atmosphere to form sulfuric acid (H_2SO_4). H_2SO_4 in turn mainly condenses onto existing particles when particle loadings are high, or nucleates to form new particles under lower concentration conditions. Thus, of the gas-phase SO_X species, only SO_2 is emitted in the tropospheric boundary layer at concentrations of concern for environmental exposures.

NH_3, the gas-phase precursor for NH_4^+, plays a key role in neutralizing acidity in ambient particles and in cloud, fog, and rain water. NH_3 is also involved in the ternary nucleation of new particles and reacts with gas-phase HNO_3 to form NH_4NO_3, and with SO_4^{2-} to form ammonium bisulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$), three significant components of N and S deposition across the landscape. The NO_X-SO_2-NH_X cycles and phase-changes are schematized in Figure 2-16.



Source: Adapted from Meng et al. (1997) and Warneck and used courtesy of R. Mathur and R. Dennis, U.S. EPA /ORD / NERL / ASMD.

Figure 2-16. The combined NO_X+SO_X+NH_X System showing how atmospheric fates and lifetimes of reduced and oxidized N components are linked.

2.6.2. NO_X Chemistry

NO_X is emitted by combustion sources mainly as NO with ~5 to 10% NO_2. The rapid photochemical cycle in the troposphere linking NO and NO_2 involves photolysis of NO_2 by UV-A radiation to yield NO and a ground-state oxygen atom, $O(^3P)$

$$NO_2 + hv \rightarrow NO + O(^3P)$$

Reaction 4

$O(^3P)$ can then combine with molecular oxygen (O_2) to form O_3; and, colliding with any molecule from the surrounding air (M = N_2, O_2, etc.), the newly formed O_3 molecule transfers excess energy and is stabilized by

$$O(^3P) + O_2 + M \rightarrow O_3 + M$$

Reaction 5

Reaction 5 is the only significant reaction for forming O_3 in the troposphere.

NO and O_3 react to reform NO_2

$$NO + O_3 \rightarrow NO_2 + O_2$$

Reaction 6

Reaction 6 is responsible for O_3 decreases and NO_2 increases found near sources of NO like highways. The falloff of NO_2 with distance from a road depends on wind speed and direction, and the local structure of turbulent mixing, temperature through the temperature dependence of Reaction 6 and the UVA-flux (through Reaction 4).

Oxidation of reactive VOCs leads to formation of reactive radical species that allow conversion of NO to NO_2 without participation of O_3 as in Reaction 7

$$NO \xrightarrow{HO_2,\ RO_2} NO_2$$

Reaction 7

O_3, therefore, can accumulate as NO_2 photolyzes as in Reaction 4, followed by Reaction 5. Specific mechanisms for the oxidation of a number of VOCs were discussed in the O_3 AQCD (EPA, 2006).

It is often convenient to speak about families of chemical species defined in terms of members that interconvert rapidly on time scales shorter than those for formation or destruction of the family as a whole. For example, an "odd oxygen" (O_X) family can be defined as

$$O_x = \sum(O(^3P) + O(^1D) + O_3 + NO_2)$$

Reaction 8

In much the same way, NO_X is sometimes referred to as "odd nitrogen." Hence, we see that production of O_X occurs by the schematic Reaction 7 while the sequence of reactions given by Reaction 4 through Reaction 6 represents no net production of O_X. (Definitions of species families and methods for constructing families are discussed in Jacobson (1999) and references therein.) Other families including N-containing species used later in this chapter are

$$NO_Z = \sum HNO_2 + HNO_4 + NO_3 + 2NO_2O_5 + PAN(CH_3CHO - OO - NO_2) +$$
$$\text{other organic nitrates + halogen nitrates + particulate nitrates}$$

and

$$NO_Y = NO_X + NO_Z + HONO$$

and

$$HO_X = OH + HO_2$$

NO_Z refers to the sum of all oxidation products of NO_X, but not the original NO and NO_2.

The reaction of NO_2 with O_3 leads to the formation of NO_3

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

Reaction 9

However, NO_3 reacts rapidly, having a τ of ~5 s during the photochemically most active period of the day near local solar noon, by two pathways (Atkinson, 1992)

$$NO_3 + hv \rightarrow NO + O_{2(10\%)}$$

Reaction 10

$$NO_3 + hv \rightarrow NO_2 + O(^3P)_{(90\%)}$$

Reaction 11

Because of this, NO_3 concentrations remain low during daylight hours but can increase after sunset to nighttime concentrations of 5×10^7 to 1×10^{10} molecules/cm^3 or 2 to 430 parts per trillion (ppt) over continental areas influenced by anthropogenic emissions of NO_X (Atkinson, 1986). At night, NO_3, rather than OH, is most often the primary oxidant in polluted tropospheric systems. Moreover, NO_3 can combine with NO_2 to form dinitrogen pentoxide (N_2O_5)

$$NO_3 + NO_2 \xleftrightarrow{M} N_2O_5$$

Reaction 12

and N_2O_5 both photolyzes and thermally decomposes back to NO_2 and NO_3 during the day; however, N_2O_5 can accumulate during the night to ppb levels in polluted urban atmospheres.

The tropospheric chemical removal processes for NO_X include reaction of NO_2 with OH and hydrolysis of N_2O_5 in aqueous aerosol solutions if there is no organic coating. Both of these reactions produce HNO_3

$$OH + NO_2 \xrightarrow{M} HNO_3$$

Reaction 13

$$N_2O_5 \xrightarrow{H_2O(1)} 2HNO_3$$

Reaction 14

The gas-phase reaction of OH with NO_2 (Reaction 13) is one of the major and ultimate removal processes for NO_X in the troposphere. This reaction removes OH and NO_2 in one step and competes with HC for OH in areas characterized by high NO_X concentrations such as urban centers. The τ for conversion of NO_X to HNO_3 in the PBL at 40 N latitude ranges from ~ 4 hours in July to ~ 16 hours in January. The corresponding range in τ at 25 N latitude is between 4 and 5 hours, while at 50 N latitude, HNO_3 τ ranges from about 4 to 20 hours (Martin, 2003).

In addition to gas-phase HNO_3, Golden and Smith (2000) have shown on the basis of theoretical studies that pernitrous acid (HOONO) is also produced by the reaction of NO_2 and OH; however, this production channel most likely represents a minor yield ~ 15% at the surface (Jet Propulsion Laboratory, 2003). Pernitrous acid will also thermally decompose and photolyze.

Gas-phase HNO_3 formed from Reaction 13 and Reaction 14 undergoes wet and dry deposition to the surface and uptake by ambient aerosol particles. In addition to uptake of HNO_3 on particles and in cloud drops, it photolyzes and reacts with OH

$$HNO_3 + h\nu \rightarrow OH + NO_2$$

Reaction 15a

$$HNO_3 + h\nu \longrightarrow O + HNO_2$$

Reaction 15b

$$HNO_3 + h\nu \longrightarrow H + NO_3$$

Reaction 15c

and

$$HNO_3 + OH \rightarrow NO_3 + H_2O$$

Reaction 16

(Margitan, 1982) established that Reaction 15a has a quantum yield of ~1, with only very small contributions from the two other possible photolytic pathways. The τ of HNO_3 with respect to these two reactions is long enough for HNO_3 to act somewhat as a reservoir species for NO_X during long-range transport, contributing in this way to NO_2 levels in areas remote from the source region of the NO_X that formed this HNO_3.

Geyer and Platt (2002) concluded that Reaction 14 constituted about 10% of the removal of NO_X at a site near Berlin, Germany during spring and summer. However, Dentener and Crutzen (1993) estimated 20% in summer and 80% of P(HNO_3) in winter. A modeling study by Tonnesen and Dennis (2000) reported 16 to 31% of summer HNO_3 production from Reaction 14. The importance of Reaction 14 could be much higher during winter than during summer because of the much lower concentration of OH and the enhanced stability of N_2O_5 due to lower temperatures and UV flux. Recent work in the northeastern U.S. indicates that this reaction proceeds at a faster rate in power plant plumes than in urban plumes (Brown, 2006; Brown, 2006; Frost, 2006).

OH also reacts with NO to produce nitrous acid (HNO_2).

$$OH + NO \xrightarrow{M} HNO_2$$

Reaction 17

In sunlight, HNO_2 is rapidly photolyzed back to the original reactants.

$$HNO_2 + h\nu \rightarrow OH + NO$$

Reaction 18

Reaction 17 is, however, a negligible source of HNO_2, which is formed mainly by multiphase processes. At night, heterogeneous reactions of NO_2 in aerosols or at Earth's surface result in accumulation of HNO_2 (Lammel, 1996; Jacob, 2000; Sakamaki, 1983; Pitts, 1984; Svensson, 1987; Jenkin, 1988; Lammel, 1988; Notholt, 1992; Notholt, 1992; Harris, 1982), which can be a source of morning OH to drive P(O_3).

HO_2 can react with NO_2 to produce pernitric acid (HNO_4)

$$HO_2 + NO_2 + M \rightarrow HNO_4 + M$$

Reaction 19

which then can thermally decompose and photolyze back to its original reactants. The acids formed in these gas-phase reactions are all water soluble; thus, they can be incorporated into cloud drops and in the aqueous phase of particles.

A broad range of organic N compounds are directly emitted by combustion sources or formed in the atmosphere from NO_X emissions. Organic N compounds include the PANs, nitrosamines, nitro-PAHs, and the more recently identified nitrated quinones. Oxidation of VOCs produces organic peroxy radicals (RO_2). Reaction of RO_2 radicals with NO and NO_2 produces $RONO_2$ and peroxynitrates (RO_2NO_2)

$$RO_2 + NO \xrightarrow{M} RONO_2$$

Reaction 20

$$RO_2 + NO_2 \xrightarrow{M} RO_2NO_2$$

Reaction 21

Reaction 20 is a minor branch for the reaction of RO_2 with NO; the major branch produces RO and NO_2, as discussed in the next section. However, the $RONO_2$ yield increases with carbon number (Atkinson, 2000).

The most important family of these organic nitrates is the PANs, the dominant member of the broader family of peroxyacyl nitrates which includes peroxypropionyl nitrate (PPN) of anthropogenic origin, and peroxymethacrylic nitrate (MPAN) produced from isoprene oxidation. The PANs are formed by the combination reaction of acetyl peroxy radicals with NO_2

$$CH_3C(O){-}OO + NO_2 \rightarrow CH_3C(O)OONO_2$$

Reaction 22

where the acetyl peroxy radicals are formed mainly during the oxidation of ethane (C_2H_6) along with acetaldehyde. Acetaldehyde (CH_3CHO) can be photolyzed or react with OH to yield acetyl radicals

$$CH_3{-}C(O)H + h\nu \rightarrow CH_3{-}C(O) + H$$

Reaction 23

$$CH_3{-}C(O)H + OH \rightarrow CH_3{-}C(O) + H_2O$$

Reaction 24

Acetyl radicals then react with O_2 to yield acetyl peroxy radicals.

$$CH_3{-}C(O) + O_2 + M \rightarrow CH_3C(O){-}OO + M$$

Reaction 25

However, acetyl peroxy radicals will react with NO in areas of high NO concentrations

$$CH_3(CO){-}OO + NO \rightarrow CH_3(CO){-}O + NO_2$$

Reaction 26

and the acetyl-oxy radicals will then decompose

$$CH_3(CO){-}O \rightarrow CH_3 + CO_2$$

Reaction 27

Thus, formation of PAN is favored at conditions of high ratios of NO_2 to NO which are most typically found under low total NO_X conditions. The PANs both thermally decompose and photolyze back to their reactants with τ on the order of a few hours during warm sunlit conditions: τ with respect to thermal decomposition range from ~1 hour at 298 K, to ~2.5 days at 273 K, up to several weeks at 250 K. Thus, PANs can provide a reversible sink of NO_X at cold temperatures and high solar zenith angles, allowing release of NO_2 as air masses warm. The PANs are also removed by uptake to vegetation (Sparks, 2003; Teklemariam, 2004). RO_2NO_2 produced by Reaction 21 are thermally unstable and most have very short τ of < 100 s owing to thermal decomposition back to the original reactants. They are thus not effective permanent sinks of NO_X.

2.6.2.1. O_3 Formation

O_3 is unlike most other air pollution species whose rates of formation vary directly with the emissions of their precursors in that $P(O_3)$ changes nonlinearly with the concentrations of its precursors. At the low NO_X concentrations found in most environments ranging from remote continental areas to rural and suburban areas downwind of urban centers, net $P(O_3)$ increases with increasing NO_Xlevels. At the high NO_X concentrations found in downtown metropolitan areas especially near busy streets and roadways and in power plant plumes, net destruction of O_3 by titration reaction with NO dominates. Between these two regimes is a transition stage in which $P(O_3)$ shows only a weak dependence on NO_X. In the high NO_X concentration regime, NO_2 scavenges OH (Reaction 13) which would otherwise oxidize VOCs to produce HO_2, which in turn would oxidize NO to NO_2 (Reaction 7). In the low NO_X concentration regime, VOC oxidation generates, or at least does not consume, free radicals, and $P(O_3)$ varies directly with NO_X levels. Sometimes the terms “VOC-limited” and “NO_X-limited” are used to describe these two regimes; also, the terms NO_X-limited and NO_X-saturated are used (e.g.,, Jaeglé, 2001). OH chemistry initiates HC oxidation and behaves similarly to that for O_3 with respect to NO_X concentrations (Hameed, 1979; Pinto, 1993; Poppe, 1993; Zimmermann, 1993). These considerations introduce a high degree of uncertainty into attempts to relate changes in O_3 concentration to emissions of precursors. Note that in a NO_X-limited or NO_X-sensitive regime, $P(O_3)$ is not insensitive to radical production or the flux of solar UV photons; rather, $P(O_3)$ is more sensitive to the NO_X concentrations. For example, global tropospheric O_3 is sensitive to CH_4, even though the troposphere is predominantly NO_X-limited.

Various analytical techniques have been proposed that use ambient NO_X and VOC measurements to derive information about $P(O_3)$ and particular instantiations of this O_3−NO_X-VOC sensitivity. The

National Research Council (NRC) (NRC, 1992); previously suggested that $P(O_3)$ in individual urban areas could be understood in terms of measurements of ambient NO_X and VOC during the early morning. With this approach, the summed VOC-to-NO_X unweighted by chemical reactivity is used to determine whether conditions are NO_X sensitive or VOC sensitive. However, the technique is inadequate to characterize $P(O_3)$ because it omits many factors important for $P(O_3)$, including: (1) the effect of biogenic VOCs, because they are mostly absent during early morning hours; 2) important individual differences in the ability of VOCs to generate free radicals, rather than just from total VOC, and other differences in O_3−forming potential for individual VOCs (Carter, 1995); 3) the effect of multiday transport; and (4) general changes in photochemistry as air moves downwind from urban areas (Milford et al., 1994).

Jacob et al. (1995) used a combination of field measurements and a CTM to show that $P(O_3)$ changed from NO_X-limited to NO_X-saturated as seasons changed from summer to fall at a monitoring site in Shenandoah National Park, VA. Photochemical $P(O_3)$ generally occurs together with production of other species including HNO_3, $RONO_2$, and hydrogen peroxide (H_2O_2). The relative rates of $P(O_3)$ and the production of these other species vary depending on photochemical conditions and can be used to provide information about particular O_3 precursor sensitivities.

The transition stage between NO_X-limited and NO_X-saturated is not clearly demarcated with regard to NO_X concentrations, but is highly spatially and temporally heterogeneous. In the upper troposphere, responses to NO_X additions from commercial aircraft have been found which are very similar to these in the lower troposphere. Brühl et al. (2000) found that the NO_X concentrations for determining net $P(O_3)$ or destruction are highly sensitive to the radical sources included in model calculations. Inclusion of only CH_4 and CO oxidation led to a decrease in net $P(O_3)$ in the North Atlantic flight corridor due to NO emissions from aircraft. However, inclusion of acetone photolysis shifted the maximal $P(O_3)$ to higher NO_X concentrations, thereby reducing or eliminating areas in which $P(O_3)$ rates decreased due to the aircraft NO_X emissions.

Trainer et al. (1993) suggested that the slope of the regression line between O_3 concentration and NO_Z concentration can be used to estimate the rate of $P(O_3)$ per NO_X consumed; this relationship is also known as the O_3 production efficiency (OPE). Ryerson et al. (1998; , 2001) used measured correlations between O_3 and NO_Z to identify different rates of O_3 production in plumes from large point sources. These relationships were further characterized and tested against surface concentrations with predictions from a large-scale Eulerian air quality model by Dennis et al. (2001), and Arnold, et al. (2003).

Sillman (1995) and Sillman and He (2002) identified several secondary reaction products that show different correlation patterns for NO_X-limited conditions and NO_X-saturated conditions. The most important correlations are for O_3 versus NO_Y, O_3 versus NO_Z, O_3 versus HNO_3, and H_2O_2 versus HNO_3. The correlations between O and NO_Y, and O_3 and NO_Z are especially important because measurements of NO_Y concentrations are more widely available than of other species. Ratios of measured O_3 versus NO_Z

shown in Figure 2-17 have distinctly different patterns in different locations. In rural areas and in smaller urban areas such as Nashville, TN, O_3 shows a strong correlation with NO_Z concentrations and a relatively steep slope to the regression line. By contrast, in Los Angeles O_3 concentration also increased with NO_Z, but the rate of increase was lower and the O_3 concentration for a given NO_Z concentration was generally lower. The heterogeneity of these patterns was tested in surface data at several special research sites in the southeastern U.S. and with predictions from U.S. EPA's CMAQ modeling system (Arnold, 2001; , 2003).

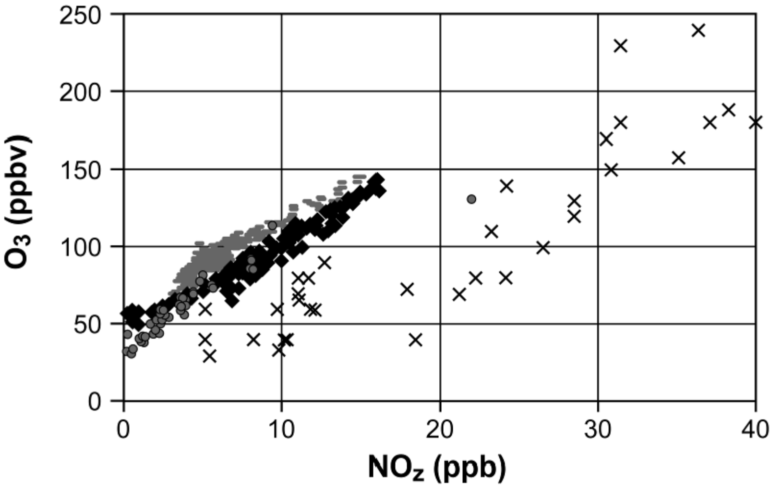


Figure 2-17. Measured values of O_3 and NO_Z ($NO_Y – NO_X$). Measured during the afternoon at rural sites in the eastern U.S. (gray circles) and in urban areas and urban plumes associated with Nashville, TN (gray dashes), Paris, FR (black diamonds) and Los Angeles, CA (Xs).

The difference between NO_X-limited and NO_X-saturated regimes is also reflected in measurements of H_2O_2 concentrations. $P(H_2O_2)$ takes place by self-reaction of photochemically generated HO_2 so H_2O_2 concentrations show a strong seasonal variance with values > 1 ppb limited mainly to summer months when photochemistry is most active (Kleinman, 1991). H_2O_2 is produced in abundance only when O_3 is produced under NO_X-limited conditions; when the photochemistry is NO_X-saturated, much less H_2O_2 is produced, owing to decreased availability of free HO_2 to self-combine. In addition, increasing NO_X concentrations tend to slow $P(H_2O_2)$ under NO_X-limited conditions. Differences between these two regimes are also related to the preferential $P(SO_4)^{2-}$ during summer and to inhibition of SO_4^{2-} and H_2O_2 production during winter (Stein, 2003). Measurements in the rural eastern U.S. (Jacob, 1995), in Nashville (Sillman, 1998), and in Los Angeles (Sakugawa, 1989) show large differences in H_2O_2 concentrations, likely due in part to differences in NO_X availability at these locations. More details on $P(O_3)$ are given in the *ISA for NO_X—Health Criteria* (EPA, 2008a).

2.6.2.2. Multiphase Interactions

Warneck (1999) constructed a box model describing the chemistry of the oxidation of NO_2 including the interactions of N species and minor processes in sunlit cumulus clouds. The relative contributions of different reactions to the oxidation of NO_2 to NO_3 10 min after cloud formation are given in Table 2-3. Where the two columns show the relative contributions with and without transition metal ions. Oxidation of NO_2 as delineated in Table 2-3 occurs mainly in the gas phase within clouds, implying that gas-phase oxidation of NO_2 by OH predominates.

Table 2-3. Relative contributions of various gas and aqueous phase reactions to aqueous NO_3 formation within a sunlit cloud, 10 minutes after cloud formation.

Reaction	% of Total [a]	% of Total [b]
Gas Phase		
$OH + NO_2 + M$	57.7	67.4
Aqueous Phase		
$N_2O_{5g} + H_2O$	8.1	11.2
$NO_3^- + Cl^-$	<0.1	0.1
$NO_3^- + SO_3^{2-}$	0.7	1.0
$NO_3^- + HCOO^-$	0.6	0.8
$HNO_4 + SO_3^{2-}$	31.9	20.5
$HOONO + NO_3^-$	0.8	<0.1
$O_3 + NO_2^-$	<0.1	<0.1

[a] In the absence of transition metals.

[b] In the presence of iron and copper ions.

Source: Adapted from Warneck (1999).

Recent laboratory studies on SO_4^{2-} and organic aerosols indicate that the reaction probability γN_2O_5 is in the range of 0.01 to 0.05 (Kane, 2001; Hallquist, 2003; Thornton, 2003). Tie et al. (2003) found that a value of 0.04 in their global model gave the best simulation of observed NO_X over the Arctic in winter. Using aircraft measurements over the northeastern U.S., Brown et al. (Brown, 2006) found that γN_2O_5 on the surfaces of particles depends strongly on their SO_4^{2-} content. They found that γN_2O_5 was highest (0.017) in regions where the aerosol SO_4^{2-} concentration was highest and lower elsewhere (< 0.0016). This result contrasts with that of Dentener and Crutzen (1993) who concluded that γN_2O_5 would be independent of aerosol composition based on a value for γN_2O_5 of 0.1, implying that the heterogeneous hydrolysis of N_2O_5 would be saturated for typical ambient aerosol surface areas. The importance of this reaction to tropospheric chemistry depends on the value of γN_2O_5. If it is 0.01 or lower, loss of NO_Y and formation of pNO_3 becomes difficult to explain, especially during winter. A decrease in

N_2O_5 concentration retards removal of NO_X by leaving more NO_2 available for reaction, and thus increases $P(O_3)$.

Based on the consistency between measurements of NO_Y partitioning and gas-phase models, Jacob (2000) considered it unlikely that HNO_3 is recycled to NO_X in the lower troposphere in significant concentrations. However, only one of the reviewed studies (Schultz, 2000) was conducted in the marine troposphere and none was conducted in the marine boundary layer (MBL). An investigation over the equatorial Pacific reported discrepancies between observations and theory (Singh, 1996), which might be explained by HNO_3 recycling. It is important to recognize that both Schultz et al. (2000) and Singh et al. (1996) involved aircraft sampling at altitude which, in the MBL, can significantly under-represent sea salt aerosols and thus most total NO_3 (defined to be HNO_3 + pNO_3) and large fractions of NO_Y in marine air (see, Huebert, 1996). Consequently, some caution is warranted in interpreting constituent ratios and NO_Y budgets based on these data.

Recent work in the Arctic has quantified significant photochemical recycling of total NO_3 to NO_X and attendant perturbations of OH chemistry in snow (Honrath, 2000; Dibb, 2002; Domine, 2002) which suggest the possibility that similar multiphase pathways could occur in aerosols. As mentioned above, NO_3 is photolytically reduced to NO_2 (Zafiriou, 1979) in acidic sea salt solutions (Anastasio, 1999). Further photolytic reduction of NO_2 to NO (Zafiriou, 1979) could provide a possible mechanism for HNO_3 recycling. Early experiments reported production of NO_X during the irradiation of artificial seawater concentrates containing NO_3 (Petriconi, 1972). Based on the above, HNO_3 recycling in sea salt aerosols is potentially important and warrants further investigation. Other possible recycling pathways involving highly acidic aerosol solutions and soot are reviewed by Jacob (2000).

Stemmler et al. (2006) studied the photosensitized reduction of NO_2 to HNO_2 on humic acid films using radiation in the UV-A through the visible spectral regions. They also found evidence for reduction occurring in the dark, reactions which may occur involving surfaces containing partly oxidized aromatic structures. For example, Simpson et al. (2006) found that aromatic compounds constituted ~20% of organic films coating windows in downtown Toronto. They calculated $p(HNO_2)$ rates compatible with observations of high HNO_2 concentrations in a variety of environments. The photolysis of HNO_2 formed this way could account for up to 60% of the integrated source of OH in the PBL. A combination of high NO_2 concentrations and surfaces of soil and buildings and other structures exposed to diesel exhaust would then be conducive to $P(HNO_2)$ and, hence, to high OH concentrations.

Ammann et al. (1998) reported the efficient conversion of NO_2 to HNO_2 on fresh soot particles in the presence of water, and suggested that interaction between NO_2 and soot particles may account for high concentrations of HNO_2 observed in urban environments. Conversion of NO_2 to HNO_2 and the subsequent photolysis of HNO_2 to NO + OH (Reaction 18) would constitute a NO_X catalyzed O_3 sink involving snow. High HNO_2 levels can lead to the rapid rise in OH shortly after sunrise, accelerating photochemical smog formation. Prolonged exposure to ambient oxidizing agents appears to deactivate this process. Bröske et al. (2003) studied the interaction of NO_2 on secondary organic aerosols and concluded that the uptake coefficients were too low for this reaction to be an important source of HNO_2 in the troposphere.

Choi and Leu (1998) evaluated interactions of HNO_3 on the model black carbon soot Degussa FW2, graphite, hexane, and kerosene soot, finding that HNO_3 decomposed to NO_2 and H_2O at higher HNO_3 surface coverages, i.e., $pHNO_3 = 10^{-4}$ Torr while none of the soot models used were reactive at $pHNO_3 = 5 \times 10^{-7}$ Torr or at temperatures below 220 K. They concluded that aircraft soot in the upper troposphere and lower stratosphere was unlikely to decrease HNO_3 concentrations.

Heterogeneous production on soot at night is believed to be the mechanism by which HNO_2 accumulates to provide an early morning source of HO_X in high NO_X environments (Harrison, 1996; Jacob, 2000). HNO_2 has been frequently observed to accumulate to levels of several ppb overnight, and this has been attributed to soot chemistry (Harris, 1982; Calvert, 1994; Jacob, 2000).

Longfellow et al. (1999) observed formation of HNO_2 when CH_4, propane, hexane, and kerosene soot were exposed to NO_2 and suggested that this reaction may account for some part of the unexplained high levels of HNO_2 observed in urban areas. However, without specific details of the surface area, porosity, and amount of soot available for this reaction, reactive uptake values cannot be estimated reliably. Longfellow, et al. (1999) noted that soot and NO_2 are produced in close proximity during combustion, and that large quantities of HNO_2 have been observed in aircraft plumes.

Saathoff et al. (2001) studied the heterogeneous loss of NO_2, HNO_3, NO_3/N_2O_5, HO_2/HO_2NO_2 on soot aerosol using a large aerosol chamber. Reaction periods of up to several days were monitored and results used to fit a detailed model. Saathoff et al. (2001) derived reaction probabilities at 294 K and 50% RH for NO_2, NO_3, HO_2, and HO_2NO_2 deposition to soot, HNO_3 reduction to NO_2, and N_2O_5 hydrolysis. When these probabilities were included in photochemical box model calculations of a 4–day smog event, the only noteworthy influence of soot was a 10% reduction in the second day maximum O_3 concentration for a soot loading of 20 $\mu g/m^3$. Note that this loading is roughly a factor of 10 greater than any observed black carbon loadings in U.S. urban areas, even during air pollution episodes.

Muñoz and Rossi (2002) conducted Knudsen cell studies of HNO_3 uptake on black and grey decane soot produced in lean and rich flames, respectively and observed HNO_2 as the chief species released following HNO_3 uptake on gray soot, with NO and traces of NO_2 from black soot. They concluded that these reactions would have relevance only in special situations in urban settings where soot and HNO_3 are present in high concentrations simultaneously.

The biosphere also interacts with NO_X through HC emissions and their subsequent reactions to form multi-functional $RONO_2$, of which isoprene nitrates are an important class. Isoprene reacts with OH to form a radical that adds NO_2 to form a hydroxyalkyl nitrate. The combination of OH and NO_3

functional groups makes these compounds especially soluble with low vapor pressures and they likely deposit rapidly (Shepson, 1996; Treves, 2000). Many other unsaturated HCs react by analogous routes. Observations at Harvard Forest show a substantial fraction of total NO_Y not accounted for by NO, NO_2 and PAN, and attribute the missing fraction to $RONO_2$ (Munger, 1998; Horii, 2006). Furthermore, the total NO_Y flux there exceeds the sum of HNO_3, NO_X, and PAN, which implies that the $RONO_2$ are a substantial fraction of N deposition. Other observations that show evidence of hydoxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

HNO_2 formation on vegetative surfaces at night has long been observed based on measurements of positive gradients (Harrison, 1994). Surface reactions of NO_2 enhanced by moisture have been proposed to explain these results. Production was evident at sites with high ambient NO_2 concentrations; at low NO_2 concentrations, uptake of HNO_2 exceeded the source. Daytime observations of HNO_2 when rapid photolysis depletes ambient concentrations to very low levels implies large sources of photo-induced HNO_2 could be present at a variety of forested sites where measurements have been made. Emissions rates ranging from 200–1800 ppt/h have been estimated (Zhou, 2003; Zhou, 2002), which are ~20 times faster than all nighttime sources of HNO_2 formation. Reliable estimates to extend this emissions rate nationwide have not been made. Additional evidence of light-dependent reactions to produce HNO_2 comes from discovery of a HNO_2 artifact in pyrex sample inlet lines exposed to ambient light. Either covering the inlet or washing it eliminated the HNO_2 formation (Zhou, 2002). Similar reactions might serve to explain observations of UV-dependent production of NO_X in empty foliar cuvettes exposed to ambient air (Hari, 2003; Raivonen, 2003).

Production of HNO_2 in the dark is currently believed to occur via a heterogeneous reaction involving NO_2 on wet surfaces (Jenkin, 1988; Pitts, 1984; He, 2006; Sakamaki, 1983), with a mechanism that is first-order in both NO_2 and H_2O (Kleffmann, 1998; Svensson, 1987) despite the stoichiometry. However, the molecular pathway of the mechanism is still under debate. Jenkin et al. (1988) postulated a $H_2O{\cdot}NO_2$ water complex reacting with gas phase NO_2 to produce HNO_2, which is inconsistent with the formation of an N_2O_4 intermediate leading to HNO_2 as proposed by Finlayson-Pitts et al. (2003). Another uncertainty is whether the reaction forming HNO_2 is dependent on water vapor (Svensson, 1987; Stutz, 2004) or water adsorbed on surfaces (Kleffmann, 1998). Furthermore, the composition of the surface and the available amount of surface or surface-to-volume ratio can significantly influence the HNO_2 production rates (Kaiser, 1977; Kleffmann, 1998; Svensson, 1987), which may explain the difference in the rates observed between laboratory and atmospheric measurements.

There is no consensus on a chemical mechanism for photo-induced HNO_2 production. Photolysis of HNO_3 or NO_3^- absorbed on ice or in surface water films has been proposed (Honrath, 2002; Ramazan, 2004; Zhou, 2001; Zhou, 2003), but alternative pathways include NO_2 interaction with organic surfaces such as humic substances (George, 2005; Stemmler, 2006). Note that either NO_3 photolysis or heterogeneous reaction of NO_2 are routes for recycling deposited NO_X back to the atmosphere in an active form. NO_3 photolysis would return N that heretofore was considered irreversibly lost, while surface reactions between NO_2 and water films or organic molecules would decrease the effectiveness of observed NO_2 deposition if the HNO_2 were re-emitted.

Halogen Chemistry

Four decades of observational data on O_3 in the troposphere have revealed numerous anomalies not easily explained by gas-phase HO_X-NO_X photochemistry. The best-known example is the dramatic decrease in ground-level O_3 during polar sunrise due to multiphase catalytic cycles involving inorganic Br and Cl radicals (Barrie, 1988; Martinez, 1999; Foster, 2001). Other examples of anomalies in tropospheric O_3 at lower latitudes include O_3 concentrations < 10 ppb in the MBL and overlying free troposphere (FT) at times over large portions of the tropical Pacific (Kley, 1996) as well as post-sunrise O_3 decreases over the western subtropical Pacific Ocean (Nagao, 1999), the temperate Southern Ocean (Galbally, 2000), and the tropical Indian Ocean (Dickerson, 1999). The observed O_3 depletions in near-surface marine air are generally consistent with the model-predicted volatilization of Br_2, BrCl, and Cl_2 from sea salt aerosols through autocatalytic halogen "activation" mechanisms (see e.g., 1996; Von Glasow, 2002) involving these aqueous-phase reactions

$$HOBr + Br^{-} + H^{+} \rightarrow Br_2 + H_2O$$

Reaction 28

$$HOCL + Br^{-} + H^{+} \rightarrow BrC1 + H_2O$$

Reaction 29

$$HOC1 + C1^{-} + H^{+} \rightarrow C1_2 + H_2O$$

Reaction 30

In polluted marine regions at night, the heterogeneous reaction

$$N_2O_5 + C1^{-} \rightarrow C1NO_2 + NO_3^{-}$$

Reaction 31

may also be important (Finlayson-Pitts, 1989; Behnke, 1997; Erickson, 1999). Br_2, BrCl, Cl_2, and $ClNO_2$ volatilize and photolyze in sunlight to produce atomic Br and Cl. The acidification of sea salt aerosol via incorporation of HNO_3 and other acid leads to volatilization of HCl (Erickson, 1999)

$$HNO_3 + Cl^- \rightarrow HCl + NO_3^-$$

Reaction 32

and the corresponding shift in phase partitioning can accelerate deposition flux to the surface of total pNO_3 (Russell, 2003; Fischer, 2006).

The set of N reactions with aerosol salts in marine atmospheres sketched briefly here was reviewed in detail by De Haan et al. (De Haan, 1999). This chemistry remains important not only for halogen cycling and atmospheric oxidation reactions (Andreae, 1997), but also because through them NO3 can be shifted from gas-phase HNO3 or from fine-mode aerosol after dissociation of NH4NO3, for example, to coarse-mode particles, thereby enhancing the potential for local N deposition to coastal regions. The actual areal extent of N deposition resulting from gas-to-particle $NO3^-$ conversion, however, is a complex function of local wind speeds, as shown by Pryor and Sørensen (2000): with moderate winds of 3.5–10 m/s, gas-phase HNO3 V_d exceeded that of an average NaNO3 particle, whereas at higher and lower wind speeds the reverse was true. This means that as a result of gas-to-particle NO3 conversion, under commonly moderate winds, less N would be deposited locally and more would be available for transport and deposition in a larger area of extent.

In polluted coastal regions where HCl from Reaction 33 often exceeds 1 ppb, significant additional atomic Cl^- is produced (Singh, 1988; Keene, 2007).

$$HCl + OH \rightarrow Cl + H_2O$$

Reaction 33

Following production, Br and Cl atoms catalytically destroy O_3

$$X + O_3 \rightarrow XO + O_2$$

Reaction 34

$$XO + HO_2 \rightarrow HOX + O_2$$

Reaction 35

$$HOX + h\nu \rightarrow OH + X$$

Reaction 36

where X = Br and Cl.

Formation of Br and Cl nitrates via

$$XO + NO_2 \rightarrow XNO_3$$

Reaction 37

and the subsequent reaction of XNO_3 with sea salt and sulfate aerosols

$$XNO_3 + H_2O \rightarrow HOX + H^+ + NO_3^-$$

Reaction 38

and

$$XNO_3 + Y^- \rightarrow XY + NO_3^-$$

Reaction 39

where Y = Cl, Br, or I accelerates conversion of NO_X to pNO_3 and thereby contributes indirectly to net O_3 destruction (Sander, 1999; Vogt, 1999; Pszenny, 2004).

Most XNO_3 reacts via Reaction 38 on sea salt whereas Reaction 39 is more important on pSO_4. Partitioning of HCl on pSO_4 following Henry's Law provides Cl^- for Reaction 39 to form BrCl. Product NO_3^- from both Reaction 38 and Reaction 39 partitions with the gas-phase HNO_3 following Henry's Law. Because most aerosol size fractions in the MBL are near equilibrium with respect to HNO_3 (Erickson, 1999; Keene, 2004), both pSO_4 and sea salt aerosol can sustain the catalytic removal of NO_X and re-activation of Cl and Br with no detectable change in composition. The photolytic reduction of NO_3 in sea salt aerosol solutions recycles NO_X to the gas phase (Pszenny, 2004). Halogen chemistry also affects O_3 indirectly by altering OH-to-HO_2 ratios through the steps of Reactions 33 through 34 (e.g.,, Stutz, 1999; Bloss, 2005).

In addition to O_3 destruction via Reaction 34, atomic Cl^- oxidizes HCs primarily via H abstraction to form HCl vapor and organic products (Jobson, 1994; Pszenny, 2006). The enhanced supply of odd-H radicals from HC oxidation leads to net $P(O_3)$ in the presence of sufficient NO_X (Pszenny, 1993). Available evidence suggests that Cl^- chemistry may be a significant net source for O_3 in polluted coastal urban air (Tanaka, 2003; e.g.,, Finley, 2006).

An analogous autocatalyic O_3 destruction cycle involving multiphase I chemistry also operates in the marine atmosphere (Alicke, 1999; Vogt, 1999; McFiggans, 2000; Ashworth, 2002). In this case, the primary source of I is believed to be either photolysis of CH_2I_2, other I-containing gases (Carpenter, 1999; Carpenter, 2003), or perhaps I_2 (Saiz-Lopez, 2004; McFiggans, 2005; McFiggans, 2004) emitted by micro-and macro flora. Sea salt and pSO_4 provide substrates for multiphase reactions that sustain the catalytic I-IO cycle. The reaction of IO with NO_2 followed by uptake of INO_3 into aerosols accelerates conversion of NO_X to pNO_3, contributing to net O_3 destruction and changing the deposition of N compounds as described above.

2.6.2.3. Nitro-PAH Formation

Nitro-PAHs are generated from incomplete combustion processes through electrophilic reactions of PAHs in the presence of NO_2 (International Agency for Research on Cancer (IARC) (1989), 1989; World Health Organization (WHO), 2003 (2003); structures for example nitro-PAHs are shown in Figure 2-18. Among combustion sources, diesel emissions have been identified as the major source of nitro-PAHs in ambient air (Bezabeh, 2003; Gibson, 1983; Schuetzle, 1983; Tokiwa, 1986). Direct emissions of nitro-PAHs in PM vary with type of fuel, vehicle maintenance, and ambient conditions.

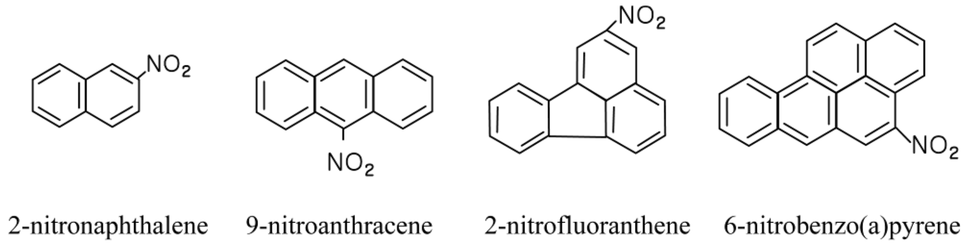


Figure 2-18. Structures of some nitro-PAHs.

In addition to being directly emitted, nitro-PAHs are formed from both gas-phase and heterogeneous reactions of PAHs with gaseous N pollutants (Arey, 1998; Arey, 1986; Perrini, 2005; Pitts, 1987; Sasaki, 1997; Zielinska, 1989). Different isomers of nitro-PAHs are formed through different formation processes. For example, the most abundant nitro-PAH in diesel particles is 1–nitropyene (1NP), followed by 3–nitrofluoranthene (3NF) and 8–nitrofluoranthene (8NF) (Bezabeh, 2003; Gibson, 1983; Schuetzle, 1983; Tokiwa, 1986; Zielinska, 1989). However, in ambient particulate organic matter (POM), 2–nitrofluoranthene (2NF) is the dominant compound, followed by 1NP and 2–nitropyrene (2NP) (Arey, 1989; Arey, 1989; Bamford, 2003; Reisen, 2005), although 2NF and 2NP are not directly emitted from primary combustion emissions. Reaction mechanisms for various nitro-PAH formation processes are schematized in Figure 2-19.

The dominant process for the formation of nitro-PAHs in the atmosphere is gas-phase reaction of PAHs with OH in the presence of NO_X (Arey, 1986, 1998; Atkinson, 1994; Ramdahl, 1986; Sasaki, 1997). The postulated reaction mechanism of OH with PAHs involves addition of OH at the site of highest electron density of the aromatic ring, for example, the 1-position for pyrene (PY) and the 3-position for fluoranthene (FL), followed by addition of NO_2 to the OH-PAH adduct and elimination of water to form the nitroarenes (as in Figure 2-19) (Arey, 1986; Atkinson, 1990; Pitts, 1987). After formation, nitro-PAHs with low vapor pressures (such as 2NF and 2NP) immediately migrate to particles under ambient conditions (Fan, 1995; Feilberg, 1999). The second order rate-constants for the reactions of OH with most PAHs range from 10^{-10} to 10^{-12}/cm/molecule/s at 298 K with the yields ranging from ~0.06

to ~5% (Atkinson, 1994). 2NF and 2NP have been found to be the most abundant nitro-PAHs formed via reactions of OH with gaseous PY and FL, respectively, in ambient air.

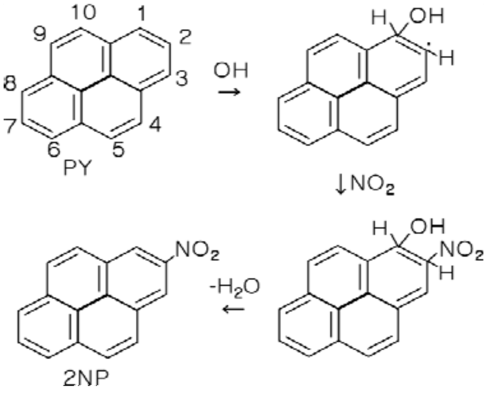


Figure 2-19. Formation of 2NP from the reaction of OH with gaseous PY.

The concentrations for most nitro-PAHs found in ambient air are much lower than 1 pg/m^3, except NNs, 1NP, and 2NF, which can be present at several pg/m^3. These concentrations are lower by as much as a factor of 2 to 1000 than their parent PAHs; however, nitro-PAHs are much more toxic than PAHs (Durant, 1996; Grosovsky, 1999; Salmeen, 1982; Tokiwa, 1998; Tokiwa, 1986), and are present on particles with a mass median diameter < 0.1 µm, perhaps altering their delivery to susceptible organisms in the environment.

Additional information on nitro-PAHs is included in Chapter 2 and Annex B of the latest *ISA for Oxides of NO$_X$—Human Health Criteria* (EPA, 2008a).

2.6.3. SO$_X$ Chemistry

Gas phase oxidation of SO_2 is initiated by the reaction

$$SO_2 + OH + M \rightarrow HSO_3 + M$$

Reaction 40

followed by

$$HSO_3 + O_2 \rightarrow SO_3 + HO_2$$

Reaction 41

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Reaction 42

Because the saturation vapor pressure of H_2SO_4 is extremely low, it will be removed rapidly by transfer to the aqueous phase of aerosol particles and cloud droplets. Depending on atmospheric conditions and the concentrations of other ambient particles and gas-phase species that can participate in new particle formation, it can also nucleate to form new particles. Rate coefficients for the reactions of SO_2 with either HO_2 or NO_3 (Jet Propulsion Laboratory, 2003) are too low to be significant.

SO_2 is chiefly but not exclusively primary in origin; it is also produced by the photochemical oxidation of reduced sulfur compounds such as dimethyl sulfide ($CH_3{-}S{-}CH_3$), hydrogen sulfide (H_2S), carbon disulfide (CS_2), carbonyl sulfide (OCS), methyl mercaptan ($CH_3{-}S{-}H$), and dimethyl disulfide ($CH_3{-}S{-}S{-}CH_3$) which are all mainly biogenic in origin. Their sources are discussed in Section 2.3.2 just above. Table 2-4 lists the atmospheric lifetimes of reduced sulfur species with respect to reaction with various oxidants. Except for OCS, which is lost mainly by photolysis (τ~6 months), these species are lost mainly by reaction with OH and NO_3.

Because OCS is relatively long-lived in the troposphere, it can be transported upwards into the stratosphere.

Table 2-4. Atmospheric lifetimes of SO_2 and reduced sulfur species with respect to reaction with OH, NO_3, and Cl radicals.

Compound	OH		NO_3		CL	
	k x 10^{12}	T	k x 10^{12}	T	k x 10^{12}	T
SO_2	1.6	7.2 d	NA		NA	
$CH_3{-}S{-}CH_3$	5.0	2.3 d	1.0	1.1–h	400	29 d
H_2S	4.7	2.2 d	NA		74	157 d
CS_2	1.2	9.6 d	< 0.0004	> 116 d	< 0.004	Nr
OCS	0.0019	17 y	< 0.0001	> 1.3 y	< 0.0001	Nr
$CH_3{-}S{-}H$	33	8.4 h	0.89	1.2 h	200	58 d
$CH_3{-}S{-}S{-}CH_3$	230	1.2 h	0.53	2.1–h	NA	

[1] Rate coefficients were taken from JPL Chemical Kinetics Evaluation No. 14 (Jet Propulsion Laboratory, 2003)

NA = Reaction rate coefficient not available.

OH = 1 × 10^6/cm

NO_3 = 2.5 × 10^8/cm

Cl = 1 × 10^3/cm

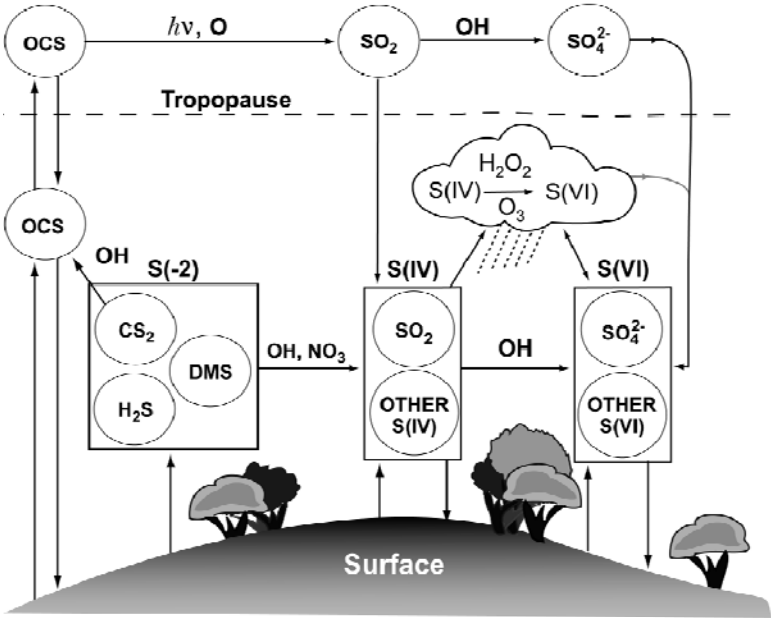
N_r = Rate coefficient too low to be relevant as an atmospheric loss mechanism. Rate coefficients were calculated at 298 K and 1 atmosphere.

Source: Seinfeld and Pandis (1998)

Crutzen (1976) proposed that its oxidation serves as the major source of SO_4^{2-} in the stratospheric Junge layer, (1961) during periods when volcanic plumes do not reach the stratosphere. However, the flux of OCS into the stratosphere is probably not sufficient to maintain this stratospheric aerosol layer. Myhre et al. (2004) proposed instead that SO_2 transported upwards from the troposphere is the most likely source since the upward flux of OCS is too small to sustain observed SO_4^{2-} loadings in the Junge layer.

In addition, in situ measurements of the isotopic composition of S do not match those of OCS (Leung, 2002).

Reaction with NO_3^- at night most likely represents the major loss process for DMS and methyl mercaptan, although the mechanisms are not well understood. Initial attack by NO_3^- and OH^- involves H atom abstraction, with a smaller branch leading to OH^- addition to the S atom. The OH^- addition branch increases in importance as temperatures decrease, becoming the major pathway below temperatures of 285 K (Ravishankara, 1997). The adduct may either decompose to form methanesulfonic acid (MSA) or undergo further reactions in the main pathway to yield dimethyl sulfoxide (Barnes, 1991). Following H atom abstraction from DMS, the main reaction products include MSA and SO_2. The ratio of MSA to SO_2 is strongly temperature dependent, varying from about 0.1 in tropical waters to about 0.4 in Antarctic waters (Seinfeld, 1998). SO_4^{2-} in excess of that expected from sea salt aerosols is related mainly to the production of SO_2 from the oxidation of DMS. These transformations among atmospheric S compounds are summarized in Figure 2-20.



Source: Adapted from Berresheim et al. (1995).

Figure 2-20. Transformations of sulfur compounds in the atmosphere.

2.6.3.1. Multi-phase SO_X Chemistry

The major S species in clouds are hydrogen sulfite (HSO_3^-) and the sulfite ion (SO_3^{2-}). Both are derived from the dissolution of SO_2 in water, and are grouped together as S(IV); bisulfate ion (HSO_4^-) and SO_4^{2-} are grouped together as S(VI). The chief species capable of oxidizing S(IV) to S(VI) in cloud water are O_3, H_2O_2 or organic peroxides, OH^-, and ions of transition metals such as iron (Fe), manganese

(Mn) and copper (Cu) in the presence of O_2. The basic mechanism of the aqueous phase oxidation of SO_2 has long been studied and can be found in numerous texts on atmospheric chemistry; see for example, Seinfeld and Pandis (1998), Finlayson-Pitts and Pitts (1999, Jacob (1999, and Jacobson (2002). Following Jacobson (2002, the steps involved in the aqueous phase oxidation of SO_2 can be summarized as: (1) dissolution of SO_2

$$SO_2(g) \Leftrightarrow SO_2(aq)$$

Reaction 43

and (2) formation and dissociation of H_2SO_3

$$SO_2(aq) + H_2O(aq) \Leftrightarrow H_2SO_3 \Leftrightarrow H^+ + HSO_3{}^- \Leftrightarrow 2H^+ + SO_3{}^{2-}$$

Reaction 44

In the pH range commonly found in rainwater, pH 2 to 6, the most important reaction converting S(IV) to S(VI) is

$$HSO_3{}^- + H_2O_2 + H^+ \Leftrightarrow SO_4{}^{2-} + H_2O + 2H^+$$

Reaction 45

as $SO_3{}^{2-}$ is much less abundant than $HSO_3{}^-$.

Another pathway to aqueous-phase oxidation of S(IV) is reaction with O_3

$$HSO_3{}^- + O_3 + OH^- \rightarrow SO_4{}^{2-} + H_2O + O_2$$

Reaction 46

But while the gas-phase reaction of SO_2 with O_3 is slow, the rate coefficient for Reaction 46 in the aqueous phase is rapid, and increases up to a value of ~5 x 10-3 with increasing pH between 1 and 3 (Finlayson-Pitts, 2000). Major pathways for the aqueous-phase oxidation of S(IV) to S(VI) as a function of pH are shown in Figure 2-21.

For pH up to about 5.3, H_2O_2 is the dominant oxidant converting S(IV) to S(VI), while at pH > 5.3, O_3 becomes dominant, followed by Fe(III), using characteristic values found in Seinfeld and Pandis (1998). However, differences in concentrations of oxidants result in differences in the pH at which this transition occurs. It should also be noted that the oxidation of SO_2 by O_3 and O_2 tends to be self-limiting: as $SO_4{}^{2-}$ is formed, the pH decreases and the rates of these reactions decrease. Higher pH levels are expected to be found mainly in marine aerosols. However, in marine aerosols, the Cl^-catalyzed oxidation of S(IV) may be more important (Zhang, 1991; Hoppel, 2005). Because $NH_4{}^+$ is so effective in neutralizing acidity, it, too, affects the rate of oxidation of S(IV) to S(VI) and the rate of dissolution of SO_2 in particles and cloud droplets.

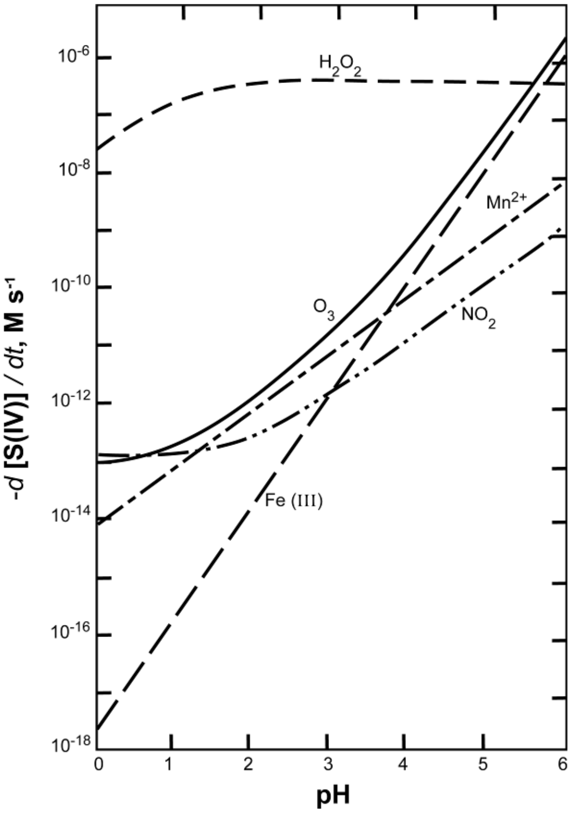


Figure 2-21. Comparison of aqueous-phase oxidation paths. The rate of conversion of S(IV) to S(VI) is shown as a function of pH. Conditions assumed are: $[SO_{2(g)}]$ = 5 ppb; $[NO_{2(g)}]$ = 1 ppb; $[H_2O_{2(g)}]$ = 1 ppb; $[O_{3(g)}]$ = 50 ppb; $[Fe(III)_{(aq)}]$ = 0.3 µM; $[Mn(II)_{(aq)}]$ = 0.3 µM.

A comparison of the relative rates of oxidation by gas and aqueous phase reactions by Warneck (1999) indicates that on average only ~ 20% of SO_2 is oxidized by gas-phase reactions; the remainder is oxidized by aqueous phase reactions. Warneck's box model (1999) describing the chemistry of the oxidation of SO_2 and NO_2 includes interactions of S species and minor processes in sunlit cumulus clouds. The relative contributions of different reactions to the oxidation of S(IV) species to S(VI) 10 min after cloud formation are given in Table 2-5. The two columns show the relative contributions with and without transition metal ions. As can be seen from Table 2-5, SO_2 within a cloud (gas + cloud drops) is oxidized mainly by H_2O_2 in the aqueous phase, while and the gas-phase oxidation by OH is small by comparison. A much smaller contribution in the aqueous phase is made by methyl hydroperoxide (CH_3OOH) because it is formed mainly in the gas phase and its Henry's Law constant is several orders of magnitude smaller that of H_2O_2. After H_2O_2, HNO_4 is the major contributor to S(IV) oxidation.

The values shown in Table 2-5 here and Table 2-3 above for NO_3 indicate that gas-phase oxidation accounts for only ~ 20% of SO_2 oxidation but ~ 90% of NO_2 oxidation.

Table 2-5. Relative contributions of various reactions to the total S(IV) oxidation rate within a sunlit cloud, 10 min after cloud formation.

Reaction	% of Total [a]	% of Total [b]
Gas Phase		
$OH + NO_2 + M$	57.7	67.4
Aqueous Phase		
$N_2O_{5g} + H_2O$	8.1	11.2
$NO_3 + Cl^-$	<0.1	0.1
$NO_3 + SO_3^{2-}$	0.7	1.0
$NO_3 + HCOO^-$	0.6	0.8
$HNO_4 + SO_3^{2-}$	31.9	20.5
$HOONO + NO_3^-$	0.8	<0.1
$O_3 + NO_2^-$	<0.1	<0.1

[a] In the absence of transition metals.

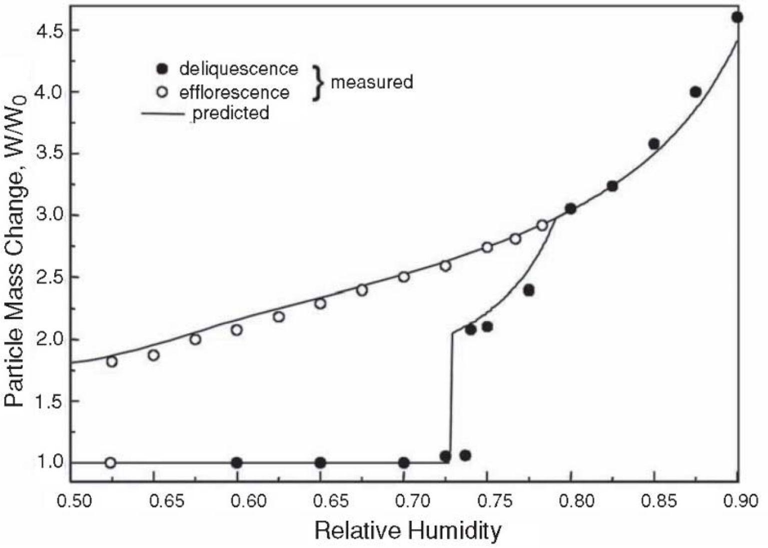
[b] In the presence of iron and copper ions.

Source: Adapted from Warneck (1999).

In areas away from strong pollution sources, the SO_2 τ is ~7 days, based on measurements of the rate constant for Reaction 41 (Jet Propulsion Laboratory, 2003) and a nominal OH concentration of $10^6/cm^3$. However, the mechanism of SO_2 oxidation at a particular location depends on local environmental conditions. For example, near stacks, oxidants such as OH are depleted and almost no SO_2 is oxidized in the gas phase. Further downwind, as the plume is diluted with background air, the gas phase oxidation of SO_2 increases in importance. Finally, even further downwind when conditions in the plume can become more oxidizing than in background air, the SO_2 oxidation rate could exceed that in background air. SO_2 in the PBL is also removed from the atmosphere by dry deposition to moist surfaces, resulting in an atmospheric τ with respect to dry deposition of ~ 1 day to 1 week. Wet deposition of S naturally depends on the variable nature of rainfall, but in general results in a τ of SO_2 ~7 days, too. These two processes, oxidation and deposition, lead to an overall τ of SO_2 in the atmosphere of 3 to 4 days.

Multiphase chemical transformations involving inorganic halogenated compounds effect changes in the multiphase cycling of SO_X in ways analogous to their effects on NO_X. Oxidation of dimethylsulfide $(CH_3)_2S$ by BrO produces dimethylsulfoxide $(CH_3)_2SO$ (Barnes, 1991; Toumi, 1994), and oxidation by Cl leads to formation of SO_2 (Keene, 1996). $(CH_3)_2SO$ and SO_2 are precursors for methanesulfonic acid (CH_3SO_3H) and H_2SO_4. In the MBL, virtually all H_2SO_4 and CH_3SO_3H vapor condenses onto existing aerosols or cloud droplets, which subsequently evaporate, thereby contributing to aerosol growth and acidification. Unlike CH_3SO_3H, H_2SO_4 also has the potential to produce new particles (Korhonen, 1999; Kulmala, 2000), which in marine regions is thought to occur primarily in the FT.

Excepting H_2SO_4, inorganic particles are solid at low RH, and their composition determines their deliquescence thresholds for forming saturated aqueous solutions. Crystallization is not simply the reverse of deliquescence but is a process subject to hysteresis; see the NaCl+Na_2SO_4 example in Figure 2-22, and Tang and Munkelwitz (1993) for deliquescence RH points of other inorganic particles.



Source: Pandis, 2004, in McMurry et al., 2004.

Figure 2-22. Relative humidity (RH) effects on deliquescence and efflorescence points for a NaCl+Na_2SO_4 particle, indicating deliquescence at ~72% RH and re-crystallization at ~52% RH. Points are measurements from Tang (1997); solid line is aerosol thermodynamic model prediction of (Ansari, 2000).

Particles with several components behave similarly to the example of Na_2SO_4 but with more complex curves and generally have deliquescence RH points below these of their constituent components (Wexler, 1991).

Saiz-Lopez et al. (2004) estimated that observed levels of BrO at Mace Head Atmospheric Research Station in Ireland would oxidize $(CH_3)_2S$ ~6 times faster than OH and thereby substantially increase $P(H_2SO_4)$ and other condensible S species in the MBL. SO_2 is also scavenged by deliquesced aerosols and oxidized to H_2SO_4 in the aqueous phase by several strongly pH-dependent pathways (Chameides, 1992; Keene, 1998; Vogt, 1996). Model calculations indicate that oxidation of S(IV) by O_3 dominates in fresh, alkaline sea salt aerosols, whereas oxidation by hypohalous acids, primarily HOCl, dominates in moderately acidic solutions. Additional non-sea salt (nss) pSO_4 is generated by SO_2 oxidation in cloud droplets (Clegg, 1998). Ion-balance calculations indicate that most of the nss pSO_4 in short-lived sea salt size fractions accumulates in acidic aerosol solutions or in acidic aerosols processed through clouds or both (e.g.,, Keene, 2004). The production, cycling, and associated radiative effects of S-containing aerosols in marine and coastal air are regulated in part by chemical transformations involving inorganic halogens (Von Glasow, 2002). These transformations include: dry-deposition fluxes of nss pSO_4 in marine air dominated, naturally, by the sea salt size fractions (Huebert, 1996; Turekian, 2001) HCl phase partitioning that regulates sea salt pH and associated pH-dependent pathways for S(IV) oxidation (Keene, 2002; Pszenny, 2004) and potentially important oxidative reactions with reactive halogens for

$(CH_3)2S$ and S(IV). However, both the absolute magnitudes and relative importance of these processes in MBL S cycling are poorly understood.

Iodine chemistry has been linked to ultrafine particle bursts at Mace Head (O'Dowd, 2002; O'Dowd, 1999). Observed bursts coincide with the elevated IO concentration and are characterized by particle concentrations increasing from background levels to up to 300,000/cm^3 on a time scale of seconds to minutes. This newly identified source of marine aerosol would provide additional aerosol surface area for condensation of SO_X and thereby presumably diminish the potential for nucleation pathways involving H_2SO_4. However, a subsequent investigation in polluted air along the New England, USA coast found no correlation between periods of nanoparticle growth and corresponding concentrations of I oxides (Fehsenfeld, 2006).

2.6.4. NH_X Interactions

Figure 2-17 above illustrated the central role NH_3 can play in the atmospheric chemistry of NO_X and SO_X. This results in part from its being the most common soluble base in the atmosphere and a range of chemical reactions. OH attack on NH_3 proceeds by

$$NH_3 + OH \rightarrow NH_2 + H_2O$$

Reaction 47

$$k^{298K}_{37} = 1.6 \times 10^{-13}\ molec/cm^3/s$$

Reaction 48

The fate of the NH_2 radical is not known with certainty, but in polluted atmospheres can be

$$NH_2 + O_3 \rightarrow NH, NHO, NO$$

Reaction 49

$$NH_2 + NO_2 \rightarrow N_2$$

Reaction 50

$$NH_2 + NO_2 \rightarrow N_2O + H_2O$$

Reaction 51

However, with typical OH concentration of 1 to 2 x 10^6/cm^3, the τ of NH_3 against the initial reaction is ~ 30 to 70 days, sufficiently long that this is a small sink compared to NH_3 uptake by cloud droplets where it is reduced to NH_4^+

$$NH_3(g) + H_2O \leftrightarrow NH_3{\cdot}H_2O(aq) \leftrightarrow NH_4^+ + OH$$

Reaction 52

Gas-phase NH_3 also reacts with gas-phase HNO_3 to form particulate NH_4NO_3

$$NH_3 + HNO_3 \leftrightarrow NH_4NO_3$$

Reaction 53

and with aqueous-phase H_2SO_4 to from particulate and aqueous-phase NH_4HSO_4 and $(NH_4)_2SO_4$

$$NH_3(g) + H_2SO_4(l) \rightarrow NH_4HSO_4\ (s,l)$$

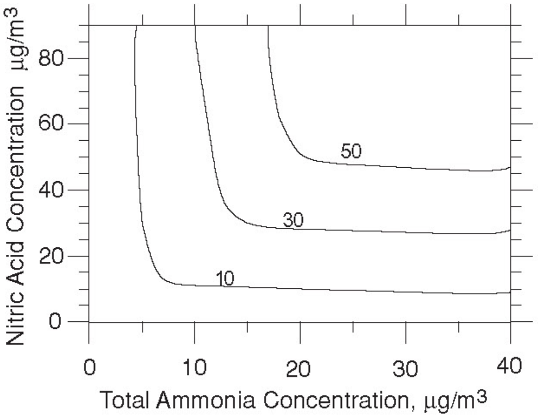
Reaction 54

$$NH_3(g) + NH_4HSO_4(l) \rightarrow (NH_4)_2SO_4(s,l)$$

Reaction 55

These products are of special note because submicron pNH_4HSO_4 and $(pNH_4)_2SO_4$ can act as cloud condensation nuclei, but the H_2SO_4+H_2O system does not readily undergo nucleation without addition of NH_4^+ (Coffman, 1995; Kulmala, 2007). They are also of note because Reaction 53 and Reaction 54 are not reversible under typical ambient conditions while Reaction 52 resulting in creation of NH_4NO_3 is reversible. The pNO_4NO_3 is in a thermodynamic equilibrium with NH_4^+ and HNO_3 in the gas phase such that lower temperatures shift the equilibrium toward greater production of pNH_4NO_3 and away from the gas phase. Higher RH also shifts the equilibrium toward liquid-phase pNH_4NO_3. For these reasons, and because gas-phase NH_3 will neutralize SO_4^{2-} preferentially first, pNH_4NO_3 can only form when an excess of gas-phase NH_3 first exists.

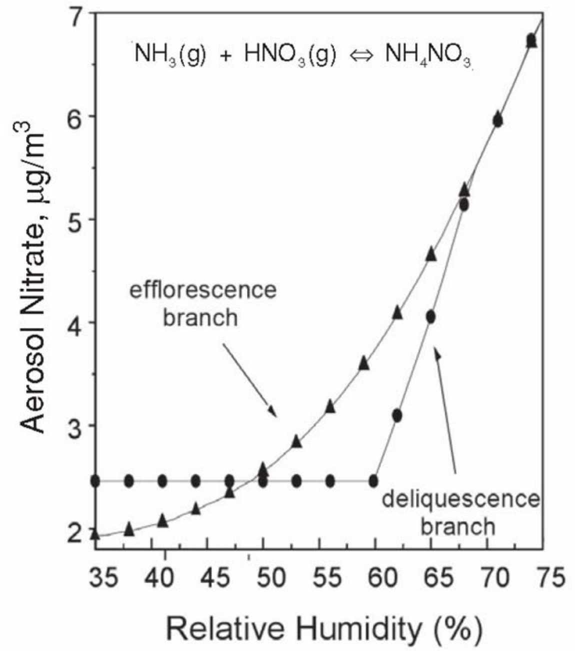
Along with HNO_3 and H_2SO_4, NH_3 can be limiting in the formation of secondary atmospheric particles containing NO_3 and SO_4^{2-}. Measurements and thermodynamics models of free and condensed-phase precursors have been used to predict the limiting reactant under different atmospheric conditions (Watson, 1994; Blanchard, 2000; Dennis, 2001). Figure 2-23 shows results from one application of this technique from Blanchard et al. (2000) with isopleths of NO_3 as predicted from total (gas and particulate phase) HNO_3 and NH_3, with 25 ug/m^3 SO_4^{2-} and 2 ug/m^3 total Cl. Formation of pNO_3 is limited by total NH_3 availability but not HNO_3 where isolines are vertical. NO_3 exists predominately in the condensed phase where isolines are horizontal, and formation is not limited by NH_3 there. These relationships have also been confirmed in field measurements like those reported for NO_3 aloft in Arnold and Luke (2007).



Source: Adapted from Blanchard et al. (2000).

Figure 2-23. Predicted isolines of particulate NO_3 concentrations (ug/m^3) as a function of total HNO_3 and NH_3 at 293 K and 80 percent relative humidity, and with 25 ug/m^3 SO_4^{2-} and 2 ug/m^3 total Cl.

Changing RH and particle water content also changes the partitioning between gas and condensed phases for semivolatile species like atmosphere NO_3; see Figure 2-24 for the example of NH_4NO_3.



Source: Pandis, 2004, in McMurry et al., 2004.

Figure 2-24. Predicted particulate NO_3 concentration as a function of relative humidity for a typical environment. Actual measured values depend on aging characteristics of the particle.

The phase partitioning of NH_3 with deliquesced aerosol solutions is controlled primarily by the thermodynamic properties of the system

$$NH_{3g} \overset{K_H}{\leftrightarrow} [NH_{3aq}] \overset{K_b}{\leftrightarrow} [NH_4^+] + K_W/[H^+]$$

Reaction 56

where K_H and K_b are the temperature-dependent Henry's Law and dissociation constants (62 M/atm) (1.8 × 10^{-5} M), respectively, for NH_3, and K_w is the ion product of water (1.0 × 10^{-14} M) (Chameides, 1984). For a given NH_X concentration, increasing aqueous concentrations of particulate H^+ will shift the partitioning of NH_3 towards the condensed phase. Consequently, under the more polluted conditions characterized by higher pSO_4 concentration, ratios of gaseous NH_3 to particulate NH_4^+ decrease (Smith, 2007). It also follows that in marine air, where aerosol acidity varies substantially as a function of particle size, NH_3 partitions preferentially to the more acidic submicron size fractions (e.g., (Keene, 2004; Smith, 2007).

Because the dry V_d of gaseous NH_3 to the surface is substantially greater than that for the submicron pSO_4 size factions with which most particulate NH_4^+ is associated, dry deposition fluxes of total NH_3 are dominated by the gas-phase fraction (Russell, 2003; Smith, 2007). Consequently, partitioning with acidic pSO_4 effectively increases the atmospheric lifetime of total NH_3 against dry deposition.

This shift has important consequences for NH_3 cycling in the atmosphere and potential ecological effects. In coastal New England during summer, air transported from rural eastern Canada contains relatively low concentrations of nss pSO_4 and total NH_3 (Smith, 2007). Under these conditions, the roughly equal partitioning of total NH_3 between the gas and particulate phases sustains substantial dry deposition fluxes of total NH_3 with a median value of 10.7 $\mu M/m^2/day$ to the coastal ocean. In contrast, heavily polluted air transported from the industrialized midwestern U.S. contains median concentrations of nss pSO_4 and total NH_3 a factor of ~3 greater. Under these conditions, > 85% of total NH_3 partitions to the acidic pSO_4 size fractions and, consequently, the median dry-deposition flux of total NH_3 is 30% lower than that under the cleaner northerly flow regime. The relatively longer atmospheric τ of total NH_3 against dry deposition under more polluted conditions implies that, on average, total NH_3 would accumulate to higher atmospheric concentrations under these conditions and also be subject to atmospheric transport over longer distances. Consequently, the importance of NH_X removal via wet deposition would also increase. Because of the inherently sporadic character of precipitation, greater heterogeneity may exist in NH_3 deposition fields and any potential biological responses downwind of major S-emission regions.

2.6.5. Transport-related Effects

Convective processes and small-scale turbulence transport pollutants both upward and downward throughout the planetary boundary layer and the free troposphere. NO_X, SO_X, VOCs, and CO can be transported vertically by convection into upper part of the mixed layer on one day, then transported overnight as a layer of elevated mixing ratios, perhaps by a nocturnal low-level jet, and then entrained into a growing convective boundary layer downwind and brought back to the surface.

Because NO and NO_2 are only slightly soluble, they can be transported over longer distances in the gas phase than can more soluble species which can be depleted by deposition to moist surfaces, or taken up more readily on aqueous surfaces of particles. During transport, they can be transformed into reservoir species such as HNO_3, PANs, and N_2O_5. These species can then contribute to local NO_X concentrations in remote areas. For example, it is now well established that PAN decomposition provides a major source of NO_X in the remote troposphere (Staudt, 2003). PAN decomposition in subsiding air masses from Asia over the eastern Pacific could make an important contribution to O_3 and NO_X enhancement in the U.S. (Kotchenruther, 2001; Hudman, 2004). Further details about mechanisms for transporting O_3 and its precursors were described at length in O_3 AQCD (2006).

Major episodes of high pollution concentrations in the eastern United Sates and in Europe are often associated with slow moving high-pressure systems. High-pressure systems during the warmer seasons are associated with subsidence, resulting in warm, generally cloudless conditions with light winds. The subsidence results in stable conditions near the surface, which inhibit or reduce the vertical mixing of NO_X, SO_X, VOCs and CO. Photochemical activity is enhanced because of higher temperatures and the availability of sunlight.

However, it is becoming increasingly apparent that transport of O_3 and NO_X and VOC from distant sources can provide significant contributions to local O_3 concentrations even in areas where there is substantial photochemical production. A number of transport phenomena occur either in the upper boundary layer or in the FT which can contribute to high O_3 concentrations at the surface. These phenomena include stratospheric-tropospheric exchange (STE), deep and shallow convection, low-level jets, and the so-called “conveyor belts” that serve to characterize flows around frontal systems.

Crutzen and Gidel (1983), Gidel (1983), and Chatfield and Crutzen (1984) hypothesized that convective clouds played an important role in rapid atmospheric vertical transport of trace species and first tested simple parameterizations of convective transport in atmospheric chemical models. At nearly the same time, evidence was shown of venting the boundary layer by shallow, fair weather cumulus clouds (e.g.,, Greenhut, 1986; Greenhut, 1984). Field experiments were conducted in 1985 which resulted in verification of the hypothesis that deep convective clouds are instrumental in atmospheric transport of trace constituents (Dickerson, 1987). Once pollutants are lofted to the middle and upper troposphere, they typically have a much longer chemical τ and with the generally stronger winds at these altitudes, they can be transported large distances from their source regions. Transport of NO_X from the boundary layer to the upper troposphere by convection tends to dilute concentrations and extend the NO_X τ from less than 24 hours to several days. Photochemical reactions occur during this long-range transport. Pickering et al. (1990) demonstrated that venting of boundary layer NO_X by convective clouds (both shallow and deep) causes enhanced $P(O_3)$ in the FT. NO_X at the surface can often increase $P(O_3)$ efficiency. Therefore, convection aids in the transformation of local pollution into a contribution to global atmospheric pollution. Downdrafts within thunderstorms tend to bring air with less NO_X from the middle troposphere into the boundary layer. Lightning produces NO which is directly injected chiefly into the middle and upper troposphere. As described in Section 2.2.2.4 the total global production of NO by lightning remains uncertain, but is on the order of 10% of the total.

The first unequivocal observations of deep convective transport of boundary layer pollutants to the upper troposphere were documented by Dickerson et al. (1987). Instrumentation aboard three research aircraft measured CO, O_3, NO, NO_X, NO_Y, and HCs in the vicinity of an active mesoscale convective system near the border of Oklahoma and Arkansas during the 1985 PRE-STORM experiment. Anvil penetrations about two hours after maturity found greatly enhanced mixing ratios inside the cloud of all of the aforementioned species compared with outside it. NO mixing ratios in the anvil averaged 3 to 4 ppb, with individual 3-min observations reaching 6 ppb; boundary layer NO_X was typically 1.5 ppb or less outside the cloud. Therefore, the anvil observations represent a mixture of boundary layer NO_X and NO_X contributed by lightning. Luke et al. (1992) summarized the air chemistry data from all 18 flights during PRE-STORM by categorizing each case according to synoptic flow patterns. Storms in the maritime tropical flow regime transported large amounts of CO, O_3, and NO_Y into the upper troposphere with the midtroposphere remaining relatively clean. During frontal passages a combination of stratiform and convective clouds mixed pollutants more uniformly into the middle and upper levels.

Prather and Jacob (1997) and Jaeglé et al. (1997) noted that precursors of HO_X are also transported to the upper troposphere by deep convection, in addition to the primary pollutants. The HO_X precursors of most importance are water vapor, formaldehyde, H_2O_2, acetaldehyde, and acetone.

Over remote marine areas, the effects of deep convection on trace gas distributions differ from those over moderately polluted continental regions. Chemical measurements taken by the NASA ER-2 aircraft during the Stratosphere-Troposphere Exchange Project (STEP) off the northern coast of Australia show the influence of very deep convective events. Between 14.5 and 16.5 km on the February 2–3, 1987 flight, chemical profiles that included pronounced maxima in CO, water vapor, and CCN, and minima of NO_Y, and O_3 (Pickering, 1993). Trajectory analysis showed that these air parcels likely were transported from convective cells 800–900 km upstream. Very low marine boundary layer mixing ratios of NO_Y and O_3 in this remote region were apparently transported upward in the convection. A similar result was noted in Central Equatorial Pacific Experiment (CEPEX`; see, Kley, 1996) and in Indian Ocean Experiment

(INDOEX; see (De Laat, 1999) where a series of ozonesonde ascents showed very low upper tropospheric O_3 following deep convection. It is likely that similar transport of low O_3 concentrations tropical marine boundary layer air to the upper troposphere occurs in thunderstorms along the east coast of Florida. Deep convection occurs frequently over the tropical Pacific. Low O_3 concentrations and low NO_X convective outflow likely will descend in the subsidence region of the subtropical eastern Pacific, leading to some of the cleanest air that arrives at the west coast of the U.S.

The discussion above relates to the effects of specific convective events. Observations have also been conducted by NASA aircraft in survey mode, in which the regional effects of many convective events can be measured. The Subsonic Assessment Ozone and Nitrogen Oxides Experiment (SONEX) field program in 1997 conducted primarily upper tropospheric measurements over the North Atlantic. The regional effects of convection over North America and the Western Atlantic on upper tropospheric NO_X were pronounced (Crawford, 2000; Allen, 2000).

Thunderstorm clouds are optically very thick, and, therefore, have major effects on radiative fluxes and photolysis rates. Madronich (1987) provided modeling estimates of the effects of clouds of various optical depths on photolysis rates. In the upper portion of a thunderstorm anvil, photolysis is likely to be enhanced by a factor of 2 or more due to multiple reflections off the ice crystals. In the lower portion and beneath the cloud, photolysis is substantially decreased. With enhanced photolysis rates, the NO-to-NO_2 ratio in the upper troposphere is driven to larger values than under clear-sky conditions.

Thunderstorm updraft regions, which contain copious amounts of water, are regions where efficient scavenging of soluble species can occur (Balkanski, 1993). NO_2 itself is not very soluble and therefore wet scavenging is not a major removal process for it. However, a major NO_X reservoir species, HNO_3 is extremely soluble. Very few direct field measurements of the amounts of specific trace gases that are scavenged in storms are available. Pickering et al. (Pickering, 2001) used a combination of model estimates of soluble species that did not include wet scavenging and observations of these species from the upper tropospheric outflow region of a major line of convection observed near Fiji. Over 90% of the NO_X in the outflow air appeared to have been removed by the storm; about 50% of acetaldehyde and about 80% of formaldehyde had been lost.

2.7. Sampling and Analysis Techniques

2.7.1. Methods for Relevant Gas-Phase N Species

Separate sections here on field-deployed measurement techniques focus on current methods and promising new technologies so no attempt is made to cover development of these methods or methods no longer in widespread use. Rather, the descriptions in this chapter concern chiefly the Federal Reference Methods and Federal Equivalent Methods (FRM and FEM, respectively). More detailed discussions of the FRM, FEM, and other, newer methods including issues about their field use is found in (Clemitshaw, 2004; McClenny, 2000; Parrish, 2000; , 1996; EPA, 2008; Edgerton, 2006; Edgerton, 2007).

2.7.1.1. NO and NO_2

NO can be measured reliably using the principle of gas-phase chemiluminescence (CL) induced by the reaction of NO with O_3 at low pressure. Modern commercial NO_X analyzers have sufficient sensitivity and specificity for adequate measurement in urban and many rural locations (EPA, 1993; U.S. Environmental Protection Agency, 2006). Research grade CL instruments have been compared under realistic field conditions to spectroscopic instruments, and the results indicate that both methods are reliable (at concentrations relevant to smog studies) to better than 15 percent with 95 percent confidence. Response times are on the order of 60 s (e.g.,, Crosley, 1996). Near-source, urban, and rural and remote concentrations of NO are routinely measured using CL. However, Cardelino and Chameides (2000) reported that measured NO concentrations during the afternoon was frequently at or below the operational limit of detection (LOD), ~1 ppb, of the regulatory NO_X instruments even in large metropolitan regions such as Washington, DC, Houston, TX, and New York, NY, where NO_X concentrations from mobile sources would be high.

The FRM for NO_2 also makes use of this NO detection technique using a prerequisite step to reduce NO_2 to NO on the surface of a molybdenum oxide (MoO_X) substrate heated to ~340 EC. Because the FRM monitor cannot detect NO_2 directly, the NO_2 level is determined as the difference between the sample passed over the heated MoO_X substrate (the NO_X total) and the sample not so reduced (the NO alone). Reduction of NO_2 to NO on the MoO_X substrate is not specific to NO_2; hence, the CL analyzers are subject to varying interferences produced by the presence in the sample of the other oxidized N compounds (the NO_Z species shown in the outer box of Figure 2-15). This interference is often termed a "positive artifact" in the NO_2 concentration estimate, since the presence of NO_Z always results in an over-estimate of the NO_2 concentration in the reported measurement. This interference by NO_Z compounds has long been known (Fehsenfeld, 1987; EPA, 2008; Steinbacher, 2007, 2006JD007971; , 2007; , 2007; Rodgers, 1989; Crosley, 1996; Nunnermacker, 1998; Parrish, 2000; McClenny, 2002,. These studies have relied on intercomparisons of measurements using the FRM and other techniques for measuring NO_2. The sensitivity of the FRM to potential interference by individual NO_Z compounds is variable and also depends in part on characteristics of individual monitors, such as the design of the instrument inlet, the temperature and composition of the reducing substrate, and on the interactions of atmospheric species with the reducing substrate. Only recently have attempts been made to systematically quantify the magnitude and variability of the interference by NO_Z species in ambient measurements of NO_2. Dunlea et al. (2007; , 2007) found an average of ~22% of ambient NO_2 (~9 to 50 parts per billion [ppb]) measured in Mexico City was due to interference from NO_Z compounds; that is to say, the actual NO_2 concentration was ~22% lower than what was reported at monitors using the difference technique. Comparable levels of NO_2 are found in many locations in the U.S., but the same comparison for distinct places in the U.S. is difficult to make because significant uncertainty remains in determining the concentrations of the higher oxidation NO_Z products since they are not routinely measured. Dunlea et al. (2007; , 2007) compared NO_2 measured using the conventional chemiluminescent instrument with other (optical) techniques. The main sources of interference were HNO_3 and various organic nitrates ($RONO_2$) which can be converted to NO on the catalyst with varying rates of efficiency. In this study, the efficiency of conversion on the catalyst — that is, how much of the compound introduced to the catalyst was converted to NO — was estimated to be ~38% for HNO_3; for PAN, ~95% and ~ 95% for other $RONO_2$. Peak interference (over-estimation) in the reported estimate of NO_2 concentrations from the presence of NO_Z compounds of up to 50% was found during afternoon hours and was associated with O_3 and NO_Z compounds such as HNO_3 and the alkyl and multifunctional alkyl nitrates.

In a study in rural Switzerland, Steinbacher et al. (2007, 2006) compared measurements of NO_2 continuously measured using a conventional NO_X monitor and measurements in which NO_2 was photolyzed to NO. They found the conventional technique using catalytic reduction overestimated the reported NO_2 concentration using the photolytic technique on average by 10% during winter and 50% during summer.

Another approach to estimating the measurement interference is to use model calculations in conjunction with known data on the reduction efficiencies of NO_Z species on the MoO_X converters as described above. Lamsal et al. (2008) used the conversion efficiencies noted above along with output for NO_Y species from the GEOS-Chem CTM to derive seasonal correction factors for the ambient monitoring data across the U.S. These factors range from < 10% in winter in the East to > 80% in the West, with the highest values found during summer in relatively unpopulated areas. Lamsal et al. (2008) also used these corrected data to determine the feasibility of using satellite data to supplement ground based data. However, the current generation of satellite monitors are in low earth orbit and so the NO_2 values are restricted to time of satellite overpass in early afternoon. Future generations of geostationary satellites are planned that will obtain more continuous data across the U.S. throughout the day.

Calculations using CMAQ for the Mid-Atlantic region in a domain extending from Virginia to southern New Jersey were made at much higher spatial resolution than the GEOS-Chem simulations (see http://www.mde.state.md.us/Programs/AirPrograms/air_planning/index.asp). The daily average interference for an episode during the summer of 2002 estimated using model-derived concentration fields for NO_Z species and using the conversion efficiencies for NO_Z species given above, ranged from ~20% in Baltimore to ~80% in Madison, VA. Highest values were found during the afternoon, when photochemical activity is highest and production and accumulation of the higher oxidized NO_Z compounds is greatest, and lowest values during the middle of the night when photochemistry stops. The model calculations showed episode averages of the NO_Z/NO_2 ratio ranging from 0.26 to 3.6 in rural Virginia; the highest ratios were in rural areas, and lowest were in urban centers closer to sources of fresh NO_X emissions. (The capabilities of three-dimensional CTMs such as GEOS-CHEM and CMAQ and issues associated with their use are presented below.)

On the whole, the current method of determining ambient NO_X and then reporting NO_2 concentrations by subtraction of NO is subject to a consistently positive interference by NO_X oxidation products, chiefly HNO_3 and PAN as well as other oxidized N-containing compounds, though the magnitude of this positive bias is largely unknown and can be changing rapidly. Measurements of these higher-order oxidation products in urban areas are sparse. Concentrations of these oxidation products are expected to peak in the afternoon because of the continued oxidation of NO_2 emitted during the morning rush hours and during conditions conducive to photochemistry in areas well downwind of sources, particularly during summer.

Within the urban core of metropolitan areas, where many of the ambient monitors are sited close to strong NO_X sources such as motor vehicles on busy streets and highways, the positive artifacts due to the NO_2 oxidation products are much smaller on a relative basis, typically <.10%. Conversely, the positive artifacts are larger in locations more distant from NO_X sources where NO_2 concentrations are lowest and could exceed 50%. Therefore, variable, positive artifacts associated with measuring NO_2 using the Federal Reference Method (FRM) severely hamper its ability to serve as an accurate and precise indicator of NO_2 concentrations at the typical ambient levels generally encountered outside of urban cores where they would be most relevant for environmental exposures.

NO has also been successfully measured in ambient air with direct spectroscopic methods; these include two-photon laser-induced fluorescence (TPLIF), tunable diode laser absorption spectroscopy (TDLAS), and two-tone frequency-modulated spectroscopy (TTFMS). These were reviewed thoroughly in the 2008 NO_2 ISA for human health. The spectroscopic methods demonstrate excellent sensitivity and selectivity for NO with detection limits on the order of 10 ppt for integration times of 1 min. Spectroscopic methods compare well with the CL method for NO in controlled laboratory air, ambient air, and heavily polluted air (e.g.,, Walega, 1984; Kireev, 1999; Gregory, 1990). These spectroscopic methods remain in the research arena due to their complexity, size, and cost, but are essential for demonstrating that CL methods are reliable for monitoring NO concentrations involved in O_3 formation, from around 20 ppt to several hundred of ppb.

There are approaches to measuring NO_2 not affected by the artifacts mentioned above. For example, NO_2 can be photolytically reduced to NO with an efficiency of ~70% as used in the Steinbacher et al. (2007, 2006 study. Ryerson et al. (2000) developed a gas-phase CL method using a photolytic converter based on a Hg lamp with increased radiant intensity in the region of peak NO_2 photolysis (350 to 400 nm) and producing conversion efficiencies of 70% or more in less than 1 s. Metal halide lamps with conversion efficiency of about 50% and accuracy on the order of 20% (Nakamura, 2003) have been used. Because the converter produces little radiation at wavelengths less than 350 nm, interferences from HNO_3 and PAN are minimal. This method requires additional development to ensure its cost effectiveness and reliability for extensive field deployment. The relatively low and variable conversion efficiency of this technique would necessitate more frequent calibration. Optical methods such as those using differential optical absorption spectroscopy (DOAS) or laser induced fluorescence (LIF) are also available. However, these particular methods are more expensive than either the FRM monitors or photolytic reduction technique and require specialized expertise to operate. Moreover, the DOAS obtains an area-integrated measurement rather than a point measurement. Cavity attenuated phase shift (CAPS) monitors are an alternative optical approach that is potentially less costly than DOAS or LIF (Kebabian, 2007; Kebabian, 2007). However, this technique is not highly specific to NO_2 and is subject to interference by other species absorbing at 440 nm, such as the 1,2–dicarbonyl compounds. The extent of this interference and the potential of the CAPS technique for extensive field deployment have not been evaluated.

A DOAS system manufactured by OPSIS is designated as a FEM for measuring NO_2. DOAS systems can also be configured to measure NO, HONO, and NO_3 radicals. Typical detection limits are 0.2 to 0.3 ppb for NO, 0.05 to 0.1 ppb for NO_2, 0.05 to 0.1 ppb for HONO, and 0.001 to 0.002 ppb for NO_3, at path lengths of 0.2, 5, 5, and 10 km, respectively. The obvious advantage compared to fixed point measurements is that concentrations relevant to a much larger area are obtained, especially if multiple targets are used. At the same time, any microenvironmental artifacts are minimized over the long path integration. However, comparisons to other measurements made at point not a real location are difficult. A major limitation in this technique had involved inadequate knowledge of absorption cross sections. Harder et al. (1997) conducted an experiment in rural Colorado involving simultaneous measurements of NO_2 by DOAS and by photolysis followed by chemiluminescence. They found differences of as much as 110% in clean air from the west, but for NO_2 mixing ratios in excess of 300 ppt, the two methods agreed to better than 10%. Stutz et al. (2000) cites two intercomparisons of note. NO was measured by DOAS, by photolysis of NO_2 followed by chemiluminescence, and by LIF during July 1999 as part of the SOS in Nashville, TN. On average, the three methods agreed to within 2%, with some larger differences likely caused by spatial variability over the DOAS path. In another study in Europe, and a multi-reflection set-up over a 15 km path, negated the problem of spatial averaging here agreement with the CL detector following photolytic conversion was excellent (slope = 1.006 ± 0.005; intercept = 0.036 ± 0.019; r = 0.99) over a concentration range from about 0.2 to 20 ppb.

The paucity of specific in situ NO_2 measurements motivates the inference of ground level NO_2 concentrations from satellite measurements of tropospheric NO_2 columns. This prospect would take advantage of the greater sensitivity of tropospheric NO_2 columns to NO_X in the lower troposphere than in the upper troposphere as discussed earlier. Tropospheric NO_2 columns show a strong correlation with in situ NO_2 measurements in northern Italy (Ordonez, 2006). Quantitative calculation of surface NO_2 concentrations from a tropospheric NO_2 column requires information on the relative vertical profile. Comparison of vertical profiles of NO_2 in a CTM (GEOS-Chem) versus in situ measurements over and downwind of North America shows a high degree of consistency (Martin, 2004; Martin, 2006; Martin, 2004; Martin, 2006), suggesting that CTM could be used to infer the relationship between surface NO_2 concentrations and satellite observations of the tropospheric NO_2 column.

Table 2-6 contains an overview of the three satellite instruments that are used retrieve tropospheric NO_2 columns from measurements of solar backscatter. All three instruments are in polar sun-synchronous orbits with global measurements in the late morning and early afternoon. The spatial resolution of the measurement from SCIAMACHY is 7 times better than that from Ozone Monitoring Instrument (GOME), and that from Ozone Monitoring Instrument (OMI) is 40 times better than that from GOME.

Figure 2-25 shows tropospheric NO_2 columns retrieved from SCIAMACHY. Pronounced enhancements are evident over major urban and industrial emissions. The high degree of spatial heterogeneity over the southwestern U.S. provides empirical evidence that most of the tropospheric NO_2 column is concentrated in the lower troposphere. Tropospheric NO_2 columns are more sensitive to NO_X in the lower troposphere than in the upper troposphere (Martin, 2002). This sensitivity to NO_X in the lower troposphere is due to the factor of 25 decrease in the NO_2-to-NO ratio from the surface to the upper troposphere (Bradshaw, 1999) that is driven by the temperature dependence of the NO + O_3 reaction. Martin et al. (2004) integrated in situ airborne measurements of NO_2 and found that during summer the lower mixed layer contains 75% of the tropospheric NO_2 column over Houston and Nashville. However, it should be noted that these measurements are also sensitive to surface albedo and aerosol loading.

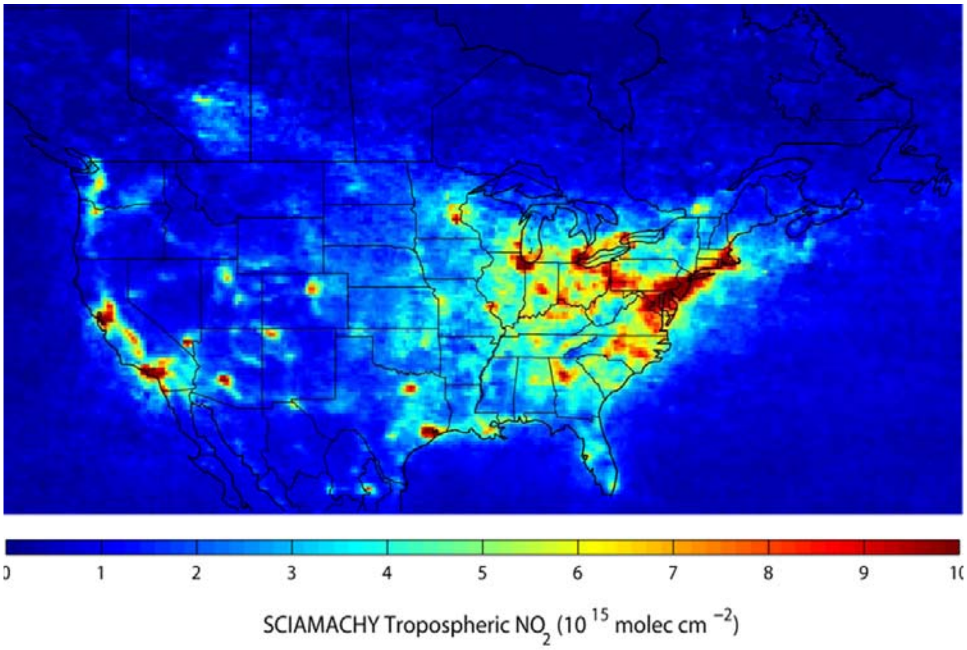
Table 2-6. Satellite instruments used to retrieve tropospheric NO_2 columns.

Instrument	Coverage	Typical U.S. Measurement Time	Typical Resolution (km)	Return Time (days)[1]	Instrument Overview
GOME	1995–2002	10:30–11:30 AM	320 × 40	3	Burrows et al. (1999)
SCIAMACHY	2002–	10:00–11:00 AM	30 × 60	6	Bovensmann et al. (1999)
OMI	2004–	12:45–1:45 PM	13 × 24	1	Levelt et al. (2006)

[1] Return time is reported here for cloud-free conditions. Note that due to precession of the satellite's orbit, return measurements are close to but not made over the same location. In practice, clouds decrease observation frequency by a factor of 2.

Table 2-7. Characteristics of principal airsheds for reduced-N deposition.

Watershed	Principal Red-N Airshed Area (km^2)	Red-N Area as % of O_X-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH_3 Emission as % of E. North American Emissions
Chesapeake Bay	668,000	64%	55%	11%
Pamlico Sound	406,000	61%	60%	6.8%
Apalachee Bay	310,000	70%	45–50% est.	4.3%



Source: Martin et al. (2006).

Figure 2-25. Tropospheric NO_2 columns (molecules NO_2/cm^2) retrieved from the SCIAMACHY satellite instrument for 2004–2005.

2.7.1.2. NO_Y

Commercially available NO_X monitors have been converted to NO_Y monitors by moving the MoO_X convertor to interface directly with the sample inlet. Because of losses on inlet surfaces and differences in the efficiency of reduction of NO_Z compounds on the heated MoO_X substrate, NO_X cannot be considered as a universal surrogate for NO_Y. However, in settings close to relatively high-concentration, fresh emissions like those during urban rush hour, most of the NO_Y is present as NO_X. Measurements of total NO_Y characterize the entire suite of oxidized N compounds to which humans are exposed. Reliable measurements of NO_Y and NO_2, especially at the low concentrations observed in many areas remote from sources are also crucial for evaluating the performance of three-dimensional, chemical transport models of oxidant and acid production in the atmosphere.

Gold-catalyzed CO or H_2 reduction or conversion on heated MoO_X have been used to reduce total NO_Y to NO before detection by CL (Fehsenfeld, 1987; Crosley, 1996). Both techniques offer generally reliable measurements, with response times on the order of 60 s and a linear dynamic range demonstrated in field intercomparisons from ~10 ppt to 10s of ppb. Under some conditions, hydrogen cyanide (HCN), NH_3, alkyl nitrates (RNO_2), and acetonitrile (CH_3CN) can be converted to NO; but at normal concentrations and humidity, and when convertor temperature is closely monitored, these are minor interferants. Thermal decomposition followed by LIF has also been used for NO_Y detection. In field comparisons, instruments based on these two principles generally showed good agreement (Day, 2002) with experimental uncertainty estimated to be on the order of 15 to 30%.

2.7.1.3. HNO_3

A major issue to be considered when measuring NO_X and NO_Y is the possibility that HNO_3, a major component of NO_Y, is sometimes lost in inlet tubes and not measured (Luke, 1998; Parrish, 2000). This problem is especially critical if measured NO_Y is used to identify NO_X-limited versus NO_X-saturated conditions. The problem is substantially alleviated although not necessarily completely solved by using much shorter inlets on NO_Y monitors than on NO_X monitors and by the use of surfaces less likely to take up HNO_3. The correlation between O_3 and NO_Y differs for NO_X-limited versus NO_X-saturated locations, but this difference is driven primarily by differences in the ratio of O_3 to HNO_3. If HNO_3 were omitted from the NO_Y measurements, then the measurements would represent a severely biased estimate and their use would be problematic.

Accurate measurement of HNO_3 has presented a long-standing analytical challenge. To understand why, it is useful to consider the major factors that control HNO_3 partitioning between the gas and deliquesced-particulate phases in ambient air

$$HNO_{3(g)} \overset{K_H}{\leftrightarrow} [HNO_{3(aq)}] \overset{K_a}{\leftrightarrow} [H^+]+[NO_3^-]$$

Reaction 57

where K_H is the Henry's Law constant in M/atm and K_a is the acid dissociation constant in M. Thus, the primary controls on HNO_3 phase partitioning are its thermodynamic properties, aerosol liquid water content (LWC), solution pH, and kinetics. Aerosol LWC and pH are controlled by the relative mix of acids and bases in the system, the hygroscopic properties of condensed compounds, and meteorological conditions, chiefly RH, temperature, and pressure.

In the presence of chemically distinct aerosols of varying acidities (e.g., super-µm, predominantly sea salt; and sub-µm, predominantly pSO_4), HNO_3 should partition preferentially to the less-acidic particles, and observations are consistent with this (see. e.g.,, Huebert, 1996; Keene, 1998). The kinetics of this phase partitioning are controlled by atmospheric concentrations of HNO_3 vapor and pNO_3, and the size distribution and τ of the particles against deposition. Sub-µm diameter aerosols typically equilibrate with the gas phase in seconds to minutes while super-µm aerosols require hours to a day or more see, e.g., Meng and Seinfeld (1996) and Erickson et al. (1999). Consequently, smaller aerosol size fractions are typically close to thermodynamic equilibrium with respect to HNO_3, whereas larger size fractions, for which τ against deposition range from hours to a few days, are often undersaturated (e.g.,, Keene, 1998; Erickson, 1999).

Methods used widely for measuring HNO_3 include standard filterpacks configured with nylon or alkaline-impregnated filters (see, e.g.,, Goldan, 1983; Bardwell, 1990), annular denuders like EPA method IP-9, and standard mist chambers (e.g.,, Talbot, 1990). Samples from these instruments are typically analyzed by ion chromatography. Intercomparisons of these measurement techniques by Hering et al. (1988), Tanner et al. (1989), and Talbot et al. (1990) reported differences on the order of a factor of 2 or more. In part, this variance is due to nonsystematic sampling error. When chemically distinct aerosols with different pHs, for example, sea salt and pSO_4, mix together on a bulk filter, the acidity of the bulk mixture will be greater than that of the less-acidic aerosols with which most of the NO_3^- is associated. This change in pH may cause the bulk mix to be supersaturated with respect to HNO_3 leading to volatilization and, thus, to a positive measurement bias in HNO_3 sampled downstream. Alternatively, when undersaturated super-µm size fractions like sea salt accumulate on a bulk filter and chemically interact over time with HNO_3 in the sample air stream, scavenging may lead to a negative bias in the HNO_3 sampled downstream. Because the magnitude of both effects will vary as functions of the overall composition and thermodynamic state of the multiphase systems, the combined influence can cause net positive or net negative measurement bias in data with unknown frequencies. Pressure drops across particle filters can also lead to artifact volatilization and associated positive bias in HNO_3 concentrations measured downstream.

Recently, sensitive HNO_3 measurements based on the principle of chemical ionization mass spectroscopy (CIMS) have been reported; see, e.g., Huey et al. (1998), Mauldin et al. (1998), Furutani and Akimoto (2002), and Neuman et al. (2002). The CIMS relies on selective formation of ions such as $SiF_5^- \cdot HNO_3$ or $HSO_4^- \cdot HNO_3$ followed by detection via mass spectroscopy. Two CIMS techniques and a filter pack technique were intercompared in Boulder, CO (Fehsenfeld, 1998). Results indicated agreement to within 15% between the two CIMS instruments and between the CIMS and filterpack methods under relatively clean conditions with HNO_3 mixing ratios between 50 and 400 ppt. In more polluted air, the filterpack technique generally yielded higher values than the CIMS, suggesting that interactions between chemically distinct particles on bulk filters is a more important source of bias in polluted continental air. Differences were also greater at lower temperature when pNO_3 corresponded to relatively greater fractions of total NO_3.

Three semi-continuous methods for detecting HNO_3 were tested against the annular denuder filter pack (ADS) integrated collection technique at the Tampa Bay Regional Atmospheric Chemistry Experiment (BRACE) Sydney research station ~20 km downwind of the Tampa, Florida, urban core (Arnold, 2007). The semi-continuous instruments included: two slightly differing implementations of the NO_Y-NO_{Y*} (total oxides of nitrogen minus that total denuded of HNO_3) denuder difference technique, one from the NOAA Air Resources Lab (ARL), and one from Atmospheric Research and Analysis, Inc. (ARA); the parallel plate wet diffusion scrubber online ion chromatography technique from Texas Tech University (TTU); and the chemical ionization mass spectrometer from the Georgia Institute of Technology (GIT). Twelve hour ADS samples were collected by the University of South Florida (USF). Results for 10 min samples computed from the various higher sampling frequencies of each semi-continuous instrument showed good agreement ($R^2 > 0.7$) for afternoon periods of the highest production and accumulation of HNO_3. Further, agreement was within ± 30% for these instruments even at HNO_3 concentrations < 0.30 ppb. The USF ADS results were biased low, however, by 44%, on average, compared to the corporate 12 h aggregated means from the semi-continuous methods, and by >600% for the nighttime samples; ADS results were below the corporate mean maximum HNO_3 concentration by >30% as well. The four instruments using semi-continuous methods, by contrast, were all within 10% of each other's 12 h mean mixing ratios. While only ARA employed a formal minimum detection limit at 0.050 ppb, error analysis with the other techniques established that at the same level of precision, TTU's effective limit was approximately the same as ARA's and that ARL's limit was 0.030 ppb; analysis for GIT showed no apparent effective limit at the levels of HNO_3 encountered in this field study. The importance of sample inlet height for HNO_3 measurements was indirectly shown through comparison to previous field work at this site when sample inlet heights ranged from 1.5–10 m and produced systematic discrepancies in HNO_3 concentrations correlated with height of more than a factor of 2.

2.7.1.4. Other Nitrates

Methods for sampling and analysis of $RONO_2$ in the atmosphere have been reviewed by Parrish and Fehsenfeld (2000). PAN, PPN, and MPAN are typically measured using a gas chromatograph followed by electron capture detectors (GC-ECD) (see, e.g.,, Gaffney, 1998), although other techniques such as Fourrier Transform InfraRed (FTIR) analysis can also be used. Field measurements made using GC-ECD have reported a total uncertainty of ±5 ppt + 15% (1998). Additional descriptions of specific techniques for $RONO_2$ and some of the issues involved with using data taken with them appear in Section

2.10, accompanying descriptions of the methods used routinely to monitor ambient air concentrations and deposition amounts of $RONO_2$, and in the *ISA for NO_X—Health Criteria* (EPA, 2008a).

2.7.1.5. NH_3

Because NH_3 plays a key role in the atmospheric chemistry of particle formation, several methods have been developed for ambient and higher-level concentrations; see, for example, (Appel, 1988; Allegrini, 1991; Genfa, 1989; Williams, 1992; Wyers, 1993; Mennen, 1996; Asman, 1998; Pryor, 2001; Schwab, 2007; Fehsenfeld, 2002). Measurement of NH_3 is made difficult by its chemistry, whereby it forms strong H bonds with itself and water, and can be lost either partly reversibly (i.e., with hysteresis) or irreversibly to many instrument surfaces. Moreoever, the range of atmospheric NH_3 extends over 4 or 5 orders of magnitude. Because of these challenges, many NH_3 techniques remain "research-grade" with steep requirements of time, care, and technical experience. However, U.S. EPA has proposed to include ambient NH_3 measurements in its new National Core (NCore) monitoring network (EPA, 2005) and this has motivated additional development and testing of NH_3 monitors.

The U.S. EPA Environmental Technology Verification (ETV) Program's Advanced Monitoring Systems (AMS) Center, has verified the performance of seven ambient NH_3 monitors[1] for use at confined animal feeding operations (CAFOs). In collaboration with the U.S. Department of Agriculture (USDA), the AMS Center verified the seven ambient NH_3 monitors (see Table 2-8) in two phases of testing, each at separate CAFOs. Phase I was conducted at a swine finishing farm, and Phase II was conducted at a cattle feedlot. These sites were selected to provide realistic testing conditions and a wide range of NH_3 concentrations. Table 2-9 summarizes some of the performance data for the individual technologies. (The full verification reports can be found at http://www.epa.gov/nrmrl/std/etv/vt-ams.html under ambient NH_3 sensors category.)

Ambient NH_3 monitors utilize a wide range of analytical methods. These methods include direct detection by spectroscopic techniques or indirect detection of NH_3 using selective membrane permeation with conductivity detection, catalytic conversion with CL detection, treatment with a chemical dopant followed by ion mobility detection, or other techniques. Ambient NH_3 monitors also can provide specialized features that can be valuable in specific uses, such as long-term monitoring or determining NH_3 fluxes and emission rates.

For example, monitors that collect high-speed, sub-second response time NH_3 concentration data can be used with simultaneous three-dimensional windspeed and direction data to determine NH_3 flux. Alternatively, open-path monitors can be used to calculate emission rates from CAFOs, since these monitors measure the average NH_3 concentration over a 1 to 100 meter path. Some monitors also are suitable for long-term monitoring, since they can be operated without user intervention for weeks at a time.

Table 2-8. Verified ambient NH_3 monitors.

Technology Name	Description
Aerodyne Research, Inc. QC-TILDAS	An infrared laser spectrometer, based on pulsed quantum cascade laser technology; continuous measurement
Bruker Daltonics OPAG 22 Open-Path Gas Analyzer	A broadband, open-path, Fourier transform infrared spectrometer for remote sensing continuous measurement
Molecular Analytics IonPro-IMSNH_3 Analyzer	An ion mobility spectrometer; continuous measurement
Omnisens SA TGA310 NH_3 Analyzer	A trace gas analyzer that uses photoacoustic spectrometry; continuous measurement
Pranalytica, Inc. NitroluxTM 1000 Ambient NH_3 Analyzer	A resonant photoacoustic spectrometer with a line-tunable CO_2 laser; continuous measurement
Mechatronics Instruments BV AiRRmonia NH_3 Analyzer	A single-point monitor composed of a membrane diffusion sampler, a detector block with a diffusion membrane, and two conductivity cells; continuous measurement
Thermo Electron Corp. Model 17C NH_3 Analyzer	A CL analyzer that uses NO and ozone (O_3) reactions; time-averaged measurement

Table 2-9. Performance characteristics of the 7 EPA ETV tested NH_3 methods.

Vendor[a]	Testing	Average Relative Accuracy[b]	Relative Precision[b]	Response Time (95%)	Linearity			Comparability[c]		
					Slope	Intercept	r^2	Slope	Intercept	r^2
A	Phase I & Phase II	3.7 to 10.5%	0.3%	3 to 76 min	0.90 to 1.03	-24 to -0.6	1.000	0.86 to 1.20	-0.5 to 16	0.984 to 0.990
B	Phase I & Phase II	2.4 to 34%	0.7 to 2.1%	8 to 20 min	1.02 to 1.28	-2.4 to 136	0.9957 to 0.9999	0.41 to 1.18	-1.4 to 58	0.538 to 0.9755
C	Phase I & Phase II	10 to 44%	0.2 to 1.3%	1 to 32 min	0.716 to 1.25	-58.5 to 167	0.9854 to 0.9997	0.646 to 1.83	-6.7 to 21.6	0.9794 to 0.9842
D	Phase II	2.2%	0.9%	2 to 2.6 min	0.966	15.9	1.000	1.15	-4.1	0.994
E	Phase II	18.3%	1.0%	2.5 to 17 min	0.815	1.08	1.000	1.565	-16.5	0.994
F	Phase II	26%	1.8%	4 to 14 sec	0.583	24.9	0.9144	Not reported	Not reported	Not reported
G	Phase I & Phase II	4.7 to 10%	1.9 to 2.5%	0.8 to 66 sec	0.840 to 0.962	-8.8 to 35	0.9989 to 0.9998	0.984 to 1.09	-9.5 to 14.4	0.9943 to 0.9982

[a] Because the ETV Program does not compare technologies, the performance results shown in this table do not identify the vendor associated with each result and are not in the same order as the list of technologies in Table 2-8.

[b] A result of 0% indicates perfect accuracy or precision.

[c] The comparability of the verified technology with a standard reference method was established by comparing the average NH_3 sensors readings with time-integrated NH_3 samples collected using citric-acid-coated denuders. The reference samples were collected based on procedures described in the EPA Compendium Method IO-4.2, Determination of Reactive Acidic and Basic Gases and Acidity of Fine Particles (<2.5 µm). Comparability between the NH_3 sensors results and the reference method results with respect to ambient air was assessed by linear regression using the reference method NH_3 concentrations as the independent variable and results from the NH_3 sensor as the dependent variable.

In addition to the elevation by EPA, ETV, a laboratory-based intercomparison of real-time ambient NH_3 instruments was conducted and reported by Schwab et al., (2007) with seven instruments using six methods. The methods were these: the tunable diode laser (TDL) absorption spectrometer, the wet scrubbing long-path absorption photometer (LOPAP), the wet effusive diffusion denuder (WEDD), the ion mobility spectrometer (IMS), the Nitrolux laser acousto-optical absorption analyzer, and a modified CL analyzer. Schwab et al. (2007) reported that all instruments performed well and agreed to within ~25% of the expected calibration value, with the exception of the CL analyzer which suffered from problems related to its MoOx conversion of NO_Z to NO. (Work with a modification of this technique has been continuing with the Aerosol Research Inhalation Epidemiology Study (ARIES); see Blanchard and Hidy (2003).

Instrument response time is known to be a crucial feature for ambient NH_3 measurements, and Schwab et al. (2007) showed response time to be sensitive to measurement history as well as the sample handling materials. Shortest response was for the TDL; the Nitrolux and IMS and WEDD instruments had unacceptably long time responses under some environmental conditions which rendered correlations across instruments meaningless. The TDL and LOPAP reported values closest to delivered concentration values; the IMS exhibited bias of ~ +25%; the Nitrolux bias was ~ −25%. Schwab et al. (2007) concluded that sub-ppb ambient NH_3 measurements can be taken reliably with some of these instruments, but that special care must still be exercised to ensure high-quality data.

These and other recent intercomparisons of ambient NH_3 instruments have confirmed that no single technique has yet been identified for automated, fast-response, low-concentration, high-quality continuous data.

2.7.2. Methods for Relevant Gas-phase S Species

Currently, ambient SO_2 is measured using instruments based on pulsed fluorescence. The UV fluorescence monitoring method for atmospheric SO_2 was developed to improve upon the flame photometric detection (FPD) method for SO_2, which in turn had displaced the pararosaniline wet chemical method for SO_2 measurement. The pararosaniline method is still the FRM for atmospheric SO_2, but is rarely used because of its complexity and slow response, even in its automated forms. Both the UV fluorescence and FPD methods are designated as FEMs by the EPA, but UV fluorescence has largely supplanted the FPD approach because of the UV method's inherent linearity, sensitivity, and the absence of consumables, such as the H gas needed for the FPD method.

The LOD for a non-trace-level SO_2 analyzer is 10 ppb (CFR, 2006). However, most commercial analyzers report operational detection limits of ~3 ppb. This concentration is very near the current ambient annual average concentration of SO_2 of ~4 ppb.

SO_2 molecules absorb ultraviolet (UV) light at one wavelength and emit UV light at longer wavelengths. This fluorescence involves excitation of the SO_2 molecule to a higher energy (singlet) electronic state. Once excited, the molecule decays non-radiatively to a lower energy electronic state from which it then decays to the original, or ground, electronic state by emitting a photon of light at a longer wavelength (i.e., lower energy) than the original, incident photon. The process can be summarized by the following equations

$$SO_2 + h\nu_1 \rightarrow SO_2*$$

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$$SO_2* \rightarrow SO_2 + h\nu_2$$

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where SO_2* represents the excited state of SO_2, $h\nu_1$, and $h\nu_2$ represent the energy of the excitation and fluorescence photons, respectively, and $h\nu_2 < h\nu_1$. The intensity of the emitted light is proportional to the number of SO_2 molecules in the sample gas. Additional information is found in the 2008 ISA for SO_2 human health effects.

2.7.2.1. Positive Interference

Luke (1997) reported the positive artifacts of a modified pulsed fluorescence detector generated by the co-existence of NO, CS_2, and a number of highly fluorescent aromatic HCs such as benzene, toluene, o-xylene, m-xylene, p-xylene, m-ethyltoluene, ethylbenzene, and 1,2,4–trimethylbenzene. The positive artifacts could be reduced by using a HC “kicker” membrane. At a flow rate of 300 standard cc/min and a pressure drop of 645 torr across the kicker, the interference from ppm levels of many aromatic HCs was eliminated entirely. More details appear in the *ISA for* SO_X *—Health Criteria* (EPA, 2008b).

2.7.2.2. Negative Interference

Nonradiative deactivation (quenching) of excited SO_2 molecules can occur from collisions with common molecules in air, including N, O_2, and water. During collisional quenching, the excited SO_2 molecule transfers energy, kinetically allowing the SO_2 molecule to return to the original lower energy state without emitting a photon. Collisional quenching results in a decrease in the SO_2 fluorescence and results in the underestimation of SO_2 concentration in the air sample. The concentrations of N_2 and O_2 are constant in the ambient air, so quenching from those species at a surface site is also constant, but the water vapor content of air can vary. Luke (1997) reported that the response of the detector could be reduced by about 7% and 15% at water vapor mixing ratios of 1 and 1.5 mole percent (RH = 35 to 50% at 20–25°C and 1 atm for a modified pulsed fluorescence detector (Thermo Environmental Instruments, Model 43s). At very high SO_2 concentrations, reactions between electronically excited SO_2 and ground state SO_2 to form SO_3 and SO might occur (Calvert, 1978) However, this possibility has not been examined.

2.7.2.3. Other Methods

A more sensitive SO_2 measurement method than the UV-fluorescence method was reported by Thornton et al. (2002) using of an atmospheric pressure ionization mass spectrometer. The high measurement precision and instrument sensitivity were achieved by adding isotopically labeled SO_2 ($^{34}S^{16}O_2$) continuously to the manifold as an internal standard. Field studies showed that the method precision was better than 10% and the limit of SO_2 can be measured by LIF at around 220 nm (Matsumi, 2005). Because the laser wavelength is alternately tuned to an SO_2 absorption peak at 220.6 and trough at 220.2 nm, and the difference signal at the two wavelengths is used to extract the SO_2 concentration, the technique eliminates interference from either absorption or fluorescence by other species and has high sensitivity (5 ppt in 60 s).

SO_2 can also be measured by the same DOAS instrument that can measure NO_2. Photoacoustic techniques have been employed for SO_2 detection, but they generally have detection limits suitable only for source monitoring (Gondal, 1997; Gondal, 2001).

CIMS techniques for SO_2 have been shown to have high sensitivity, 10 ppt or better, with uncertainty of ~15% when a charcoal scrubber is used for zeroing and the sensitivity is measured with isotopically labeled $^{34}SO_2$ (Hanke, 2003; Hennigan, 2006; Huey, 2004).

2.7.3. Methods for Relevant Aerosol-phase N and S Species

SO_4^{2-} is commonly present in $PM_{2.5}$. Most $PM_{2.5}$ samplers have a size-separation device to separate particles so that only those particles approximately 2.5 µm or less are collected on the sample filter. Air is drawn through the sample filter at a controlled flow rate by a pump located downstream of the sample filter. The systems have two critical flow rate components for the capture of fine particulate: (1) the flow of air through the sampler must be at a flow rate that ensures that the size cut at 2.5 µm occurs; and (2) the flow rate must be optimized to capture the desired amount of particulate loading with respect to the analytical method detection limits.

When using the system described above to collect pSO_4 sampling artifacts can occur because of: (1) positive sampling artifact for pSO_4, NO_3, and particulate ammonium due to chemical reaction; and (2) negative sampling artifact for NO_3 and ammonium due to the decomposition and evaporation.

Several traditional and new methods could be used to quantify elemental S collected on filters: energy dispersive X-ray fluorescence, synchrotron induced X-ray fluorescence, proton induced X-ray emission (PIXE), total reflection X-ray fluorescence, and scanning electron microscopy. Energy dispersive X-ray fluorescence (EDXRF) (Method IO-3.3, EPA, 1997; see 2004 PM CD for details) and PIXE are the most commonly used methods. Since sample filters often contain very small amounts of particle deposits, preference is given to methods that can accommodate small sample sizes and require little or no sample preparation or operator time after the samples are placed into the analyzer. X-ray fluorescence (XRF) meets these needs and leaves the sample intact after analysis so it can be submitted for additional examinations by other methods as needed. To obtain the greatest efficiency and sensitivity, XRF typically places the filters in a vacuum which may cause volatile compounds (nitrates and organics) to evaporate. As a result, species that can volatilize such as ammonium nitrate and certain organic compounds can be lost during the analysis. The effects of this volatilization are important if the PTFE filter is to be subjected to subsequent analyses of volatile species.

Polyatomic ions such as SO_4^{2-}, NO_3, and ammonium are quantified by methods such as ion chromatography (IC) (an alternative method commonly used for ammonium analysis is automated colorimetry). All ion analysis methods require a fraction of the filter to be extracted in deionized distilled water for SO_4^{2-} and $NaCO_3/NaHCO_3$ solution for NO_3 and then filtered to remove insoluble residues prior to analysis. The extraction volume should be as small as possible to avoid over-diluting the solution and inhibiting the detection of the desired constituents at levels typical of those found in ambient $PM_{2.5}$ samples.

Continuous methods for the quantification of aerosol sulfur compounds first remove gaseous sulfur (e.g., SO_2, H_2S) from the sample stream by a diffusion tube denuder followed by the analysis of particulate sulfur (Cobourn, 1978; Durham, 1978; Huntzicker, 1978; Mueller, 1980; Tanner, 1980). Another approach is to measure total sulfur and gaseous sulfur separately by alternately removing particles from the sample stream. Particulate sulfur is obtained as the difference between the total and gaseous sulfur (Kittelson, 1978). The total sulfur content is measured by a flame photometric detector (FPD) by introducing the sampling stream into a fuel-rich, hydrogen-air flame (e.g.,, Farwell, 1976; Stevens, 1969) that reduces sulfur compounds and measures the intensity of the CL from electronically excited sulfur molecules (S2*). Sensitivities for particulate sulfur as low as 0.1 μg/m^3, with time resolution ranging from 1 to 30 min, have been reported. Continuous measurements of particulate sulfur content have also been obtained by on-line XRF analysis with resolution of 30 min or less (Jaklevic, 1981). During a field-intercomparison study of five different sulfur instruments, Camp et al. (1982) four out of five FPD systems agreed to within ± 5% during a 1–week sampling period.

There are two major PM speciation ambient air-monitoring networks in the U.S.: the Chemical Speciation Network (CSN, which now includes the former Speciation Trends Network [STN]), and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The current CSN samplers sample on a 1-in-3 days cycle using three filters: (1) Teflon for equilibrated mass and elemental analysis including elemental S; 2) a HNO_3-denuded nylon filter for ion analysis including NO_3 and SO_4^{2-}, (3) a quartz-fiber filter for elemental and organic carbon (EC and OC, respectively). The IMPROVE sampler, which collects two 24-h samples per week, simultaneously collects one sample of PM_{10} on a Teflon filter, and three samples of $PM_{2.5}$ on Teflon, nylon, and quartz filters. $PM_{2.5}$ mass concentrations are determined gravimetrically from the $PM_{2.5}$ Teflon filter sample. The $PM_{2.5}$ Teflon filter sample is also used to determine concentrations of selected elements. The $PM_{2.5}$ nylon filter sample, which is preceded by a denuder to remove acidic gases, is analyzed to determine NO_3 and pSO_4 concentrations. Finally, the $PM_{2.5}$ quartz filter sample is analyzed for OC and EC using the thermal-optical reflectance (TOR) method for IMPROVE and thermal-optical transmittance (TOT) for CSN, though this network is in a transition stage to TOR.

In a side-by-side comparison of two of the chief aerosol monitoring techniques, $PM_{2.5}$ mass and major contributing species were moderately well correlated among the different methods with $r > 0.8$ (Hains, 2007). Agreement was good for total mass, SO_4^{2-}, OC, total carbon (TC), and NH_4^+, while NO_3^- and black carbon (BC) showed less-good fits. Based on reported uncertainties, however, even daily concentrations of $PM_{2.5}$ mass and major contributing species were often significantly different at the 95% confidence level. The CSN methods reported generally higher values of $PM_{2.5}$ total mass and of individual species than did the IMPROVE-like ones.

2.7.3.1. Artifacts

The reaction of SO_2 and other acid gases with basic coarse particles on the filter leads to formation of nonvolatile pSO_4, pNO_3, and Cl salts. These positive artifacts lead to the overestimates of the concentrations of PM total mass and SO_4^{2-} and likely NO_3^- as well. These problems were largely overcome by changing to quartz fiber or Teflon filters and by the separate collection of the $PM_{2.5}$ fraction. However, the possible reaction of acidic gases with basic coarse particles remains a possibility, especially with PM_{10} and $PM_{10-2.5}$ measurements. These positive artifacts could be effectively eliminated by removing acidic gases in the sampling line with denuders coated with NaCl or Na_2CO_3.

Positive sampling artifacts also occur during measurement of pNH_4. The reaction of NH_3 with acidic particles

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$$

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either during sampling or during transportation, storage, and equilibration could lead to an overestimation of pNH_4 concentrations. Techniques have been developed to overcome this problem, including using a denuder coated with hydrofluoric, citric, or phosphoric acid to remove NH_3 during sampling and to protect the collected PM from NH_3 (Suh, 1992; Suh, 1994; Brauer, 1991; Koutrakis, 1988; Koutrakis, 1988; Possanzini, 1999; Winberry, 1999; Keck, 2006). Positive artifacts for pNH_4 can also develop during sample handling due to contamination with NH_3 emitted directly from human sweat, breath, and tobacco smoking to form $(NH_4)_2SO_4$ or NH_4HSO_4 if the filter is improperly handled (Sutton, 2000).

Although pSO_4 is relatively stable on a Teflon filter, it is now well known that volatilization losses of pNO_3 occur during sampling. For pNO_3, the effect on the accuracy of atmospheric measurements from these volatilization losses is more significant for $PM_{2.5}$ than for PM_{10}, partly because NO_3^- contributes a smaller fraction to PM_{10} and partly because NO_X is present in a non-volatile form such as $NaNO_3$, in the coarse mode.

Sampling artifacts resulting from the loss of pNO_3 species represents a significant problem in areas such as southern California that experience high total NO_3 loadings. Hering and Cass (1999) discussed errors in $PM_{2.5}$ mass measurements owing to the volatilization of pNO_3 using data from two field measurement campaigns conducted in southern California: (1) the Southern California Air Quality Study (SCAQS) (Lawson, 1990); and (2) the 1986 California Institute of Technology (CalTech) study (Solomon, 1992). In both studies, side-by-side sampling of $PM_{2.5}$ was conducted with one sampler collecting particles directly onto a Teflon filter and a second using an MgO-coated denuder (Appel, 1981) to remove gaseous HNO_3, followed by a nylon filter to absorb the evaporating HNO_3. In both studies, the $PM_{2.5}$ mass lost from NH_4NO_3 volatilization represented a significant fraction of the total $PM_{2.5}$ mass, and these losses were greater during summer than fall: 17% (summer) versus 9% (fall) during SCAQS, and 21% (summer) versus 13% (fall) during CalTech. With regard to percentage loss of pNO_3, as contrasted to percentage loss of mass discussed above, (Hering, 1999) found that the amount of pNO_3 remaining on the Teflon filter samples was, on average, 28% less than that on the HNO_3-denuded nylon filters.

Hering and Cass (1999) also analyzed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model used by Hering and Cass (1999) takes into account the dissociation of collected particulate ammonium nitrate on Teflon filters into HNO_3 and NH_3 via three mechanisms: (1) the scrubbing of HNO_3 and NH_3 in the sampler inlet (John, 1988 showed that clean PM_{10} inlet surfaces serve as an effective denuder for HNO_3; 2) the heating of the filter substrate above ambient temperature by sampling; and (3) the pressure drop across the Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured to be less than 0.02 atm, and the corresponding change in vapor pressure was 2%, so losses driven by pressure drop were not considered to be significant in this work. Losses from Teflon filters were found to be higher during the summer than during the winter, higher during the day compared to night, and reasonably consistent with modeled predictions.

Finally, during the SCAQS (Lawson, 1990), particulate samples also were collected using a Berner impactor and greased Tedlar substrates in size ranges from 0.05 to 10 µm in aerodynamic diameter. The Berner impactor $PM_{2.5}$ NO_3 values were much closer to those from the denuded nylon filter than those from the Teflon filter, the impactor NO_3 values being ~2% lower than the nylon filter NO_3 for the fall measurements and ~7% lower for the summer measurements. When the impactor collection was compared to the Teflon filter collection for a nonvolatile species (sulfate), the results were in agreement. Chang et al. (2000) discuss reasons for reduced loss of NO_3 from impactors.

Brook and Dann (1999) observed much higher NO_3 losses during a study in which they measured particulate NO_3 in Windsor and Hamilton, Ontario, Canada, by three techniques: (1) a single Teflon filter in a dichotomous sampler, (2) the Teflon filter in an annular denuder system (ADS), and (3) total NO_3 including both the Teflon filter and the nylon back-up filter from the ADS. The Teflon filter from the dichotomous sampler averaged only 13% of the total NO_3, whereas the Teflon filter from the ADS averaged 46% of the total NO_3. The authors concluded that considerable NO_3 was lost from the dichotomous sampler filters during handling, which included weighing and XRF measurement in a vacuum.

Kim et al. (1999) also examined NO_3-sampling artifacts by comparing denuded and non-denuded quartz and nylon filters during the PM_{10} Technical Enhancement Program (PTEP) in the California South Coast Air Basin. They observed negative NO_3 losses for most measurements; however, for a significant number of measurements, they observed positive NO_3 artifacts. Kim et al. (1999) pointed out that random measurement errors make it difficult to measure true amounts of NO_3 loss.

Diffusion denuder samplers, developed primarily to measure particle strong acidity (Koutrakis, 1988; Koutrakis, 1992), also can be used to study NO_3^- volatilization. Measurements were made with two versions of the Harvard-EPA Annular Denuder System (HEADS) for which HNO_3 vapor was removed by a Na_2CO_3-coated denuder and the remaining pNO_3 was reported either as the sum of nonvolatile NO_3 collected on a Teflon filter and volatized NO_3^- collected on a Na_2CO_3–coated filter downstream of the Teflon filter (full HEADS), or on a Nylon filter downstream of the Teflon filter (Nylon HEADS). The full HEADS consistently underestimated the total pNO_3 by ~20% compared to the Nylon HEADS.

This comparison technique was then used to measure loss of pNO_3^- from Teflon filters in seven U.S. cities. (Babich, 2000). Babich et al. (2000) found significant NO_3^- losses in Riverside, CA, Philadelphia, PA, and Boston, MA, but not in Bakersfield, CA, Chicago, IL, Dallas, TX, or Phoenix, AZ, where measurements were made only during winter.

Negative sampling artifacts due to decomposition and volatilization are also significant for pNH_4 more often when it appears as NH_4NO_3 since $(NH_4)_2SO_4$ is much more stable. The presence and deposition of NH_4NO_3 is highly sensitive to environmental factors such as temperature, relative humidity, acidity of aerosols, as well as to filter type (Spurny, 1999; Keck, 2005). Any change in these parameters during the sampling period influences the position of the equilibrium between the particle and gas phases. Keck and Wittmaack (2005) observed that at temperatures < 0 EC, acetate-NO_3, quartz fiber, and Teflon filters could properly collect pNH_4, NH_3, and Cl; but at temperatures > 0 EC, the salts were lost from quartz fiber and Teflon filters, more so at higher temperatures and with no significant difference between quartz fiber and Teflon filters. The salts were lost completely from denuded quartz fiber filters at temperatures above ~20 EC, and from non-undenuded quartz fiber and Teflon filters at temperatures above ~25 EC. It is anticipated that current sampling techniques underestimate pNH_4 levels due to volatilization, but fine particle mass contains many acidic compounds, and, as consequence, a fraction of volatilized NH_4^+ in the form of NH_3 can be retained on the Teflon filter by reactions with them. Owing to these positive and negative interference effects, the magnitude of pNH_4 remains largely unknown. However, techniques have been applied to pNH_4 sampling to correct its concentrations due to evaporation using a backup filter coated with hydrofluoric acid, citric acid, or phosphorous acid to absorb the evaporated NH_4 as NH_3.

Volatile compounds can also leave the filter after sampling and prior to filter weighing or chemical analysis. Losses of NO_3, NH_4, and Cl from glass and quartz-fiber filters that were stored in unsealed containers at ambient air temperatures for 2 to 4 weeks prior to analysis exceeded 50% (Witz, 1990).

2.7.3.2. Other Methods

An integrated collection and vaporization cell was developed by Stolzenburg and Hering (2000) that provides automated, 10–min resolution monitoring of fine-particulate NO_3. In this system, particles are collected by a humidified impaction process and analyzed in place by flash vaporization and CL detection of the evolved NO_X. In field tests in which the system was collocated with two FRM samplers, the automated pNO_3 sampler results followed the results from the FRM, but were offset lower. The system also was collocated with a HEADS and a SASS speciation sampler (MetOne Instruments). In all these tests, the automated sampler was well correlated to other samplers with slopes near 1, ranging from 0.95 for the FRM to 1.06 for the HEADS and correlation coefficients ranging from 0.94 to 0.996. During the Northern Front Range Air Quality Study in Colorado (Watson, 1998), the automated pNO_3 monitor captured the 12–min variability in pNO_3 concentrations with a precision of approximately $\pm$ 0.5 $\mu g/m^3$ (Chow, 1998). A comparison with denuded filter measurements followed by IC analysis (Chow, 1999) showed agreement within $\pm$ 0.6 $\mu g/m^3$ for most of the measurements, but exhibited a discrepancy of a factor of two for the periods of high pNO_3 concentrations. More recent intercomparisons took place during the 1997 Southern California Ozone Study (SCOS97) in Riverside, CA. Comparisons with 14 days of 24–h denuder-filter sampling gave a correlation coefficient of $R^2 = 0.87$ and showed no significant bias. As currently configured, the system has a detection limit of 0.7 $\mu g/m^3$ and a precision of 0.2 $\mu g/m^3$.

The extent to which sampling artifacts for pNH_4^+ have been adequately addressed in the current networks is not clear. Recently, new denuder-filter sampling systems have been developed to measure pSO_4^{2-}, pNO_3, and pNH_4^+ with an adequate correction of NH_4^+ sampling artifacts. The denuder-filter system, Chembcomb Model 3500 speciation sampling cartridge developed by Rupprecht & Patashnick Co, Inc. could be used to collect NO_3, SO_4^{2-}, and ammonium simultaneously. The sampling system contains a single-nozzle size-selective inlet, two honeycomb denuders, the aerosol filter and two backup filters (Keck, 2005). The first denuder in the system is coated with 0.5% sodium carbonate and 1% glycerol and collects acid gases such as HCl, SO_2, HNO_2, and HNO_3. The second denuder is coated with 0.5% phosphoric acid in methanol for collecting NH_3. Backup filters collect the gases behind denuded filters. The backup filters are coated with the same solutions as the denuders. A similar system based on the same principle was applied by Possanzini et al. (1999). The system contains two $NaCl^-$coated annular denuders followed by other two denuders coated with $NaCO_3$/glycerol and citric acid, respectively. This configuration was adopted to remove HNO_3 quantitatively on the first NaCl denuder. The third and forth denuder remove SO_2 and NH_3, respectively. A polyethylene cyclone and a two-stage filter holder containing three filters is placed downstream of the denuders. Aerosol fine particles are collected on a Teflon membrane. A backup nylon filter and a subsequent citric acid impregnated filter paper collect dissociation products HNO_3 and NH_3 of NH_4NO_3 evaporated from the filtered particulate matter.

2.8. Methods to Compute NO_X and SO_X Concentrations, Chemical Interactions, and Deposition

2.8.1. CTMs

CTMs are the prime tools used to compute the interactions among NO_X, SO_X, other pollutants and their precursors, the transport and transformation of air toxics, the production of secondary aerosols, the evolution of the particle size distribution, and deposition of pollutants. CTMs are driven by emissions inventories for primary species such as NO_X, SO_X, NH_3, and primary PM, and by meteorological fields produced by other numerical prediction models. Meteorological quantities such as winds and temperatures are taken from operational analyses, reanalyses, or weather circulation models. In most cases, these are off-line meteorological analyses, meaning that they are not modified by radiatively active species generated by the air quality model (AQM).

Emissions of precursor compounds can be divided into anthropogenic and biogenic source categories, and biogenic sources can be further divided into biotic (vegetation, microbes, animals) and abiotic (biomass burning, lightning) categories as presented above. However, the distinction between biogenic sources and anthropogenic sources is often difficult to make, as human activities affect directly or indirectly emissions from what would have been considered biogenic sources during the preindustrial era. Thus, emissions from plants and animals used in agriculture have been referred to as anthropogenic or biogenic in different applications. Wildfire emissions may be considered to be biogenic, except that forest management practices may have led to the buildup of fuels on the forest floor, thereby altering the frequency and severity of forest fires.

The initial conditions, or starting concentration fields of all species computed by a model, and the boundary conditions, or concentrations of species along the horizontal and upper boundaries of the model domain throughout the simulation, must be specified at the beginning of the simulation. Both initial and boundary conditions can be estimated from models or data or, more generally, model+data hybrids. Because data for vertical profiles of most species of interest are sparse, results of model simulations over larger, usually global, domains are often used. As might be expected, the influence of boundary conditions depends on the τ of the species under consideration and the time scales for transport from the boundaries to the interior of the model.

Each of the model components described above has associated uncertainties and the relative importance of these uncertainties varies with the modeling application. The largest errors in photochemical modeling are still thought to arise from the meteorological and emissions inputs to the model (Russell, 2000). Within the model itself, horizontal advection algorithms are still thought to be significant source of uncertainty (see e.g.,, Chock, 1994), though more recently, those errors are thought to have been reduced (see e.g.,, Odman, 1996). There are also indications that problems with mass conservation continue to be present in photochemical and meteorological models (see e.g.,, Odman, 1999) and can result in significant simulation errors. The effects of errors in initial conditions can be minimized by including several days spin-up time in a simulation to allow the model to be driven by emitted species before the simulation of the period of interest begins.

While the effects of poorly specified boundary conditions propagate through the model's domain, the effects of these errors remain undetermined. Because many meteorological processes occur on spatial scales which are smaller than the model grid spacing (either horizontally or vertically) and thus are not calculated explicitly, parameterizations of these processes must be used and these introduce additional uncertainty.

Specific uncertainty also arises in modeling the chemistry of NO_X transformations because they are strongly nonlinear. Thus, the volume of the grid cell into which emissions are injected is important because, for example, O_3 production or loss depends in a complicated way on the concentrations of NO_X and OH as explained above. Use of ever-finer grid spacing allows more valid separations of regions of high NO_X concentrations from low NO_X regions and from regions were NO_X concentrations are optimal for $P(O_3)$.

The use of grid spacing fine enough to resolve the chemistry in individual power-plant plumes is too demanding of computer resources for this to be attempted in most simulations. Instead, parameterizations of the effects of sub-grid-scale processes such as these must be developed, else serious errors can result if emissions are allowed to mix through an excessively large grid volume before the chemistry step in a model calculation is performed. In light of the significant differences between atmospheric chemistry taking place within and outside of a power plant plume identified by Ryerson et al.

(1998), inclusion of a separate module for treating large, tight plumes can be useful. Because the photochemistry of NO_X transformation is nonlinear, emissions correctly modeled in a tight plume may be incorrectly modeled in a more dilute plume. Fortunately, it appears that the chemical mechanism used to follow a plume's development need not be as detailed as that used to simulate the rest of the domain, as the inorganic reactions are the most important in the plume (see e.g.,, Kumar, 1996).

Because the chemical production and loss terms in the continuity equations for individual species are coupled, the chemical calculations must be performed iteratively until calculated concentrations converge to within some preset criterion. The number of iterations and the convergence criteria chosen also can introduce error.

CTMs have been developed for application over a wide range of spatial scales ranging up from neighborhood to global. CTMs are used to: (1) obtain better understanding of the processes controlling the formation, transport, and destruction of gas- and particle-phase criteria and hazardous air pollutants; 2) understand the relations between concentrations of secondary pollutant products and concentrations of their precursors such as NO_X and VOCs and the factors leading to acid deposition and possible damage to biota; 3) understand relations among the concentration patterns of various pollutants that may exert adverse effects; and (4) evaluate how changes in emissions propagate through the atmospheric system to secondary products and deposition.

Global-scale CTMs are used to address issues associated with climate change and stratospheric O_3 depletion, and to provide boundary conditions for the regional-scale models. The CTMs include simplified mathematical descriptions of atmospheric transport, the transfer of solar radiation through the atmosphere, chemical reactions, and removal to the surface by turbulent motions and precipitation for pollutants emitted into the model domain. The upper boundaries of the CTMs extend anywhere from the top of the mixed layer to the mesopause at ~80 km in order to obtain more realistic boundary conditions for problems involving stratospheric dynamics.

CTMs in current use mostly have one of two forms. The first, grid-based or Eulerian air quality models subdivide the region to be modeled or the modeling domain into a three-dimensional array of grid cells. Spatial derivatives in the species continuity equations are cast in finite-difference form over this grid and a system of equations for the concentrations of all the chemical species in the model are solved numerically at each grid point. Finite element Eulerian models also exist and have been exercised, but less frequently. Time dependent continuity or mass conservation equations are solved for each species including terms for transport, chemical production and destruction, and emissions and deposition (if relevant), in each cell. Chemical processes are simulated with ordinary differential equations, and transport processes are simulated with partial differential equations. Because of a number of factors such as the different time scales inherent in different processes, the coupled, nonlinear nature of the chemical process terms, and computer storage limitations, all of the terms in the equations are not solved simultaneously in three dimensions. Instead, operator splitting, in which terms in the continuity equation involving individual processes are solved sequentially, is used.

In the second common CTM formulation, trajectory or Lagrangian models, a number of hypothetical air parcels are specified as following wind trajectories. In these models, the original system of partial differential equations is transformed into a system of ordinary differential equations.

A less common approach is to use a hybrid Lagrangian/Eulerian model, in which certain aspects of atmospheric chemistry and transport are treated with a Lagrangian approach and others are treaded in an Eulerian manner (see e.g.,, Stein, 2000).

Each approach has its advantages and disadvantages. The Eulerian approach is more general in that it includes processes that mix air parcels and allows integrations to be carried out for long periods during which individual air parcels lose their identity. There are, however, techniques for including the effects of mixing in Lagrangian models such as FLEXPART (e.g.,, Zanis, 2003), ATTILA (Reithmeier, 2002), and CLaMS (McKenna, 2002).

2.8.1.1. Global Scale

The importance of global transport of O_3 and O_3 precursors and their contribution to regional O_3 levels in the U.S. is now apparent. There are at present on the order of 20 three-dimensional global models developed by various groups to address problems in tropospheric chemistry. These models resolve synoptic meteorology, O_3-NO_X-CO-HC photochemistry, have parameterizations for wet and dry deposition, and parameterize sub-grid scale vertical mixing processes such as convection. Global models have proven useful for testing and advancing scientific understanding beyond what is possible with observations alone. For example, they can calculate quantities of interest that cannot be measured directly, such as the export of pollution from one continent to the global atmosphere or the response of the atmosphere to future perturbations to anthropogenic emissions.

Global simulations are typically conducted at a horizontal resolution of 200 km^2 or more. Simulations of the effects of transport from long-range transport link multiple horizontal resolutions from the global to the local scale. Finer resolution will only improve scientific understanding to the extent that the governing processes are more accurately described at that scale. Consequently, there is a critical need for observations at the appropriate scales to evaluate the scientific understanding represented by the models.

During the recent IPCC-AR4 tropospheric chemistry study coordinated by the European Union Atmospheric Composition Change: the European Network of excellence (ACCENT), 26 atmospheric CTMs were used to estimate the impacts of three emissions scenarios on global atmospheric composition, climate, and air quality in 2030 (Dentener, 2006). All models were required to use anthropogenic emissions developed at IIASA (Dentener, 2005) and GFED version 1 biomass burning emissions (Van der

Werf, 2003) as described in Stevenson et al. (2006). The base simulations from these models were evaluated against a suite of present-day observations. Most relevant to this assessment report are the evaluations with ozone, NO_2, and N deposition (Stevenson, 2006; van Noije, 2006; Dentener, 2006), which are summarized briefly below.

An analysis of the standard deviation of zonal mean and tropospheric column O_3 reveals large inter-model variability in the tropopause region and throughout the polar troposphere, likely reflecting differences in model tropopause levels and the associated stratospheric injection of O_3 to the troposphere (Stevenson, 2006). Ozone distributions in the tropics also exhibit large standard deviations (~30%), particularly as compared to the mid-latitudes (~20%), indicating larger uncertainties in the processes that influence ozone in the tropics: deep tropical convection, lightning NO_X, isoprene emissions and chemistry, and biomass burning emissions (Stevenson, 2006).

Stevenson et al., (2006) found that the model ensemble mean (MEM) typically captures the observed seasonal cycles to within one standard deviation. The largest discrepancies between the MEM and observations include: (1) an underestimate of the amplitude of the seasonal cycle at 30°-90°N with a 10 ppb overestimate of winter ozone, possibly due to the lack of a seasonal cycle in anthropogenic emissions or to shortcomings in the stratospheric influx of O_3, and (2) an overestimate of O_3 throughout the northern tropics. However, the MEM was found to capture the observed seasonal cycles in the southern hemisphere, suggesting that the models adequately represent biomass burning and natural emissions.

The mean present-day global ozone budget across the current generation of CTMs differs substantially from that reported in the IPCC Third Assessment Report (TAR), with a 50% increase in the mean chemical production (to 5100 Tg O_3/yr), a 30% increase in the chemical and deposition loss terms (to 4650 and 1000 Tg O_3/yr, respectively) and a 30% decrease in the mean stratospheric input flux (to 550 Tg O_3/yr) (Stevenson, 2006). The larger chemical terms as compared to the IPCC TAR are attributed mainly to higher NO_X (as well as an equatorward shift in distribution) and isoprene emissions, although more detailed schemes and/or improved representations of photolysis, convection, and stratospheric-tropospheric exchange may also contribute (Stevenson, 2006).

A subset of 17 of the 26 models used in the Stevenson et al. (2006) study was used to compare with three retrievals of NO_2 columns from the GOME instrument (van Noije, 2006) for the year 2000. The higher resolution models reproduce the observed patterns better, and the correlation among simulated and retrieved columns improved for all models when simulated values are smoothed to a 5° × 5° grid, implying that the models do not accurately reproduce the small-scale features of NO_2 (van Noije, 2006). Van Noije et al. (2006) suggest that variability in simulated NO_2 columns may reflect model differences in OH distributions and the resulting NO_X lifetimes, as well as differences in vertical mixing which strongly affect partitioning between NO and NO_2. Overall, the models tend to underestimate concentrations in the retrievals in industrial regions (including the eastern U.S.) and overestimate them in biomass burning regions (van Noije, 2006).

Over the eastern U.S. and in industrial regions more generally, the spread in absolute column abundances is generally larger among the retrievals than among the models, with the discrepancy among the retrievals particularly pronounced in winter (van Noije, 2006), suggesting that the models are biased low, or that the European retrievals may be biased high as the Dalhousie SAO retrieval is closer to the model estimates. The lack of seasonal variability in fossil fuel combustion emissions may contribute to a wintertime model underestimate (van Noije, 2006) manifested most strongly over Asia. In biomass burning regions, the models generally reproduce the timing of the seasonal cycle of the retrievals, but tend to overestimate the seasonal cycle amplitude, partly due to lower values in the wet season, which may reflect an underestimate in wet season soil NO emissions (van Noije, 2006; Jaeglé, 2004; Jaeglé, 2005).

2.8.1.2. Regional Scale

Major modeling efforts within the EPA center on the Community Multiscale Air Quality modeling system (CMAQ) (Byun, 1999; Byun, 2006). A number of other modeling platforms using Lagrangian and Eulerian frameworks have been reviewed in the 2006 AQCD for O_3 (EPA, 2006) and in Russell and (2001; , 2000). The capabilities of a number of CTMs designed to study local- and regional-scale air pollution problems were summarized by Russell and Dennis (2000). Evaluations of the performance of CMAQ are given in Arnold et al. (2003, Eder and Yu, (2006, Appel et al. (2005), and Fuentes and Raftery (2005). The domain of CMAQ can extend from several hundred km to the entire hemisphere. In addition, both of these classes of models allow resolution of the calculations over specified areas to vary. CMAQ is most often driven by the MM5 mesoscale meteorological model (Seaman, 2000), though it may be driven by other meteorological models RAMS. Simulations of pollution episodes over regional domains have been performed with a horizontal resolution as low as 1 km, and smaller calculations over limited domains have been accomplished at even finer scales. However, simulations at such high resolutions require better parameterizations of meteorological processes such as boundary layer fluxes, deep convection and clouds (Seaman, 2000), as well as finer-scale emissions. Finer spatial resolution is necessary to resolve features such as urban heat island circulation; sea, bay, and land breezes; mountain and valley breezes, and the nocturnal low-level jet, all of which can affect pollutant concentrations.

The most common approach to setting up the horizontal domain is to nest a finer grid within a larger domain of coarser resolution. However, there are other strategies such as the stretched grid (e.g.,, Fox-Rabinovitz, 2002) and the adaptive grid. In a stretched grid, the grid's resolution continuously varies throughout the domain, thereby eliminating any potential problems with the sudden change from one resolution to another at the boundary. Caution should be exercised in using such a formulation, because certain parameterizations (such as for convection) valid on a relatively coarse grid scale may not be valid on finer scales. Adaptive grids are not fixed at the start of the simulation, but instead adapt to the needs of the simulation as it evolves (e.g.,, Hansen, 1994). They have the advantage that they can resolve processes at relevant spatial scales. However, they can be very slow if the situation to be modeled is complex. Additionally, if adaptive grids are used for separate meteorological, emissions, and photochemical models, there is no reason a priori why the resolution of each grid should match, and the gains realized from increased resolution in one model will be wasted in the transition to another model. The use of finer horizontal resolution in CTMs will necessitate finer-scale inventories of land use and better knowledge of the exact paths of roads, locations of factories, and, in general, better methods for locating sources and estimating their emissions.

The vertical resolution of these CTMs is variable, and usually configured to have higher resolution near the surface and decreasing aloft. Because the height of the boundary layer is of critical importance in simulations of air quality, improved resolution of the boundary layer height would likely improve air quality simulations. Additionally, current CTMs do not adequately resolve fine scale features such as the nocturnal low-level jet in part because little is known about the nighttime boundary layer.

CTMs require time-dependent, three-dimensional wind fields for the period of simulation. The winds may be generated either by a model using initial fields alone or with four-dimensional data assimilation to improve the model's performance; i.e., model equations can be updated periodically "nudged" to bring results into agreement with observations. Modeling efforts typically focus on simulations of several days' duration, the typical time scale for individual O_3 episodes; but longer term modeling series of several months or multiple seasons of the year are now common. The current trend in modeling applications is towards annual simulations. This trend is driven in part by the need to better understand observations of periods of high wintertime PM (e.g.,, Blanchard, 2002) and the need to simulate O_3 episodes occurring outside of summer.

Chemical kinetics mechanisms (a set of chemical reactions) representing the important reactions occurring in the atmosphere are used in CTMs to estimate the rates of chemical formation and destruction of each pollutant simulated as a function of time. Unfortunately, chemical mechanisms that explicitly treat the reactions of individual reactive species are too computationally demanding to be incorporated into CTMs for regulatory use. So, for example, are very extensive "master mechanisms" (Derwent, 2001) includes approximately 10,500 reactions involving 3603 chemical species (Derwent, 2001), but "lumped" mechanisms that group compounds of similar chemistry together, are used. The chemical mechanisms used in existing photochemical O_3 models contain significant uncertainties that may limit the accuracy of their predictions; the accuracy of each of these mechanisms is also limited by missing chemistry. Because of different approaches to the lumping of organic compounds into surrogate groups, chemical mechanisms can produce somewhat different results under similar conditions. The CB-IV chemical mechanism (Gery, 1989), the RADM II mechanism (Stockwell, 1990), the SAPRC (e.g.,, Wang, 2000;

Wang, 2000; Carter, 2007) and the RACM mechanisms can be used in CMAQ. Jimenez et al. (2003) provide brief descriptions of the features of the main mechanisms in use and they compared concentrations of several key species predicted by seven chemical mechanisms in a box model simulation over 24 h. The average deviation from the average of all mechanism predictions for O_3 and NO over the daylight period was less than 20%, and was 10% for NO_2 for all mechanisms. However, much larger deviations were found for HNO_3, PAN, HO_2, H_2O_2, ethylene (C_2H_4), and isoprene (C_5H_8). An analysis for OH radicals was not presented. The large deviations shown for most species imply differences between the calculated lifetimes of atmospheric species and the assignment of model simulations to either NO_X-limited or radical quantity limited regimes between mechanisms. Gross and Stockwell (2003) found small differences between mechanisms for clean conditions, with differences becoming more significant for polluted conditions, especially for NO_2 and organic peroxy radicals. Faraji et al. (2005) found differences of 40% in peak 1 h O_3 in the Houston-Galveston-Brazoria area between simulations using SAPRAC and CB4. They attributed differences in predicted O_3 concentrations to differences in the mechanisms of oxidation of aromatic HCs.

CMAQ and other state-of-the-science CTMs incorporate processes and interactions of aerosol-phase chemistry (Mebust, 2003). There have also been several attempts to study the feedbacks of chemistry on atmospheric dynamics using meteorological models, like MM5 (e.g., (e.g.,, Grell, 2000; Liu, 2001; Lu, 1997; Park, 2001). This coupling is necessary to simulate accurately feedbacks such as may be caused by the heavy aerosol loading found in forest fire plumes (Lu, 1997; Park, 2001), or in heavily polluted areas. Photolysis rates in CMAQ can now be calculated interactively with model produced O_3, NO_2, and aerosol fields (Binkowski, 2007).

Spatial and temporal characterizations of anthropogenic and biogenic precursor emissions must be specified as inputs to a CTM. Emissions inventories have been compiled on grids of varying resolution for many HCs, aldehydes, ketones, CO, NH_3, and NO_X. Emissions inventories for many species require the application of algorithms for calculating the dependence of emissions on physical variables such as temperature and to convert the inventories into formatted emission files which can be used by a CTM. For example, preprocessing of emissions data for CMAQ is done by the Spare-Matrix Operator Kernel Emissions (SMOKE) system. For many species, information concerning the temporal variability of emissions is lacking, so long-term (e.g., annual or O_3−season) averages are used in short-term, episodic simulations. Annual emissions estimates are often modified by the emissions model to produce emissions more characteristic of the time of day and season. Significant errors in emissions can occur if inappropriate time dependence or a default profile is used. Additional complexity arises in model calculations because different chemical mechanisms can include different species, and inventories constructed for use with another mechanism must be adjusted to reflect these differences. This problem also complicates comparisons of the outputs of these models because one chemical mechanism may produce some species not present in another mechanism yet neither prediction may agree with the measurements.

2.8.1.3. Sub-regional Scale

The grid spacing in regional chemistry transport models of between 1 and 12 km^2 is usually too coarse to resolve spatial variations on the neighborhood scale. The interface between regional scale models and models of personal exposure described is provided by smaller scale dispersion models. Several models could be used to simulate concentration fields near roads, each with its own set of strengths and weaknesses. For example, AERMOD (http://www.epa.gov/scram001/dispersion_prefrec.htm) is a steady-state plume model that was formulated as a replacement to the ISC3 dispersion model. In the stable boundary layer (SBL), it assumes the concentration distribution to be Gaussian in both the vertical and horizontal. In the convective boundary layer, the horizontal distribution is also assumed to be Gaussian, but the vertical distribution is described with a bi-Gaussian probability density function (pdf). AERMOD has provisions to be applied to flat and complex terrain, and multiple source types (including, point, area and volume sources) in both urban and rural areas. It incorporates air dispersion based on planetary boundary layer turbulence structure and scaling concepts, and is meant to treat both surface and elevated sources and simple and complex terrain in rural and urban areas. The dispersion of emissions from line sources like highways is treated as the sum of emissions from a number of point sources placed side by side. However, emissions are usually not in steady state and there are different functional relationships between buoyant plume rise in point and line sources. It should be remembered that NO_2 is largely secondary in nature as it is produced by Reaction 6. However, AERMOD does not have provision for including secondary sources. The more appropriate use of AERMOD would be to simulate the total of NO and NO_2, or NO_X.

There are non-steady state models that incorporate plume rise explicitly from different types of sources. For example, CALPUFF (http://www.src.com/calpuff/calpuff1.htm) is a non-steady-state puff dispersion model that simulates the effects of time- and space-varying meteorological conditions on pollution transport, transformation, and removal and has provisions for calculating dispersion from surface sources. However, it should be noted that neither model was designed to treat the dispersion of emissions from roads or to include secondary sources. In using either model, the user would have to specify dispersion parameters that are specific to traffic. The distinction between a steady–state and time varying model might not be important for long time scales; however for short time scales, the temporal variability in traffic emissions could result in underestimation of peak concentration and exposures.

2.8.1.4. Modeling Effects of Convection for Chemical Transport

The effects of deep convection can be simulated using cloud-resolving models, or in regional or global models in which the convection is parameterized. The Goddard Cumulus Ensemble (GCE) model (Tao, 1993) has been used by Pickering et al. (1991; , 1992; , 1992; , 1993; , 1996), Scala et al. (1990), and Stenchikov et al. (1996) in the analysis of convective transport of trace gases. The cloud model is nonhydrostatic and contains a detailed representation of cloud microphysical processes. Two- and three-dimensional versions of the model have been applied in transport analyses. The initial conditions for the model are usually from a sounding of temperature, water vapor and winds representative of the region of storm development. Model-generated wind fields can be used to perform air parcel trajectory analyses and tracer advection calculations.

Such methods were used by Pickering et al. (1992) to examine transport of urban plumes by deep convection. Transport of an Oklahoma City plume by the 10–11 June 1985 PRE-STORM squall line was simulated with the 2–D GCE model. This major squall line passed over the Oklahoma City metropolitan area, as well as more rural areas to the north. Chemical observations ahead of the squall line were conducted by the PRE-STORM aircraft. In this event, forward trajectories from the boundary layer at the leading edge of the storm showed that almost 75% of the low level inflow was transported to altitudes exceeding 8 km. Over 35% of the air parcels reached altitudes over 12 km. Tracer transport calculations were performed for CO, NO_X, O_3, and HCs. Rural boundary layer NO_X was only 0.9 ppb, whereas the urban plume contained about 3 ppb. In the rural case, mixing ratios of 0.6 ppb were transported up to 11 km. Cleaner air descended at the rear of the storm lowering NO_X at the surface from 0.9 to 0.5 ppb. In the urban plume, mixing ratios in the updraft core reached 1 ppb between 14 and 15 km. At the surface, the main downdraft lowered the NO_X mixing ratios from 3 to 0.7 ppb.

Regional chemical transport models have been used for applications such as simulations of photochemical O_3 production, acid deposition, and fine PM. Walcek et al. (1990) included a parameterization of cloud-scale aqueous chemistry, scavenging, and vertical mixing in the chemistry model of (Chang, 1987). The vertical distribution of cloud microphysical properties and the amount of sub-cloud-layer air lifted to each cloud layer are determined using a simple entrainment hypothesis (Walcek, 1986). Vertically integrated O_3 formation rates over the northeast U. S. were enhanced by ~50% when the in-cloud vertical motions were included in the model.

Wang et al. (1996) simulated the 10–11 June 1985 PRE-STORM squall line with the NCAR/Penn State Mesoscale Model (MM5) (Grell, 1994; Dudhia, 1993). Convection was parameterized as a sub-grid-scale process in MM5 using the Kain and Fritsch (1993) scheme. Mass fluxes and detrainment profiles from the convective parameterization were used along with the 3−D wind fields in CO tracer transport calculations for this convective event.

Convective transport in global chemistry and transport models is treated as a sub-grid-scale process that is parameterized typically using cloud mass flux information from a general circulation model or global data assimilation system. While GCMs can provide data only for a "typical" year, data assimilation systems can provide "real" day-by-day meteorological conditions, such that CTM output can be compared directly with observations of trace gases. The NASA Goddard Earth Observing System Data Assimilation System (GEOS-1 DAS and successor systems; Schubert, 1993; Bloom, 1996; Bloom, 2005) provides archived global data sets for the period 1980 to present, at 2° × 2.5° or better resolution with 20 layers or more in the vertical. Deep convection is parameterized with the Relaxed Arakawa-Schubert scheme (Moorthi, 1992) in GEOS-1 and GEOS-3 and with the Zhang and McFarlane (1995) scheme in GEOS-4. Pickering et al. (1995) showed that the cloud mass fluxes from GEOS-1 DAS are reasonable for the 10–11 June 1985 PRE-STORM squall line based on comparisons with the GCE model (cloud-resolving model) simulations of the same storm. In addition, the GEOS-1 DAS cloud mass fluxes compared favorably with the regional estimates of convective transport for the central U.S. presented by Thompson et al. (1994). However, Allen et al. (1997) have shown that the GEOS-1 DAS overestimates the amount and frequency of convection in the tropics and underestimates the convective activity over midlatitude marine storm tracks.

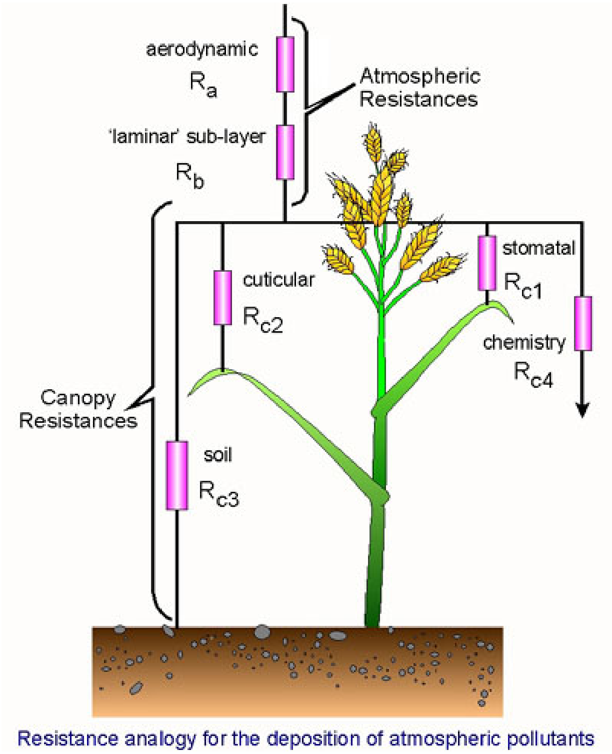
Global models with parameterized convection and lightning have been run to examine the roles of these processes over North America. Lightning contributed 23% of upper tropospheric NO_Y over the SONEX region according to the UMD-CTM modeling analysis of Allen et al. (2000). During the summer of 2004 the NASA Intercontinental Chemical Transport Experiment – North America (INTEX-NA) was conducted primarily over the eastern two-thirds of the U.S., as a part of the International Consortium for Atmospheric Research on Transport and Transformation (ICARTT). Deep convection was prevalent over this region during the experimental period. Cooper et al. (Cooper, 2006) used a particle dispersion model simulation for NO_X to show that 69–84% of the upper tropospheric O_3 enhancement over the region in summer 2004 was due to lightning NO_X. The remainder of the enhancement was due to convective transport of O_3 from the boundary layer or other sources of NO_X. Hudman et al. (2007) used a GEOS-Chem model simulation to show that lightning was the dominant source of upper tropospheric NO_X over this region during this period. Approximately 15% of North American boundary layer NO_X emissions were shown to have been vented to the free troposphere over this region based on both the observations and the model.

2.8.2. Computed Deposition

Wet and dry deposition are important removal processes for pollutants on urban and regional scales and so are included in CTMs. The general approach used in most models is the resistance-in-series method described above and represented in Reaction 61. This approach works for a range of substances, although it is inappropriate for species with substantial re-emissions from the surface or for species where deposition to the surface depends on concentrations at the surface itself. The approach is also modified somewhat for aerosols in that the terms R_b and R_c are replaced with a surface V_d to account for gravitational settling.

$$V_d=(R_a+R_b=R_c)^{-1}$$

Reaction 61



Source: Courtesy of Thomas Pierce, USEPA / ORD / NERL / Atmospheric Modeling Division.

Figure 2-26. Schematic of the resistance-in-series analogy for atmospheric deposition. Function of wind speed, solar radiation, plant characteristics, precipitation/moisture, and soil/air temperature.

where R_a, R_b, and R_c represent the resistance due to atmospheric turbulence, transport in the fluid sublayer very near the elements of surface such as leaves or soil, and the resistance to uptake of the surface itself as shown in Figure 2-26.

Weseley and Hicks (2000) listed several shortcomings of the then-current knowledge of dry deposition. Among those shortcomings were difficulties in representing dry deposition over varying terrain where horizontal advection plays a significant role in determining the magnitude of R_a and difficulties in adequately determining V_d for extremely stable conditions such as those occurring at night; see the discussion by Mahrt (1998) 1998, for example. Under optimal conditions, when a model is exercised over a relatively small area where dry deposition measurements have been made, models still generally showed uncertainties on the order of ±30% (see e.g.,, Massman, 1994; Brook, 1996; Padro, 1996). Wesely and Hicks (2000) concluded that an important result of those comparisons was that the level of sophistication of most dry deposition models was relatively low, and that deposition estimates, therefore, must rely heavily on empirical data. Still larger uncertainties exist when the surface features in the built environment are not well known or when the surface comprises a patchwork of different surface types, as is common in the eastern U.S.

2.8.2.1. N Deposition and Flux with Biota

Several reactive N are species are deposited to vegetation, among them, HNO_3, NO_2, and PAN and other $RONO_2$.

Field observations based on concentration gradients of HNO_3 and using eddy covariance techniques demonstrate rapid deposition that approaches the aerodynamic limit (as constrained by atmospheric turbulence) in the Wesely and Lesht (1989) formulation based on analogy to resistance. Surface resistance to HNO_3 uptake by vegetation is negligible. Deposition rates are independent of leaf area or stomatal conductance, implying that deposition occurs to branches, soil, and the leaf cuticle as well as leaf surfaces. The HNO_3 V_d typically exceeds 1 cm/s and exhibits a diel pattern controlled by turbulence characteristics of midday maxima and lower values at night in the more-stable boundary layer.

NO_2 interaction with vegetation is more difficult to understand than that for HNO_3, in part because very fast measurements of NO_2 flux are confounded by the rapid interconversion of NO, NO_2, and O_3 (Gao, 1991). Application of ^{15}N-labeled NO_2 demonstrates that NO_2 is absorbed and metabolized by foliage (Siegwolf, 2001; Mocker, 1998; Segschneider, 1995; Weber, 1995). Exposure to NO_2 induces activation of NO_3 reductase (Weber, 1995; Weber, 1998), a necessary enzyme for assimilating oxidized N. Understanding of NO_2 interactions with foliage is largely based on leaf cuvette and growth chamber studies which expose foliage or whole plants to controlled NO_2 concentrations and measure the fraction of NO_2 removed from the chamber air. A key finding is that the fit of NO_2 flux to NO_2, has a non-0 intercept, implying a compensation point or internal concentration. In studies at very low NO_2 concentrations, emission from foliage is observed (Teklemariam, 2006). Evidence for a compensation point is not solely based on the fitted intercept. The NO_2 uptake rate to foliage is clearly related to stomatal conductance. Internal resistance is variable, and may be associated with concentrations of reactive species such as ascorbate in the plant tissue that react with NO_2 (Teklemariam, 2006). Foliar NO_2 emissions show some dependence on N content (Teklemariam, 2006). Internal NO_2 appears to derive from plant N metabolism.

Two approaches to modeling NO_2 uptake by vegetation are the resistance-in-series analogy which considers flux (*F*) as the product of concentration (*C*) and V_d, related to the sum of aerodynamic, boundary layer, and internal resistances (R_a, R_b, and R_c, respectively); by convention, positive fluxes are in the direction of from the atmosphere to foliage. Note that this approach is the method most often used to predict deposition in AQMs, that of Wesely and Lesht (1989), as described above. These terms are related as shown in Equations 59 above and 60

$$F=CV_d$$

Reaction 62

Typically, the NO_2 V_d is less than that for O_3 due to the surface's generally higher resistance to NO_2 uptake, consistent with NO_2's lower reactivity.

Alternatively, NO_2 exchange with foliage can be modeled from a physiological standpoint where the flux from the leaf (J) is related to the stomatal conductance (g_s) and a concentration gradient between the ambient air and interstitial air in the leaf (C_a–C_i). This approach best describes results for exchange with individual foliage elements, and is expressed per unit leaf or needle area. While this approach provides linkage to leaf physiology, it is not straightforward to scale up from the leaf to the ecosystem

$$J=g_s(C_a-C_i)$$

Reaction 63

This model implicitly associates the compensation point with a finite internal concentration. Typically observed compensation points are ~1 ppb; values of internal NO_2 concentrations are consistent with metabolic pathways that include NO_X. In this formulation, the uptake will be linear with NO_2, which is typically measured in foliar chamber studies.

Several studies have shown the UV dependence of NO_2 emissions, which implies some photo-induced surface reactions to release NO_2. Rather than model this as a UV-dependent internal concentration, it would be more realistic to add an additional term to account for emission that is dependent on light levels and other surface characteristics

$$J=g_s(C_a-C_i)=J_s(UV)$$

Reaction 64

The mechanisms for surface emission are discussed below. Measurement of NO_2 flux is confounded by the rapid interconversion of NO, NO_2, and O_3 (Gao, 1991).

PAN is phytotoxic and absorbed at the leaf. Observations based on inference from concentration gradients and rates of loss at night (Shepson, 1992; Schrimpf, 1996) and from leaf chamber studies (Teklemariam, 2004) have indicated that uptake of PAN is slower than that of O_3; however, recent work in coniferous canopies with direct eddy covariance PAN flux measurements indicated a V_d more similar to that of O_3. Uptake of PAN is under stomatal control, has non-zero deposition at night, and is influenced by leaf wetness (Turnipseed, 2006). On the other hand, flux measurements determined by gradient methods over a grass surface showed a V_d closer to 0.1 cm/s, with uncertainty on the order of a factor of 10 (Doskey, 2004). Whether the discrepancies are methodological or indicate intrinsic differences between different vegetation is unknown. Uptake of PAN is a smaller loss process than its thermal decomposition in all cases.

The biosphere also interacts with NO_X through HC emissions and their subsequent reactions to form multi-functional $RONO_2$. Formation of the hydroxyalkyl nitrates occurs after OH attack on VOCs. In one sense, this mechanism is simply an alternate pathway for OH to react with NO_X to form a rapidly depositing species. If VOC were not present, OH would be available to react with NO_2 when it is present to form HNO_3.

Isoprene nitrates are an important class of $RONO_2$. Isoprene reacts with OH to form a radical that adds NO_2 to form the hydroxyalkyl nitrate. The combination of hydroxyl and NO_3 functional group makes these compounds especially soluble with low vapor pressures, so they likely deposit rapidly (Shepson, 1996; Treves, 2000). Many other unsaturated HCs react by analogous routes. Observations at Harvard Forest show a substantial fraction of the total of all gas-phase forms of oxidized N (category label is NO_Y) not accounted for by NO, NO_2 and PAN, which is attributed to the $RONO_2$ (Horii, 2006; Munger, 1998). Furthermore, the total NO_Y flux exceeds the sum of HNO_3, NO_X, and PAN, which implies that the $RONO_2$ are a substantial fraction of the total N deposition. Other observations showing evidence of hydoxyalkyl nitrates include those of Grossenbacher et al. (2001) and Day et al. (2003).

Formation of the hydroxyalkyl nitrates occurs after VOC + OH reaction. In some sense, this mechanism is just an alternate pathway for OH to react with NO_X to form a rapidly depositing species. If VOC were not present, OH would be available to react with NO_2 when it is present instead to form HNO_3.

HNO_2 formation on vegetative surfaces at night has long been observed based on measurements of positive gradients (Harrison, 1994). Surface reactions of NO_2 enhanced by moisture were proposed to explain these results. Production was evident at sites with high ambient NO_2; at low concentration, uptake of HNO_2 exceeded the source. Daytime observations of HNO_2 when rapid photolysis is expected to deplete ambient concentrations to very low levels implies a substantial source of photo-induced HNO_2 formation at a variety of forested sites where measurements have been made. Estimated source strengths are 200 to 1800 ppt/h in the surface layer (Zhou, 2003; Zhou, 2002), which is ~20 times faster than all nighttime sources.

HNO_2 sources could be important to HO_X budgets as HNO_2 is rapidly photolyzed by sunlight to OH and NO. Additional evidence of light-dependent reactions to produce HNO_2 comes from discovery of a HNO_2 artifact in pyrex sample inlet lines exposed to ambient light. Either covering the inlet or washing it eliminated the HNO_2 formation (Zhou, 2002). Similar reactions might serve to explain observations of

UV-dependent production of NO_X in empty foliar cuvettes that had been exposed to ambient air (Hari, 2003; Raivonen, 2003).

Production of HNO_2 in the dark is currently believed to occur via a heterogeneous reaction involving NO_2 on wet surfaces (He, 2006; Pitts, 1984; Sakamaki, 1983; Jenkin, 1988; Pitts, 1984), and it is proposed that the mechanism has first-order dependence in both NO_2 and H_2O (Kleffmann, 1998; Svensson, 1987) despite the stoichiometry. However, the molecular pathway of the mechanism is still under debate. Jenkin et al. (1988) postulated a $H_2O{\bullet}NO_2$ water complex reacting with gas phase NO_2 to produce HNO_2, which is inconsistent with the formation of an N_2O_4 intermediate leading to HNO_2 as proposed by Finlayson-Pitts et al. (2003). Another uncertainty is whether the reaction forming HNO_2 is dependent on water vapor (Svensson, 1987; Stutz, 2004; Svensson, 1987; Stutz, 2004) or water adsorbed on surfaces (Kleffmann, 1998). Furthermore, the composition of the surface and the available amount of surface or surface-to-volume ratio can significantly influence the HNO_2 production rates (Kaiser, 1977; Kleffmann, 1998; Svensson, 1987), which may explain the difference in the rates observed between laboratory and atmospheric measurements.

There is no consensus on a chemical mechanism for photo-induced HNO_2 production. Photolysis of HNO_3 or NO_3^- absorbed on ice or in surface water films has been proposed (Honrath, 2002; Ramazan, 2004; Zhou, 2001; Zhou, 2003). Alternative pathways include NO_2 interaction with organic surfaces such as humic substances (Stemmler, 2006; George, 2005). Note that either NO_3^- photolysis or heterogeneous reaction of NO_2 are routes for recycling deposited nitrogen oxides back to the atmosphere in an active form. NO_3 photolysis would return N that heretofore was considered irreversibly deposited, surface reactions between NO_2 and water films or organic molecules would decrease the effectiveness of observed NO_2 deposition if the HNO_2 were re-emitted.

2.8.3. Air Quality Model Evaluation

Urban and regional air quality is determined by a complex system of coupled chemical and physical processes including emissions of pollutants and pollutant precursors, complex chemical reactions, physical transport and diffusion, and wet and dry deposition. NO_X in these systems has long been known to act nonlinearly in $P(O_3)$ and other secondary pollutants (Dodge, 1977), to extend over multiple spatial and temporal scales, and to involve complicated cross-media environmental issues such as acidic or nutrient deposition to sensitive biota and degradation of visibility.

NO_Y species emitted and transformed from NO_X emissions control the production and fate of O_3 and aerosols by sustaining or suppressing OH cycling. Correctly characterizing the interrelated NO_Y and OH dynamics for O_3 formation and fate in the polluted troposphere depends on new techniques using combinations of several NO_Y species for diagnostically probing the complex atmospheric dynamics in typical urban and regional airsheds. Dennis (2002) provides more detail on measurement requirements for diagnostic model evaluation.

Because of the complexity of these atmospheric processes, compensating errors in a model's physical, chemical, or numerical representations can produce cases of model output that appears right, but for the wrong reasons. That is to say, there are cases where the model solution coheres with expectations and often even with values measured in situ from field campaigns, but where these solutions have been produced through unrevealed errors that, in essence, off-set opposing effects, balancing or buffering the final model predictions. The model performance evaluation statistics that have historically been computed for summary descriptors like bias, gross error, and peak prediction accuracy for individual species alone cannot distinguish these difficult, but frequently encountered, conditions. The regulatory use of models to predict future effects of potential control strategies means that there are no direct tests for these significant model applications. However, avoiding the potential costly errors in predicting possible effects from mandated controls, as described above, requires an accurate appraisal of the type, magnitude, and extent of these controls. Thus, model credibility and user confidence in model-predicted effects related to such controls and effects can be established only by diagnostically probing process and mechanism representations in the model, and then checking these where possible against analogous tests of photochemical dynamics in ambient atmospheres.

Arnold et al. (1998) described a model evaluation methodology that distinguished several types of AQM testing. Two components of that methodology were: (1) operational testing to judge the performance and overall behavior of a model over specific attributes; and (2) diagnostic testing to help reveal potential compensating error in model inputs or processing. Diagnostic testing is in situ testing of model components using data that emphasize atmospheric processes, often with mass balance techniques, special species ratios, and process rate and reaction rate information not typically stored by the model for output. Some of these probes have been developed through process-oriented studies using theoretical assumptions, model-derived explanations, and results from instrumented models ranging from one-dimensional box models to the full 4–dimensional photochemical modeling system (Tonnesen, 2000). Additional information on instrumenting AQMs for diagnostic analysis with model process and reaction rate information is found in Dennis et al. (2002); information pertaining to the specific implementation of these techniques in CMAQ is found in (Gipson, 1999); and results from application of diagnostic probes to modeling experiments are found in Arnold and Dennis (2006; , 2003).

Evaluation results from a recent U.S. EPA exercise of CMAQ in the Tampa Bay airshed are presented here as an example of the present level of skill of state-of-the-science AQMs for predicting atmospheric concentrations of the relevant NO_X, SO_X, and NH_X species for this NAAQS assessment. This modeling series exercised CMAQ version 4.4 and with the University of California at Davis (UCD) sectional aerosol module in place of the standard CMAQ modal module and as driven by meteorology from MM5 v3.6 and with NEI emissions as augmented by continuous emissions monitoring data where available. The CTM was run with 21 vertical layers for the month of May 2002. For this evaluation, CMAQ-UCD was run in a one-way nested series of three domains with 32 km, 8 km, and 2 km horizontal grid spacings.

Depictions of the 8 km and 2 km domains used here zoomed over the central Tampa area are shown in Figure 2-27 and Figure 2-28.

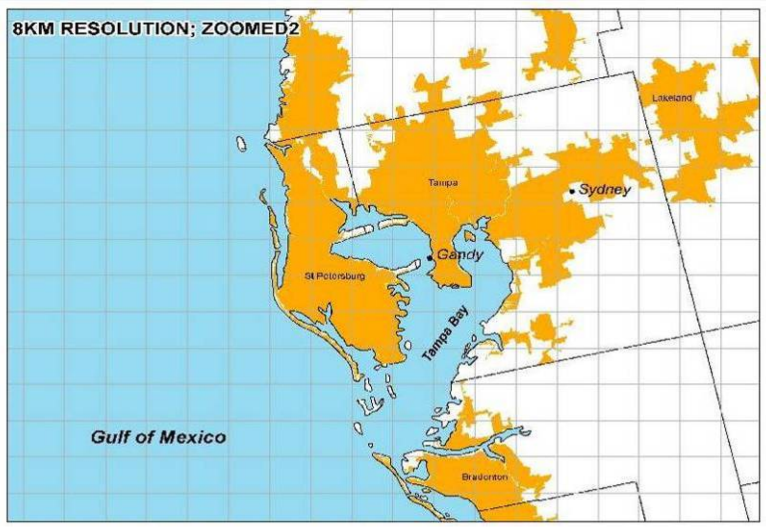


Figure 2-27. 8 km southeast U.S. CMAQ doma Function of wind speed, solar radiation, plant characteristics, precipitation/ moisture, and soil/air temperature in zoomed over Tampa Bay.

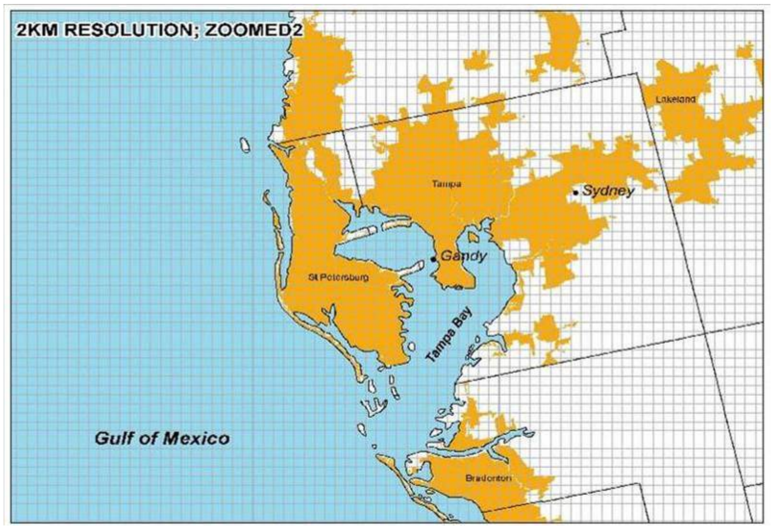
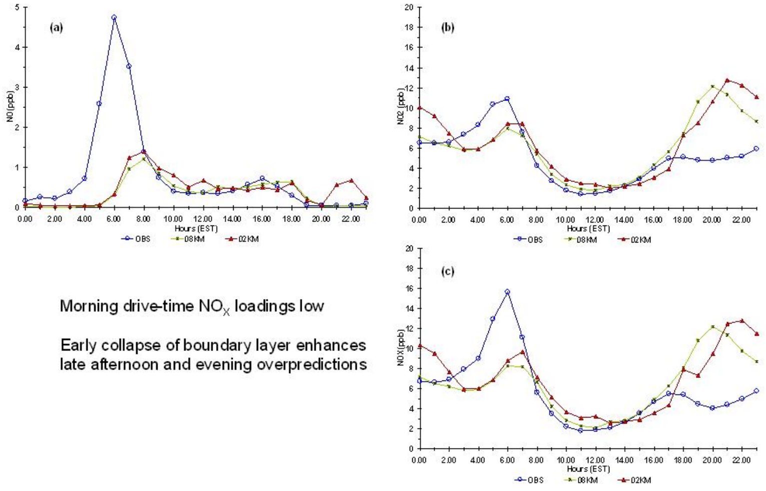


Figure 2-28. 2 km southeast U.S. CMAQ domain zoomed over Tampa Bay.

2.8.3.1. Ground-based Comparisons of Photochemical Dynamics

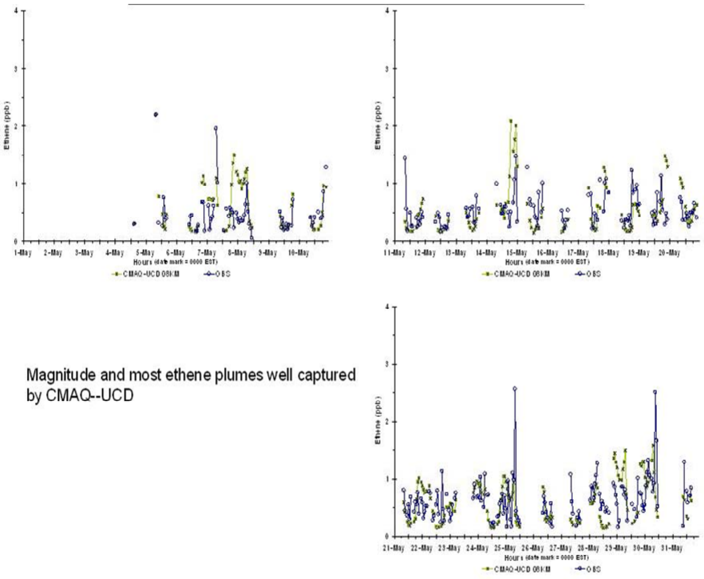
Errors in the NO_X concentrations in the model most likely from on-road emissions (Figure 2-29) affected NO_X predations, but CMAQ-UCD's general responses were reasonable. The model also replicated well anthropogenic and biogenic VOC emissions; see Figure 2-30 and Figure 2-31, respectively. After initial errors leading to underprediction in the first 21 days, CMAQ's predictions of hourly $PM_{2.5}$ concentrations and trends over the whole month also replicated the observed concentrations well; see Figure 2-32.



Morning drive-time NO_X loadings low

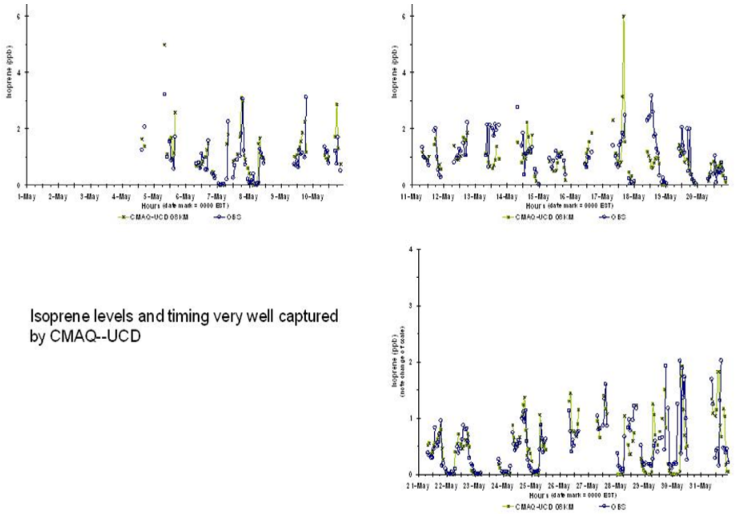
Early collapse of boundary layer enhances late afternoon and evening overpredictions

Figure 2-29. Hourly averages for 1–31 May, 2002, CMAQ 8 km and 2 km results and measured concentrations of NO (a), NO_2 (b), and total NO_X (c).



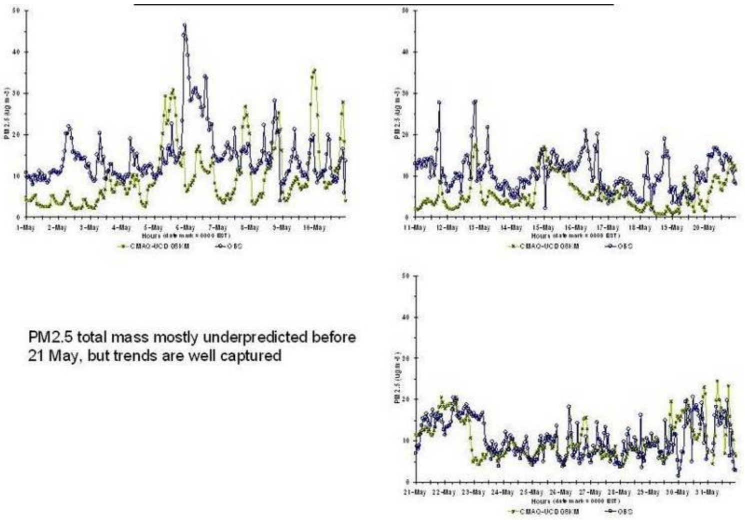
Magnitude and most ethene plumes well captured by CMAQ--UCD

Figure 2-30. May 2002 daily concentrations and 8 km CMAQ predictions for ethene at Sydney, FL.



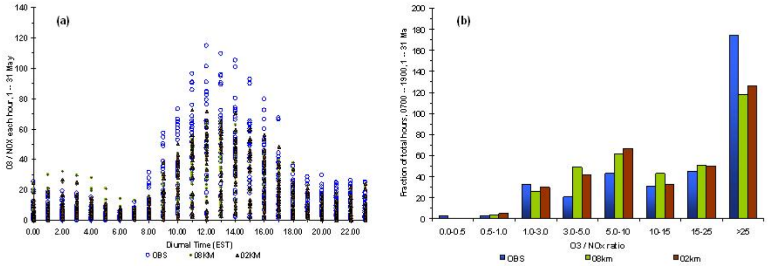
Isoprene levels and timing very well captured by CMAQ--UCD

Figure 2-31. May 2002 daily concentrations and 8 km CMAQ predictions for isoprene at Sydney, FL



PM2.5 total mass mostly underpredicted before 21 May, but trends are well captured

Figure 2-32. Observed hourly $PM_{2.5}$ concentrations at St. Petersburg, FL and results from CMAQ 8 km.

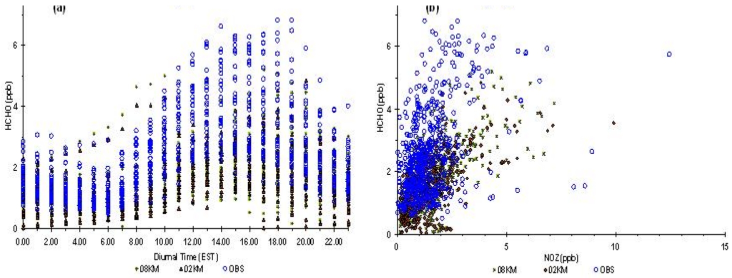


CMAQ--UCD tracks the photochemical systems across the response surface very well, but does not move them far enough into the most NO_X-limited space

Effects of the generalized NO_X overpredictions, and a slight O_3 underprediction on the few highest days, are evident here

Figure 2-33. Observed and modeled ratios of O_3 to NO_X. Diel curves from hourly averages over 1–31 May, 2002 (a), and distribution of O_3 to NO_X ratio values binned to show fractions of total daylight hours, 1–31, 2002.

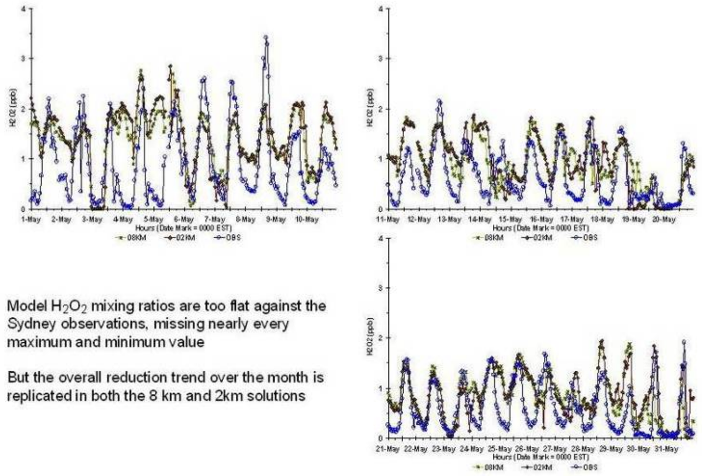
The $P(O_3)$ efficiency curves in the model agreed well with those observed at Sydney; see Figure 2-33. However, tests of CH_2O (Figure 2-34) and H_2O_2 (Figure 2-35) seemed to indicate an error in the model's OH chemistry related to these radical reservoir species since both were substantially and systematically different from the observations at the ground-based Sydney site. These species have historically been very difficult to model well, however, and the overall excellent agreement of CMAQ-UCD to production curves in relation to NO_X processing mean that this error was likely restricted to these species and of limited influence in the overall model solutions and for this evaluation.



8 km and 2 km CH_2O mixing ratios are low nearly every hour, often by more than a factor of two during the photochemically-active part of the day

Model CH_2O production is beneath the curve relative to NO_Z production in the world, too

Figure 2-34. Observed and CMAQ 8 km and 2 km predicted formaldehyde concentrations. Hourly averages from each day, 1–31 May, 2002 (a), and formaldehyde concentrations as a function of NO_Z concentrations (b).



Model H_2O_2 mixing ratios are too flat against the Sydney observations, missing nearly every maximum and minimum value

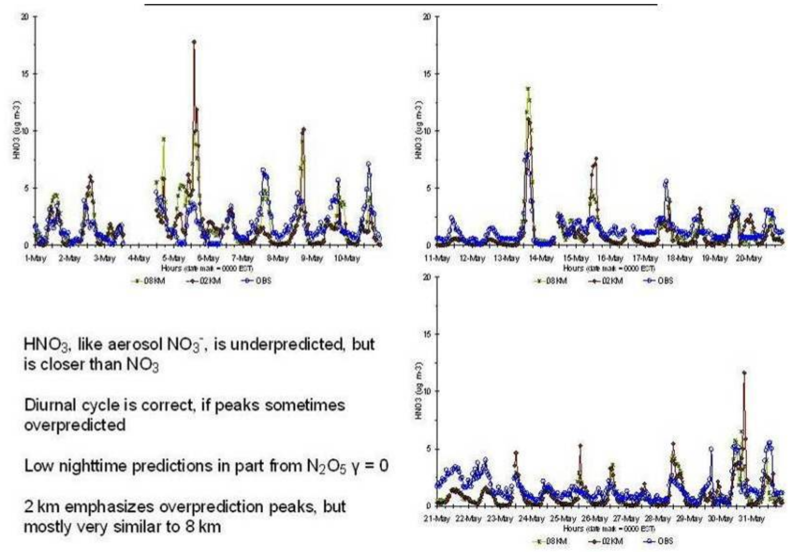
But the overall reduction trend over the month is replicated in both the 8 km and 2km solutions

Figure 2-35. Hourly concentrations of H peroxide, observed and predicted by CMAQ 8 km and 2 km, 1–31 May, 2002 at Sydney, FL.

NO_3 aerosols play a crucial and complex role in the health of aquatic and estuarine ecosystes. Gas-phase NO_3^- replacement of Cl^- on sea salt particles is often favored thermodynamically; and the deposition velocity V_d of the coarse particle NO_3^- formed through this replacement is more than an order of magnitude greater than for fine particle NO_3^-. Over open bodies of salt water such as the Gulf of Mexico and Tampa Bay, NO_3^- from this reaction dominates dry deposition, and is estimated to be of the same order as NO_3^- wet deposition.

However, aerosol NO_3^- concentrations are driven, buffered, and altered by a wide range of photochemical gas-phase reactions, heterogeneous reactions, and aerosol dynamics, making them especially difficult to model well. Because aerosol NO_3^- is derived mostly from gas-phase HNO_3 and will interact with Na^+, Cl^-, NH_4^+, and SO_4^{2-}, all these species and the physical parameters governing their creation, transport, transformation, and fate must be accurately replicated to predict NO_3^- with high fidelity. This has historically been a difficult problem for numerical process models, owing not least to the pervasive dearth of reliable ambient measurements of NO_3^- in its various forms. Normalized mean error (NME) for the large-scale Eulerian CTM-predicted pNO_3 has typically been on the order of a factor of 3 greater than the NME for pSO_4 (Odman, 2002; Pun, 2003).

SO_4^{2-}, NH_4^+, Na^+, and Cl^- were all predicted to within a factor of two and with no significant bias during the photochemical day in the 8 km CMAQ-UCD solution, although a significant bias in Na^+ and Cl^- was evident in the 2 km solution for two near water sites. This grid-size dependent bias is still being explored. Size segregation maxima were correct to within two size bins every day for which there were observations for both SO_4^{2-} and NH_4^+ (0.2 to 1.0 μm), and Na^+ and Cl^- (2.0 to 10.0 μm). Cl^- concentrations were greatly overpredicted during dark hours, but were nearer to observed values during the photochemical day. CMAQ performance for HNO_3 and NH_3 are shown in Figure 2-36 and Figure 2-37, respectively.



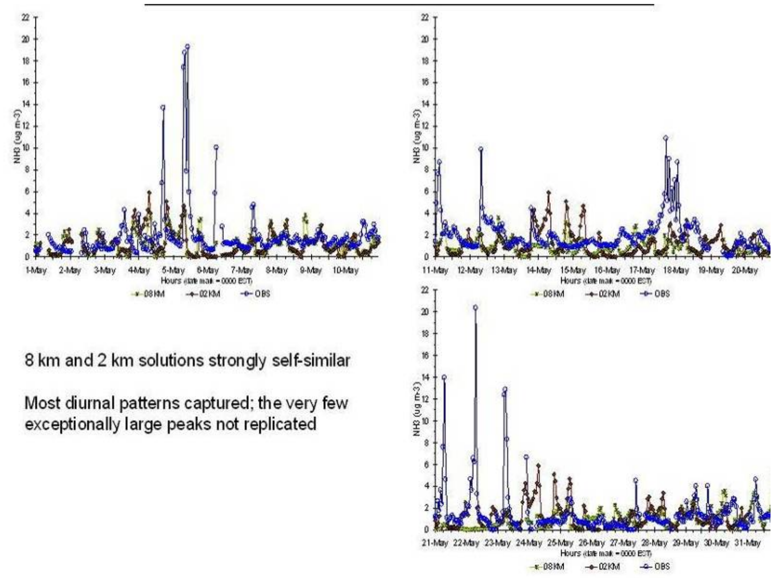
HNO_3, like aerosol NO_3^-, is underpredicted, but is closer than NO_3

Diurnal cycle is correct, if peaks sometimes overpredicted

Low nighttime predictions in part from N_2O_5 $\gamma = 0$

2 km emphasizes overprediction peaks, but mostly very similar to 8 km

Figure 2-36. Hourly and CMAQ-predicted HNO_3 concentrations at Sydney, FL, 1–31 May, 2002.



8 km and 2 km solutions strongly self-similar

Most diurnal patterns captured; the very few exceptionally large peaks not replicated

Figure 2-37. Hourly and CMAQ-predicted NH_3 concentrations at Sydney, FL, 1—31 May, 2002.

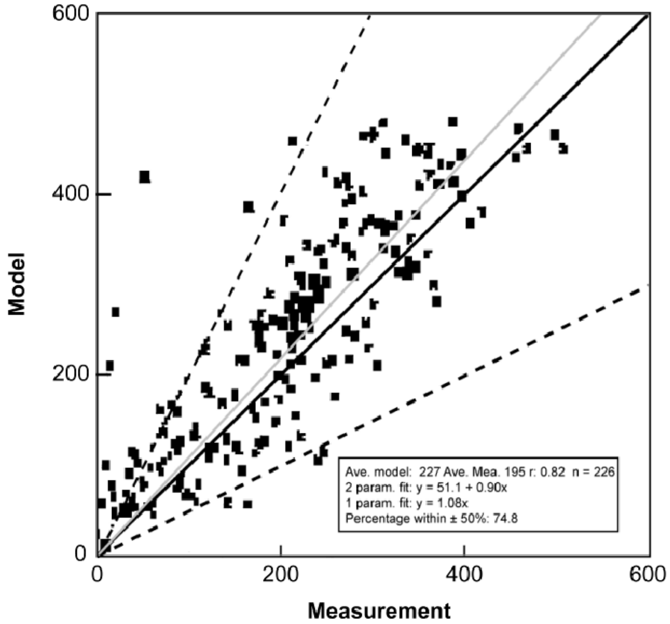
Overall, CMAQ-UCD was found to be operationally sound in this evaluation of its 8 km and 2 km solutions for the Tampa Bay airshed using the ground-based and aloft data from the May 2002 field intensive. Moreover, results from diagnostic tests of the model's photochemical dynamics were generally in excellent agreement with results from the ambient atmosphere. However, CMAQ-UCD was biased low in this application for total NO_3^- and for NO_3^- present as gas-phase HNO_3. In addition, the model was biased low for the radical reservoir species CH_2O and H_2O_2, though this bias appeared to have been limited to these species. Performance of the new UCD aerosol module was judged to be entirely adequate, allocating aerosols by chemical makeup to the appropriate size fractions. Model performance for fine-mode aerosols was also judged to be fully adequate.

2.8.3.2. Deposition with CTMs

Both wet and dry deposition are highly parameterized in CTMs. While all current models implement resistance schemes for dry deposition, the V_d generated from different models can vary highly across terrains (Stevenson, 2006). The accuracy of wet deposition in global CTMs is tied to spatial and temporal distribution of model precipitation and the treatment of chemical scavenging. Dentener et al. (Dentener, 2006) compared wet deposition across 23 models with available measurements around the globe. Source: Dentener et al. (2006).

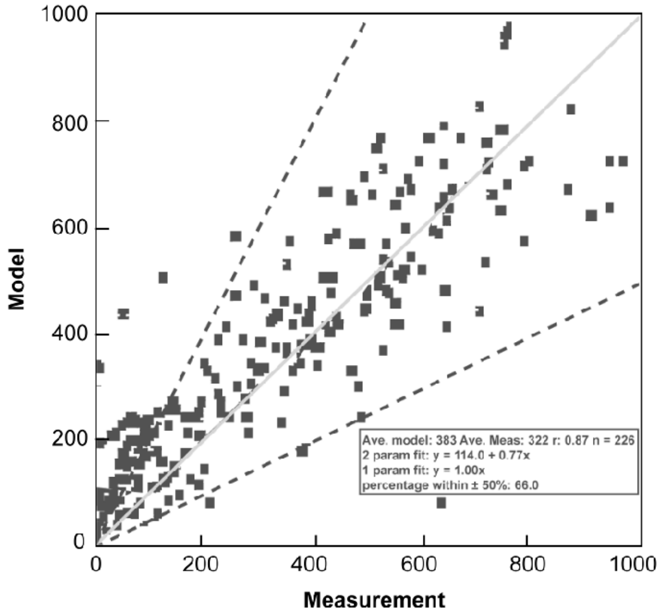
Figure 2-38 and Source: Dentener et al. (2006).

Figure 2-39 extract results of a comparison of the 23-model mean versus observations over the eastern U.S. for pNO_3 and pSO_4 deposition, respectively. The mean model results were strongly correlated with the observations ($r > 0.8$), and usually capture the magnitude of wet deposition to within a factor of 2 over the eastern U.S. Dentener et al. (2006) concluded that 60 to 70% of the participating models captured the measurements to within 50% in regions with quality controlled observations. This study then identified world regions receiving > 1000 mg $N/m^2/yr$, which they defined as the critical load, and found that 20% of non-crop, natural vegetation in the U.S. is exposed to N deposition in excess of that amount (Dentener, 2006).



Source: Dentener et al. (2006).

Figure 2-38. Scatter plot of total nitrate (HNO_3 plus aerosol nitrate) wet deposition (mg N/m^2/yr) of the mean model versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through 0.



Source: Dentener et al. (2006).

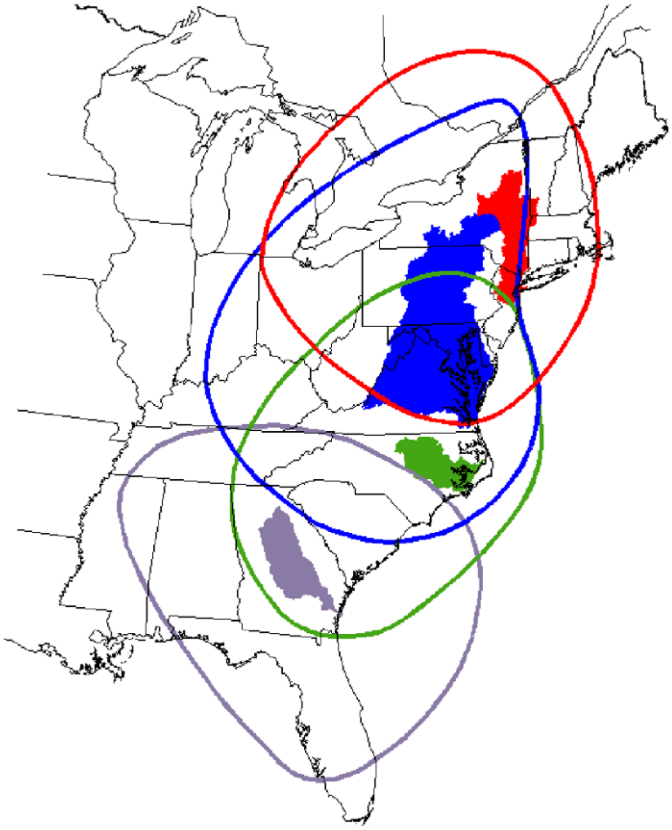
Figure 2-39. Scatter plot of total SO_4^{2-} wet deposition (mg S/m2/yr) of the mean model versus measurements for the North American Deposition Program (NADP) network. Dashed lines indicate factor of 2. The gray line is the result of a linear regression fitting through 0.

2.8.4. Computing Atmospheric Deposition to Specific Locations

Inputs of new N, i.e., non-recycled, exogenous N mostly anthropogenic in origin, are often key factors controlling primary productivity in N-sensitive estuarine and coastal waters (Paerl, 2000). Increasing trends in urbanization, agricultural intensity, and industrial expansion have led to increases in N deposited from the atmosphere on the order of a factor of 10 in the previous 100 years (Swackhamer, 2004). Direct fluxes of atmospheric N to ocean and gulf waters along the northeast and southeast U.S. are now roughly equal to or exceed the load of new N from riverine inputs at 11, 5.6, and 5.6 kg N/ha for the northeast Atlantic coast of the U.S., the southeast Atlantic coast of the U.S., and the U.S. eastern Gulf of Mexico, respectively (Paerl, 2002).

This N deposition takes different forms physically and chemically. Physically, deposition can be direct, with the loads resulting from air pollutants depositing directly to the surface of a body of water, usually a large body of water like an estuary or lake. In addition, there is an indirect deposition component derived from deposition of N or S air pollutants to the rest of the watershed, both land and water, of which some fraction is transported through runoff, rivers, streams, and groundwater to the waterbody of concern.

Direct and indirect deposition to watersheds depend on air pollutant concentrations in the airshed above the watershed. The shape and extent of the airshed is quite different from that of the watershed. In a watershed, everything that falls in its area, by definition, flows into a single body of water. An airshed, by contrast, is a theoretical concept that defines the source area containing the emissions contributing a given level, often 75%, to the deposition in a particular watershed or to a given waterbody. Hence, airsheds are modeled domains containing the sources estimated to contribute a given level of deposition from each pollutant of concern. The principal NO_X airsheds and corresponding watersheds for several regions in the eastern U.S. are shown in Figure 2-40.



Airshed extents developed and used courtesy of Robin Dennis, EPA/ORD/NERL/Atmospheric Modeling Division.

Figure 2-40. Principal airsheds and watersheds for oxides of nitrogen for estuaries. Hudson/Raritan Bay; Chesapeake Bay; Pamlico Sound; and Altamaha Sound (listed from north to south).

N inputs have been studied in several east and Gulf Coast estuaries owing to concerns about eutrophication there. N from atmospheric deposition in these locations is estimated to be 10 to 40% of the total input of N to many of these estuaries, and could be higher for some. Estimates of total N loadings to estuaries or to other large-scale elements in the landscape are then computed using measurements of wet and dry N deposition where these are available and interpolated with or without a set of air quality model predictions such as the Extended Regional Acid Deposition Model (Ext-RADM) (Mathur, 2003 Dennis, 1990; Dennis, 2001; Mathur, 2000; Dennis, 1997). Ext-RADM has been shown to capture spatial and seasonal variations in N deposition, to predict the constituent deposition species correctly, and to simulate the chemistry and physics relating reduced and oxidized forms of N with high validity.

Extensive evaluation by Mathur and Dennis (2003) of the performance of the Ext-RADM showed that model-predicted ambient levels, gas-to-particle partitioning ratios, and deposition totals were in good agreement with available measurements, having R^2 for both annual and seasonal totals in the range of 0.4 to 0.7 for most species. Ext-RADM correctly predicted that most particles in the eastern U.S. are fully neutralized, further demonstrating that most modeled chemistry is correct as judged against measurements. Experiments with Ext-RADM to characterize atmospheric conditions over the eastern U.S. in the period at the end of the 1980s and early 1990s showed that the model predicted that reduced N species were contributed 47 ± 8% of total N wet deposition, in excellent agreement with the number inferred from measurements, 43 ± 9%.

Table 2-10 lists several waterbodies for which atmospheric N inputs have been computed and ratioed to total N loads. The contribution from the atmosphere ranges from a low of 2–8% for the Guadalupe Estuary in South Texas to highs of ~38% in the New York Bight and the Albemarle-Pamlico Sound in North Carolina.

Table 2-10. Atmospheric N loads relative to total N loads in selected great waters.*

Waterbody	Total N Load (million kg/yr)	Atmospheric N Load (million kg/yr)	Percent Load from the Atmosphere
Albemarle-Pamlico Sounds	23	9	38
Chesapeake Bay	170	36	21
Delaware Bay	54	8	15
Long Island Sound	60	12	20
Narragansett Bay	5	0.6	12
New York Bight	164	62	38
Based on ADN loads from the watershed only (excluding direct N deposition to the bay surface):			
Waquoit Bay, MA	0.022	0.0065	29
Based on ADN directly to the waterbody (excluding ADN loads from the watershed):			
Delaware Inland Bays	1.3	0.28	21
Flanders Bay, NY	0.36	0.027	7
Guadalupe Estuary, TX	4.2–15.9	0.31	2–8
Massachusetts Bays	22–30	1.6–6	5–27
Narragansett Bay	9	0.4	4
Newport River Coastal Waters, NC	0.27–0.85	0.095–0.68	>35
Potomac River, MD	35.5	1.9	5
Sarasota Bay, FL	0.6	0.16	26
Tampa Bay, FL	3.8	1.1	28

ADN = atmospheric deposition of N

Source: *Table from Deposition of Air Pollutants to the Great Waters-3rd Report to Congress (EPA, 2000)

The North Carolina case is a particularly rich example of computing defined airsheds and characterizing the contributions from oxidized and reduced forms of N to underlying water bodies; see the summary reported by Dennis and Mathur (2001). The Albemarle-Pamlico principal N airsheds were computed to be 665,600 km^2 for oxidized N, and 406,400 km^2 for reduced N; these are factors of 25 and 15, respectively, larger than the watershed drainage area. NO emissions from within the oxidized N principal airshed was estimated to explain 63% of all oxidized N deposition to the Albemarle-Pamlico system, very similar to the total of 60% of all reduced N deposition accounted for by NH_3 emissions in the reduced N principal airshed. The regional component to these computed N deposition totals varied with the form of N such that local NH_3 emissions inside North Carolina were estimated to account for 45% (hence, 55% left from the regional component) of the total reduced N deposition, while local NO and NO_2 emissions accounted for only 20% of the oxidized N deposition total (hence, leaving a regional component of 80%).

Table 2-11. Natural and anthropogenic sources of atmospheric N compounds.

Chemical Form	Sources (in approximate order of importance)
Reduced N NH_3/ NH_4^+	Agricultural Livestock waste (volatilized NH_3) Chemical fertilizers (volatilized NH_3) Biomass burning Dust from deforestation and land clearing Urban and Rural (non-agricultural) Wastewater treatment (volatilized NH_3) Fossil fuel combustion (from automobile catalytic converters) Natural Biomass burning (forest and grass fire) Decomposition of organic matter Dust and aerosols Volcanism
Oxidized Nitrogen NO, NO_2, NO_3^-	Urban and Rural (non-agricultural) Fossil fuel combustion Mobile and stationary engines Powerplants and industrial Natural Biomass burning Lightning Photolysis of N_2O (air, land, water) Dust and aerosols generated by storms Microbially mediated volatilization
Organic Nitrogen (Dissolved and Particulate)	Agricultural Dust and volatilization of wastes* Urban and Rural (non-agricultural) Dust or aerosols* Natural Atmospheric photochemical and lighting Biological production in oceans*

* = possible, but little known about sources (the major chemical forms of atmospheric N compounds are the reduced, oxidized, and organic forms)

Source: Swackhamer et al. (2004).

Chemically, N deposited from the atmosphere directly or indirectly can be present as an oxide or in reduced form as NH_3 and NH_4^+ or as dissolved or particulate organic N; see the listing in Table 2-11 for a division of these and an approximate ranking of source strengths. NO and NO_2, chiefly from fossil fuel combustion, dominate total N pollution in the U.S. at ~50 to 75% of the total; see the descriptions of this chemistry in Section 2.6.2 and of sources above.

CAFOs and other intensified agricultural production methods have resulted in greatly increased volumes of animal wastes, of which 30 to 70% may be emitted as NH_3 (Whitall, 2001). The increase in reduced N deposition in the U.S. measured as increased NH_4^+ deposition correlates well with the local and regional increases in this agricultural intensity (Whitall, 2001). Moreover, the increases in NH_4^+ deposition in the U.S. track the effects in Europe where animal operations have dominated agricultural production for much of the previous 100 years and where NH_4^+ is the dominant form of N deposited from the atmosphere (Holland, 1999). Tables 2-11 and 2-12 list several important watersheds and their respective oxidized (Table 2-12) and reduced (Table 2-13) airsheds. Airsheds for oxidized N tend to be larger than those for reduced N owing to differences in the transport and deposition of NO_X and NH_X described above in Section 2.6.

Considerable uncertainty attaches to estimates of the third form of atmospherically derived N, organic N, in part because convenient methods for measurement and analysis are not widely available; see Table 2-11. Intensive studies at individual sites have shown, however, that for the North Carolina coast, for example, 30% of rain water N and deposition consisted of organic N, 20–30% of which was then available to primary producers on time scales of hours to days (Peierls, 1997).

Table 2-12. Characteristics of oxidized-nitrogen airsheds.

Watershed	Size (km²)	Size Factor Over Watershed Area	% Ox-N Deposition Explained	Airshed NO_X Emissions as % of E. North America	Efficiency of Deposition % dep. per % emiss.
Casco Bay	624,000	244	47	10	4.7
Great Bay	547,000	214	60	13	4.6
Narragansett Bay	595,200	138	73	18	4.1
Long Island Sound	905,600	22	70	23	3.0
Hudson/Raritan Bay	912,000	22	62	25	2.5
Barnegat Bay	505,600	361	67	16	4.2
Delaware Bay	729,600	22	75	26	2.9
Delaware Inland Bays	326,400	584	52	12	4.3
Chesapeake Bay	1,081,600	6.5	76	34	2.2
Pamlico Sound	665,600	25	63	18	3.5
Winyah Bay	886,400	19	69	24	2.9
Charleston Harbor	806,400	20	56	18	3.1
St. Helena Sound	588,800	48	59	11	5.4
Altamaha	678,400	18	68	13	5.2
Tampa Bay	256,000	45	76	5	15.2
Apalachee Bay	441,600	31	50	9	5.6
Apalachicola Bay	812,800	16	69	17	4.1
Mobile Bay	992,000	8.7	68	17	4.0
Lake Pontchartrain	659,200	17	63	11	5.7
Barataria-Terrebonne	409,600	55	63	8	7.9

Source: http://www.epa.gov/AMD/Multimedia/characteristicsTable.html. Table generated by Robin Dennis, NOAA/USEPA.

Table 2-13. Characteristics of principal airsheds for reduced-N deposition.

Watershed	Principal Red-N Airshed Area (km^2)	Red-N Area as % of OX-N Area	% Red-N Deposition Explained by Airshed Emissions	Airshed NH_3 Emission as % of E. North American Emissions
Chesapeake Bay	668,000	64%	55%	11%
Pamlico Sound	406,000	61%	60%	6.8%
Apalachee Bay	310,000	70%	45–50% est.	4.3%

Source: http://www.epa.gov/AMD/Multimedia/reducedTable.html; Table generated by Robin Dennis, NOAA-ARL/ USEPA-NERL.

2.8.5. PRB Concentrations of NO_X and SO_X

Background concentrations of NO_X and SO_X used for purposes of informing decisions about NAAQS are referred to as PRB concentrations. PRB concentrations are those concentrations that would occur in the U.S. in the absence of anthropogenic emissions in continental North America (defined here as the U.S., Canada, and Mexico). PRB concentrations include contributions from natural sources everywhere in the world and from anthropogenic sources outside these three countries. Biogenic emissions from agricultural activities are not considered in the formation of PRB concentrations.

Background levels so defined facilitate separation of pollution levels that can be controlled by U.S. regulations (or through international agreements with neighboring countries) from levels that are generally uncontrollable by the U.S. EPA assesses risks to human health and environmental effects from NO_2 and SO_2 levels in excess of these PRB concentrations.

The MOZART-2 global model of tropospheric chemistry (Horowitz, 2003) is used to diagnose the PRB contribution to NO_X and SO_X levels and to total (wet plus dry) deposition. The model setup for the present-day simulation has been published in a series of papers from a recent model intercomparison (Dentener, 2006; Dentener, 2006; Shindell, 2006; Stevenson, 2006; van Noije, 2006).

Background SO_2 concentrations are orders of magnitude smaller, < 10 ppt over much of the CONUS as shown in the middle panel of Figure 2-44. Maximum PRB SO_2 concentrations are 30 ppt. In the Northwest where there are geothermal sources of SO_2, the contribution of PRB to total SO_2 is 70 to 80%. However, excepting this, PRB contributes < 1% to present-day SO_2 concentrations in surface air as shown in the bottom panel Figure 2-44.

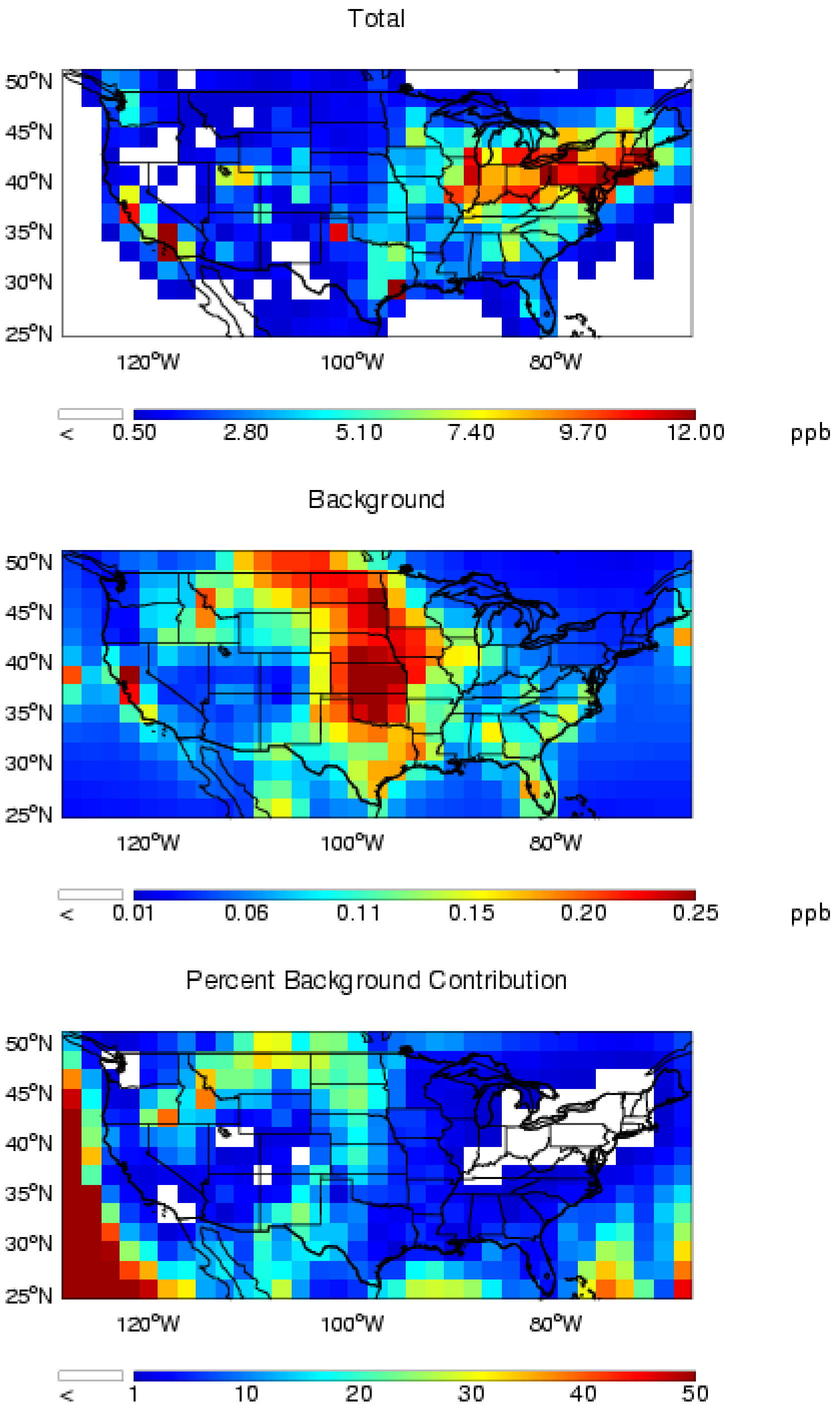
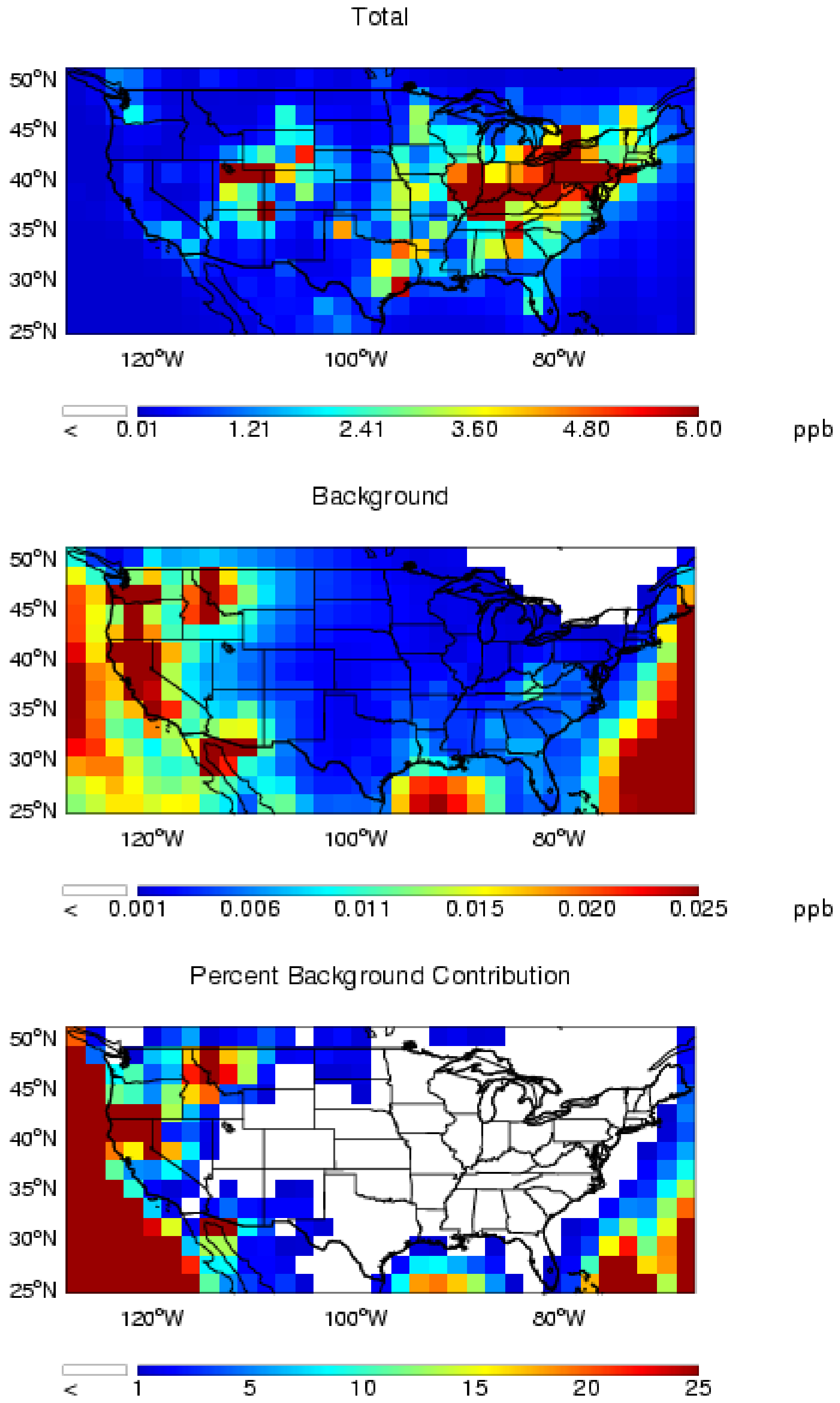


Figure 2-41. Annual mean concentrations of NO_2 (ppb) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.


Total

Background

Percent Background Contribution

Figure 2-42. Annual mean concentrations of SO_2 (ppb) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.

The spatial pattern of NO_Y (defined in the model as $HNO_3 + NH_4NO_3 + NO_X + HO_2NO_2 + RONO_2$) in wet and dry deposition is shown in Figure 2-45. The upper panel of this figure shows that highest values are found in the eastern U.S. in and downwind of the Ohio River Valley. The pattern of N deposition in the PRB simulation shown in the Figure 46 middle panel, however, shows maximum deposition centered over Texas and in the Gulf Coast region, reflecting a combination of N emissions from lightning in the Gulf region, biomass burning in the Southeast, and from microbial activity in soils with maxima in central Texas and Oklahoma. The bottom panel of Figure 2-45 shows that the PRB contribution to N deposition is < 20% over the eastern U.S., and typically < 50% in the western U.S. where NO_Y deposition is already lower at 25 to 50 mg $N/m^2/yr$.

Present-day deposition of SO_2 and pSO_4 is largest in the Ohio River Valley, due to coal-burning power plants in that region, while background deposition is typically at least an order of magnitude smaller; see Figure 2-46. Over the eastern U.S., the background contribution to SO_X deposition is < 10%, and it is even smaller, < 1%, where present-day SO_X deposition is highest. The contribution of PRB to S deposition is highest in the western U.S. at > 20% because of the geothermal sources of SO_2 and oxidation of DMS in the surface of the eastern Pacific.

Figure 2-47 shows results from MOZART-2 discussed above as compared with those from another tropospheric chemistry model, GEOS-Chem (Bey, 2001), which was previously used to diagnose PRB O_3 concentrations (Fiore, 2003; EPA, 2006). In both models, the surface PRB NO_X concentrations tend to mirror the distribution of soil NO emissions, which are highest in the Midwest. The NO emissions in GEOS-Chem are greater than those in MOZART-2 by nearly a factor of 2 reflecting different assumptions regarding the contribution to soil NO emissions largely through fertilizer, since GEOS-Chem total soil NO emissions are actually higher than MOZART-2 at 0.07 versus 0.11 Tg N over the U.S. in July. Even with the larger PRB soil NO emissions, however, surface NO_X concentrations in GEOS-Chem are typically < 500 ppt.

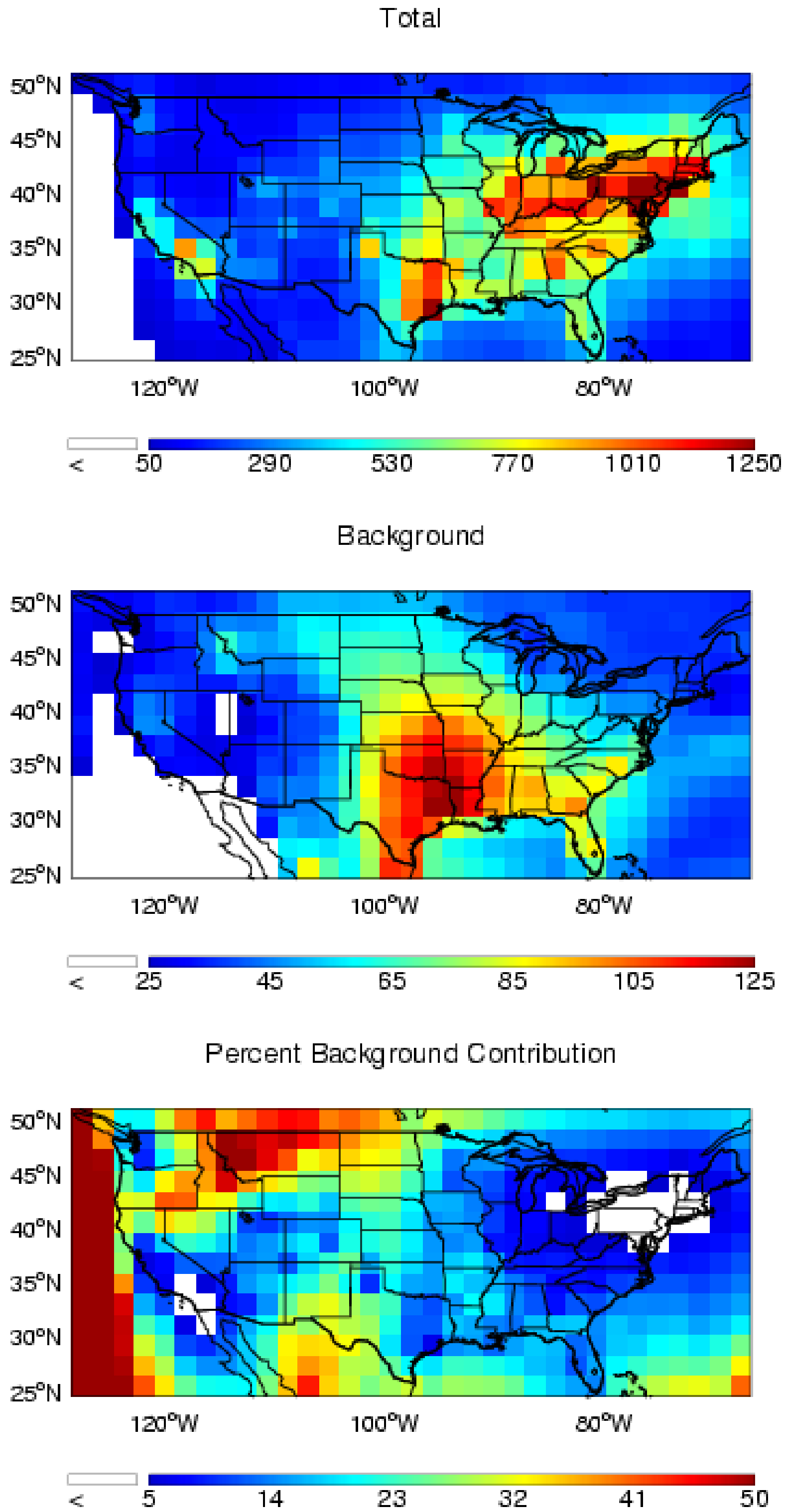


Figure 2-43. Annual mean concentrations of wet and dry deposition of HNO_3, NH_4NO_3, NO_X, HO_2NO_2, and organic nitrates (mg $N/m^2/yr$) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.

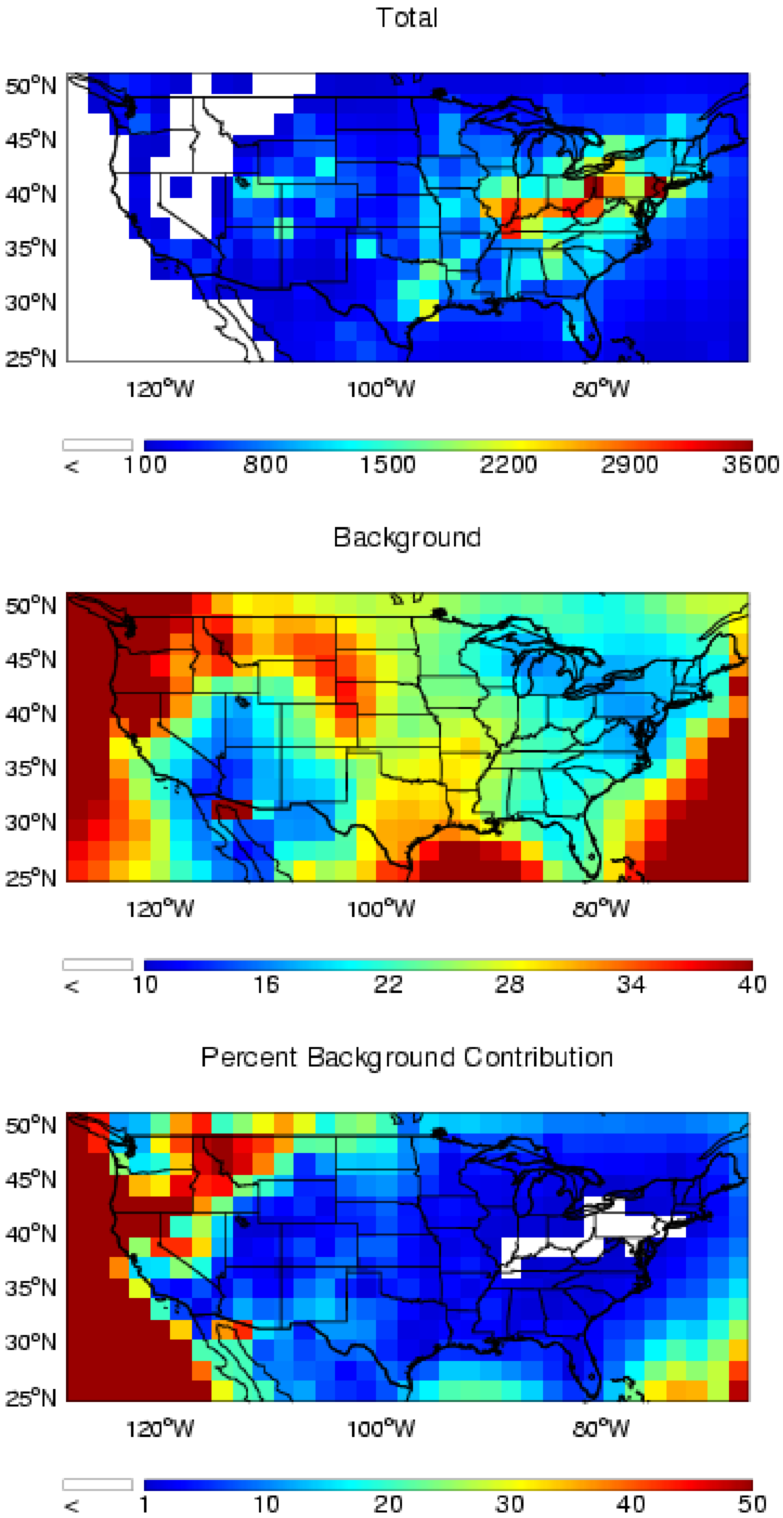


Figure 2-44. Annual mean concentrations of SO_X deposition (SO_2 + pSO_4) (mg S/m^2/yr) in surface air over the U.S. in the present-day (upper panel) and policy relevant background (middle panel) MOZART-2 simulations. The bottom panel shows the percentage contribution of the background to the present-day concentrations.

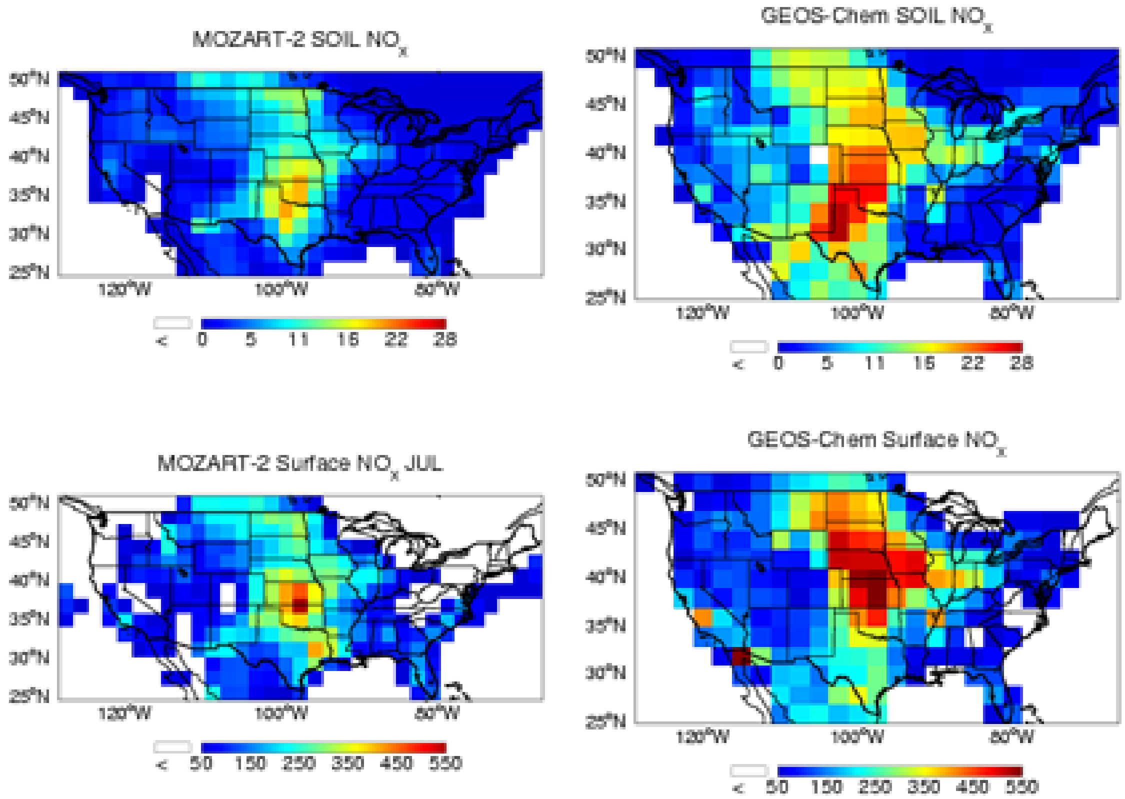


Figure 2-45. July mean soil NO emissions (upper panels; 1 × 10^9 molecules/cm^2/s) and surface PRB NO_X concentrations (lower panels; ppt) over the U.S. from MOZART-2 (left) and GEOS-Chem (right) model simulations in which anthropogenic O_3 precursor emissions were set to zero in North America.

First, the role of PRB in contributing to NO_2 and SO_2 concentrations in surface air is considered. Figure 2-41 shows the annual mean NO_2 concentration in surface air in the base case simulation (top panel) and from the PRB simulation (middle panel), along with the percentage contribution of the background to the total base case NO_2 concentrations (bottom panel). Maximum concentrations in the base case simulation occur along the Ohio River Valley and in the Los Angeles basin just as they do in reported measurements; see the section on emissions and concentrations above. While present-day concentrations are often > 5 ppb, PRB is < 300 ppt over most of the CONUS and < 100 ppt in the eastern U.S. The distribution of PRB (middle panel of Figure 2-42) largely reflects the distribution of soil NO emissions, with some local enhancements due to biomass burning such as is seen in western Montana. In the northeastern U.S., where present-day NO_2 concentrations are highest, PRB contributes < 1% to the total concentrations.

The spatial pattern of present-day SO_2 concentrations over the CONUS is similar to that of NO_2, with highest concentrations of > 5 ppb along the Ohio River Valley; see the upper panel Figure 2-43.

It is also instructive to consider measurements of SO_2 at relatively remote monitoring sites, i.e., ones located in sparsely populated areas not subject to obvious local sources of pollution. Berresheim et al. (1993) used a type of atmospheric pressure ionization mass spectrometer (APIMS) at Cheeka Peak, WA (48.30N, 124.62W, 480 m asl), in April 1991 during a field study for DMS oxidation products: SO_2 concentrations there ranged from 20 to 40 ppt. Thornton et al. (Thornton, 2002) have also used an APIMS with an isotopically labeled internal standard to determine background SO_2 levels and found 25 to 40 ppt in northwestern Nebraska in October 1999 at 150 m above ground using the NCAR C-130. These values are comparable to remote central south Pacific convective boundary layer SO_2 (Thornton, 1999).

In summary, the PRB contribution to NO_X and SO_X over the CONUS is very small, except for SO_2 in areas with volcanic activity.

2.9. Ambient Monitoring and Reported Concentrations of Relevant N and S Species

Observational systems supporting air quality and related assessments include routine regulatory networks, deposition networks, intensive field studies, remote sensing systems, sondes, aircraft campaigns, satellites, and focused fixed site special purpose networks. Major networks currently operating are emphasized; reference to other networks that have been discontinued, or that were only intended for a specific operating period, is also provided. The focus is on routinely operating North American air quality networks with limited coverage of European and international efforts relevant to North American assessments.

The scope of network coverage is broad and relatively shallow, reflecting intent to describe the observational foundation enabling integration of spatial scales, environmental media, and pollutant categories. In addition to fixed-site, surface-based air quality networks, systems providing total Earth column and vertical gradient information meteorological programs are included as well as operations designed to address climate forcing gases and aerosols, long range transport and stratospheric ozone. Cursory descriptions of recent intensive field campaigns are included to further foster integration of multiple observation platforms and air quality modeling platforms.

2.9.1. Routine Air Monitoring Networks in North America

Routine ambient air and deposition monitoring networks in North America provide more than 3000 fixed platforms measuring numerous gaseous species and aerosol properties. Many of these long-standing network systems were initialized after the 1970 CAA, subsequent CAA amendments, NAAQS reviews and National Academy of Sciences (NAS) recommendations resulting in periodic step enhancements to these routine networks. Examples include CASTNet and the National Atmospheric Deposition Program (NADP) addressing acidification; the Photochemical Assessment Monitoring Stations (PAMS) in response to persistent O_3 pollution and to monitor O_3 precursors including NO_X; and the $PM_{2.5}$ network. Table 2-14 lists the networks, sponsoring agencies, site densities, dates of operation, locations, and measurement parameters.

Table 2-14. Major routine operating air monitoring networks.[5]

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
State/Local/Federal Networks					
NCore—National Core Monitoring Network	EPA	75	2008	O_3, NO/NO_2/NO_Y, SO_2, CO, $PM_{2.5}$/PM_{10-}2.52, $PM_{2.5}$ speciation, NH_3, HNO_3, surface meteorology[3]	http://www.epa.gov/ttn/amtic/monstratdoc.htm
SLAMS—State and Local Ambient Monitoring Stations	EPA	~3000	1978	O_3, NO_X/NO_2, SO_2, $PM_{2.5}$/PM_{10}, CO, Pb	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
STN—$PM_{2.5}$ Speciation Trends Network	EPA	300	1999	$PM_{2.5}$, $PM_{2.5}$ speciation, major ions, metals	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.html
PAMS—Photochemical Assessment Monitoring Network	EPA	75	1994	O_3, NO_X/NO_Y, CO, speciated VOCs, carbonyls, surface meteorology and upper air	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
IMPROVE—Interagency Monitoring of Protected Visual Environments	NPS	110 plus 67 protocol sites	1988	$PM_{2.5}$/PM_{10}, major ions, metals, light extinction, scattering coefficient	http://vista.cira.colostate.edu/IMPROVE/
CASTNet—Clean Air Status and Trends Network	EPA	80+	1987	O_3, SO_2, major ions, calculated dry deposition, wet deposition, total deposition for S/N, surface meteorology	http://www.epa.gov/castnet/
GPMP—Gaseous Pollutant Monitoring Network	NPS	33	1987	O_3, NO_X/NO/NO_2, SO_2, CO, surface meteorology, (plus enhanced monitoring of CO, NO, NO_X, NO_Y, and SO_2 plus canister samples for VOC at three sites)	http://www2.nature.nps.gov/air/Monitoring/network.cfm#data
POMS—Portable Ozone Monitoring Stations	NPS	14	2002	O_3, surface meteorology, with CASTNet-protocol filter pack (optional) SO_4^{2-}, NO_3, ammonium, nitric acid, sulfur dioxide	http://www2.nature.nps.gov/air/studies/portO$_3$.cfm
Passive Ozone Sampler Monitoring Program	NPS	43	1995	O_3 dose (weekly)	http://www2.nature.nps.gov/air/Studies/Passives.cfm
NADP/NTN—National Atmospheric Deposition Program / National Trends Network	USGS	200+	1978	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/
NADP/MDN—National Atmospheric Deposition Program / Mercury Deposition Network	None	90+	1996	Mercury from precipitation chemistry	http://nadp.sws.uiuc.edu/mdn/
AIRMoN—National Atmospheric Deposition Program / Atmospheric Integrated Research Monitoring Network	NOAA	8	1984	Major ions from precipitation chemistry	http://nadp.sws.uiuc.edu/AIRMoN/
IADN—Integrated Atmospheric Deposition Network	EPA	20	1990	PAHs, PCBs, and organochlorine compounds are measured in air and precipitation samples	http://www.epa.gov/glnpo/monitoring/air
NAPS—National Air Pollution Surveillance Network	Canada	152+	1969	SO_2, CO, O_3, NO, NO_2, NO_X, VOCs, SVOCs, PM_{10}, $PM_{2.5}$, TSP, metals	http://www.etcentre.org/NAPS/

Network	Lead Federal Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
CAPMoN—Canadian Air and Precipitation Monitoring Network	Canada	29	2002	O_3, NO, NO_2, NO_Ymass, $PM_{2.5}$ speciation, major ions for particles and trace gases, precipitation chemistry for major ions	http://www.msc.ec.gc.ca/capmon/index_e.cfm
Mexican Metropolitan Air Quality Network	Mexico	93	???	O_3, NO_X, CO, SO_2, PM_{10}, TSP	See CEC, 19977
Air Toxics Monitoring Networks					
NATTS—National Air Toxics Trends Station	EPA	23	2005	VOCs, Carbonyls, PM_{10} metals4, Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
State/Local Air Toxics Monitoring	EPA	250+	1987	VOCs, Carbonyls, PM_{10} metals4, Hg	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htm
NDAMN—National Dioxin Air Monitoring Network	EPA	34	1998–2005	CDDs, CDFs, dioxin-like PCBs	http://cfpub2.epa.gov/ncea/cfm/recordisplay.cfm?deid=22423
Tribal Monitoring Networks					
Tribal Monitoring	EPA	120+	1995	O_3, NO_X/NO_2, SO_2, $PM_{2.5}/PM_{10}$, PAN, NH_3, $PM_{2.5}$, PM_{10} and coarse fraction CO, Pb	http://www.epa.gov/ttn/airs/airsaqs/aqsweb/aqswebhome.htmm
Industry/Research Networks					
New Source Permit Monitoring	None	variable	variable	O_3, NO_X/NO_2, SO_2, $PM_{2.5}/PM_{10}$, CO Pb	Contact specific industrial facilities
HRM Network—Houston Regional Monitoring Network	None	9	1980	O_3, NO_X, $PM_{2.5}/PM_{10}$, CO, SO_2, Pb, VOCs, surface meteorology	http://hrm.radian.com/houston/how/index.htm
ARIES / SEARCH—Aerosol Research Inhalation Epidemiology Study / Southeastern Aerosol Research and Characterization Study experiment	None	8	1992	O_3, $NO/NO_2/NO_Y$, SO_2, CO, $PM_{2.5}/PM_{10}$, $PM_{2.5}$ speciation, major ions, NH_3, HNO_3, scattering coefficient, surface meteorology	http://www.atmospheric-research.com/studies/SEARCH/index.html
SOS - SERON—Southern Oxidant Study - Southeastern Regional Oxidant Networks	EPA	~40	1990	O_3, NO, NO_Y, VOCs, CO, surface meteorology	http://www.ncsu.edu/sos/pubs/sos3/State_of_SOS_3.pdf
National/Global Radiation Networks					
RadNet—formerly Environmental Radiation Ambient Monitoring System (ERAMS)	EPA	200+	1973	Radionuclides and radiation	http://www.epa.gov/enviro/html/erams/
SASP—Surface Air Sampling Program	DHS	41	1963	89Sr, 90Sr, naturally occurring radionuclides, 7Be, 210Pb	http://www.eml.doe.gov/databases/sasp/
NEWNET—Neighborhood Environmental Watch Network	DOE	26	1993	Ionizing gamma radiation, surface meteorology	http://newnet.lanl.gov/stations.asp
CTBT—Comprehensive Nuclear Test Ban Treaty	DOE	80	1996	Radionuclides and noble gases	http://www.clw.org/archive/coalition/briefv3n14.htm
Other Networks					
UV Index—EPA Sunwise Program	EPA	–50 U.S. cities	2002	Calculated UV radiation index	http://www.epa.gov/sunwise/uvindex.html
UV Net—Ultraviolet Monitoring Program	EPA	21	2002	Ultraviolet solar radiation (UV-B and UV-A bands)	http://www.epa.gov/uvnet/access.html
UV-B Monitoring and Research Program	USDA	35	1992	UV-B radiation	http://uvb.nrel.colostate.edu/UVB/jsp/uvb_climate_network.jsp
SURFRAD—Surface Radiation Budget Network	NOAA	7	1993	Solar and infrared radiation, direct and diffuse solar radiation, photosynthetically active radiation, UVB, spectral solar, meteorological parameters	http://www.srrb.noaa.gov/surfrad/index.html
PRIMENet—Park Research & Intensive Monitoring of Ecosystems NETwork	NPS	14	1997	Ozone, wet and dry deposition, visibility, surface meteorology, and ultraviolet radiation	http://www.forestry.umt.edu/research/MFCES/programs/primenet/
BioWatch	No details				

Two important ambient air networks focused on environmental welfare effects were established in the mid-1980s. The Interagency Agency Monitoring of Protected Visual Environments (IMPROVE) network with >100 sites in National Parks and other remote locations is used primarily to assess visibility impairment, but has provided a reliable long-term record of PM mass and major speciation components and served as a model for the later deployment of STN; see Figure 2-46. STN (now part of CSN) has provided an urban complement to characterize aerosol composition; see Figure 2-47. Additional, minor networks identified in Figure 2-46 include those of the state and local air agencies deployed since the mid-1980s measuring a variety of aerosol- and gas-phase, hazardous air pollutants (HAPs) at ~200 locations, and a modest National Air Toxics Trends (NATTS) network of 23 sites.

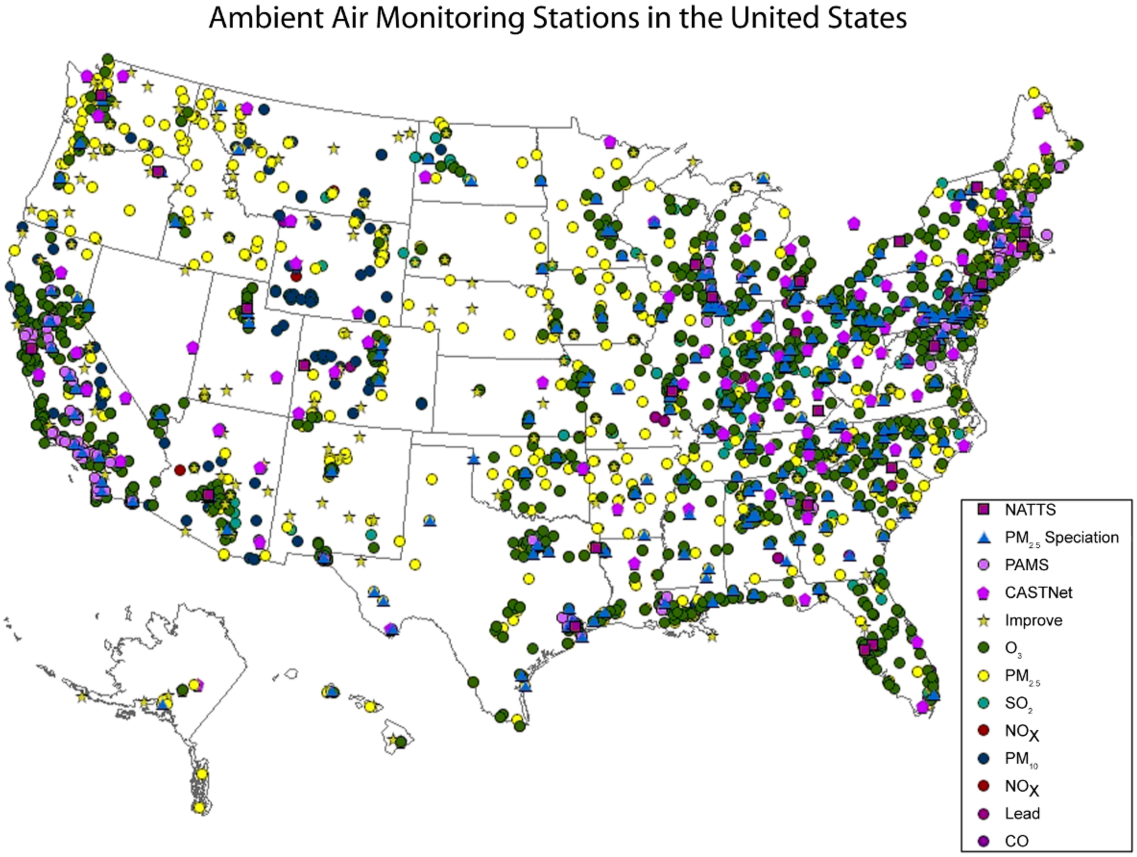
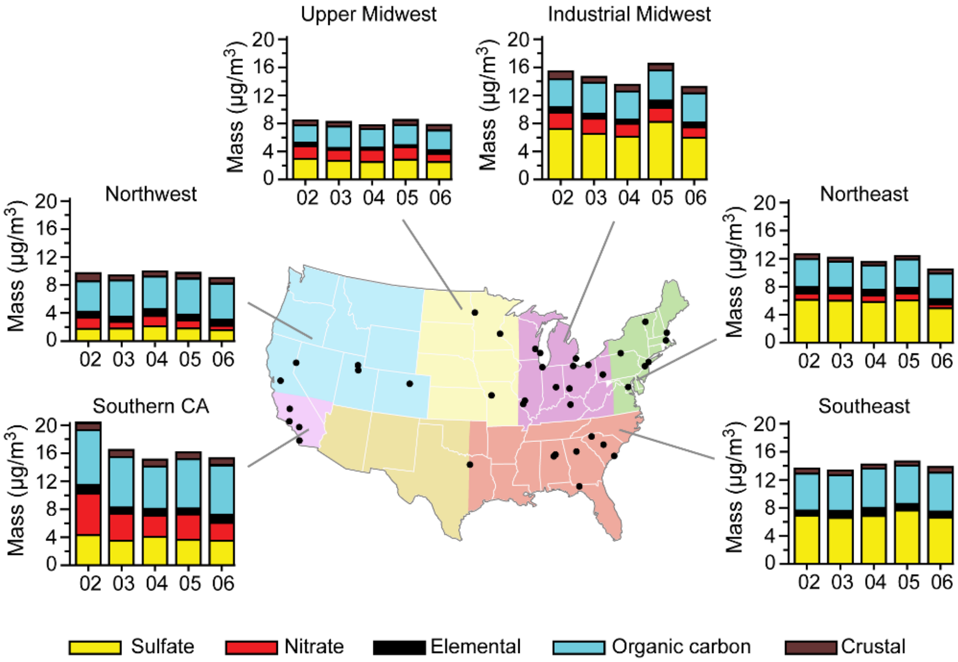


Figure 2-46. Aggregate map of the majority routine U.S. monitoring stations illustrating relatively broad coverage across the continental U.S. with noted spatial gaps in low populated areas.

CASTNET was established in the early 1990s to track changes in dry deposition of major inorganic ions and gaseous precursors associated with the CAA Title IV reductions in S and N, designed to address surface water acidification in eastern North America. Complementing ongoing precipitation measurements from NADP, CASTNET (see Figure 2-46) has provided a valuable source of model evaluation data for many of the large regional scale applications since the 1990s.



Source: 2006 EPA Air Quality Trends Report (www.epa.gov/air/airtrends/index.html).

Figure 2-47. Trends in regional chemical composition of $PM_{2.5}$ aerosols based on urban speciation sites and averaged over the entire 2006 sampling period.

Deployment of the PAMS and the $PM_{2.5}$ networks from the early 1990s through 2002 markedly enhanced the spatial, temporal, and compositional attributes of gases and aerosols, partially supporting user needs beyond NAAQS compliance (e.g., public reporting and forecasting of adverse air quality; implementation efforts including air quality model evaluation, and source apportionment and pattern (spatial and temporal) analysis of precursor species).

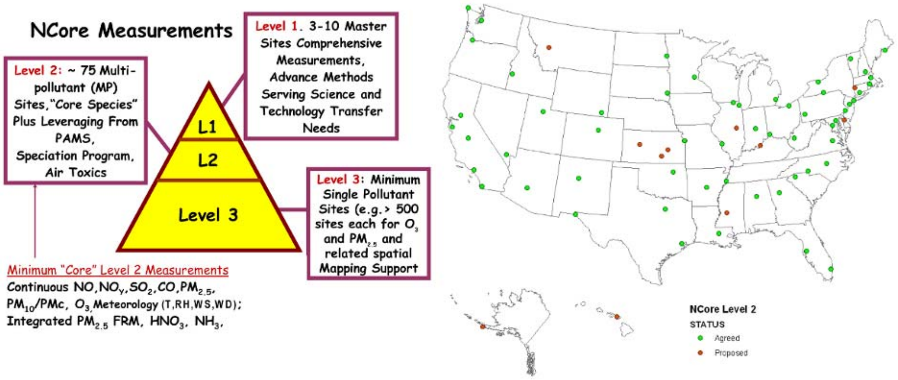


Figure 2-48. Original 3−tiered NCore design (left) and proposed site locations for Level 2 multiple pollutant sites.

A new multiple pollutant-monitoring network, NCore was begun in 2006. When finally implemented in 2009, NCore will provide a minimum of 75 Level 2 sites (Figure 2-48) in most major urban areas and important transport corridor and background locations. NCore will include a variety of trace gas, aerosol mass and speciation measurements which are intended to support multiple data user needs (e.g., air quality model evaluation, long-term epidemiological studies). In addition to establishing a multiple pollutant measurement framework, the NCore sites are intended to provide a backbone of central location sites that can be complemented by additional (existing and new) stations to address more specific spatial resolution requirements.

2.9.1.1. Pollutant Categories

Inorganic Gas-phase Species

The majority of U.S. sites measuring the criteria gases O_3, NO_X, SO_2, and CO are incorporated within the State and Local Air Monitoring Systems (SLAMS) networks. Most of the SLAMS sites are located in populated urban locations with a variety of siting requirements typically intended to site for high concentration locations resulting in an emphasis on downwind (from urban center) locations for O_3, center-city locations for NO_X, roadway intersection and canyon type locations for CO, and proximity to major power generating facilities for SO_2. Most monitoring platforms include multiple sensors to improve efficiency of network operations and adding interpretive value.

Measurements of NO_Y, HNO_3, and NH_3 are useful in a variety of ways important for assessing NO_X and SO_X environmental pollution effects; some of these ways include: (1) evaluation of emissions inventories; 2) inputs to and sources of evaluation for numerical and observation-based models; and (3) establishing baseline N budgets for watershed and field accountability assessments. NO_Y, HNO_3, and NH_3, together with true NO_2 and pNH_4, are significant components of the total N budget but remain poorly characterized at the national scale. In largest part, a lack of reliable, cost effective continuous measurement methods has hindered deployment of instruments for HNO_3 and NH_3. In the U.S., the SEARCH network of eight sites is the only source of routine, continuous ambient air measurements of NO_Y together with NH_3 and HNO_3; see discussions in Blanchard and Hidy (2003) and Zhang et al., 2006. CASTNET recently has deployed a network of inexpensive passive NH_3 samplers which have promise for characterizing broad spatial patterns, with extended averaging times beyond 24 h. This is a significant development since most other NH_3 sampling is focused on high source regions in agricultural settings designed to improve emission factors for NH_3, resulting in very limited NH_3 characterization of ambient environments.

Particulate Matter Mass

Nearly 1500 $PM_{2.5}$ gravimetric sites were established before 2000 to determine nonattainment status of counties throughout the U.S. following the 1997 promulgation of the $PM_{2.5}$ particulate matter standard. The network has evolved to add over 500 continuous $PM_{2.5}$ monitors and a reduction of 24–h gravimetric samplers below 1000 sites (see Figure 2-49) that support air quality forecasting and public notification of adverse air quality using the Air Quality Index (AQI), a generalized indicator of exposure concern linked to the NAAQS (http://www.epa.gov/airnow/). While this expansion of continuous $PM_{2.5}$ sites adds spatial coverage of highly temporally resolved information, the mix of instrument types compromises data harmonization across sites and geographic areas with different operational characteristics.

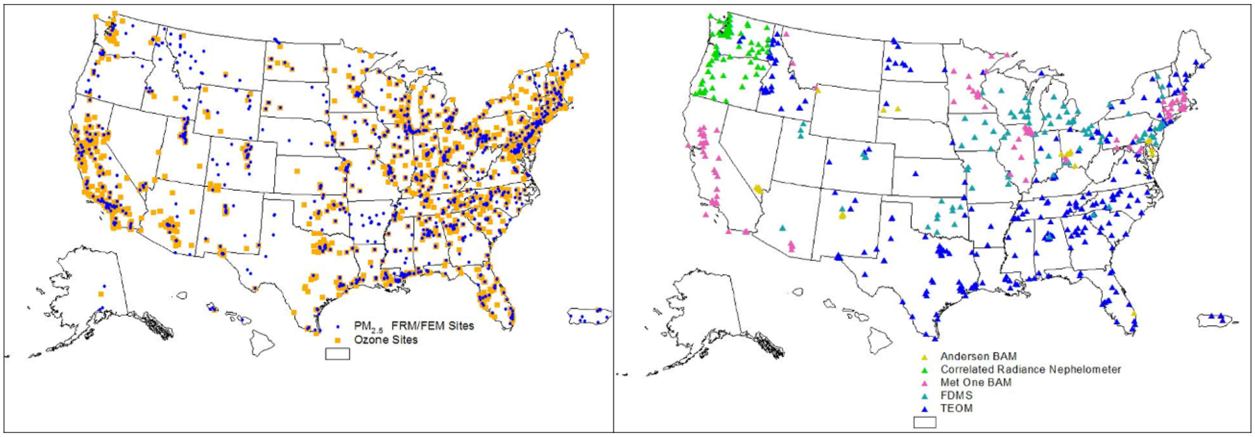


Figure 2-49. Maps illustrating breadth of $PM_{2.5}$ FRM and FEM and O_3 network (left); and $PM_{2.5}$ continuous samplers (right).

Particulate Matter Speciation

IMPROVE has provided nearly a two-decade record of major components including SO_4^{2-}, NO_3^-, OC and EC, and trace metals of $PM_{2.5}$ aerosols in pristine areas of the U.S. Over 300 speciation sites were added from 2000–2002 in urban areas of the U.S. to assist assessment efforts related to the $PM_{2.5}$ standard. This network (see Figure 2-50) across rural areas has been a widely used resource across disciplines (exposure/epidemiological, atmospheric science communities), organizations (academia, industry, government agencies), and several spatial scales of interest (long-range hemispheric transport to near source).

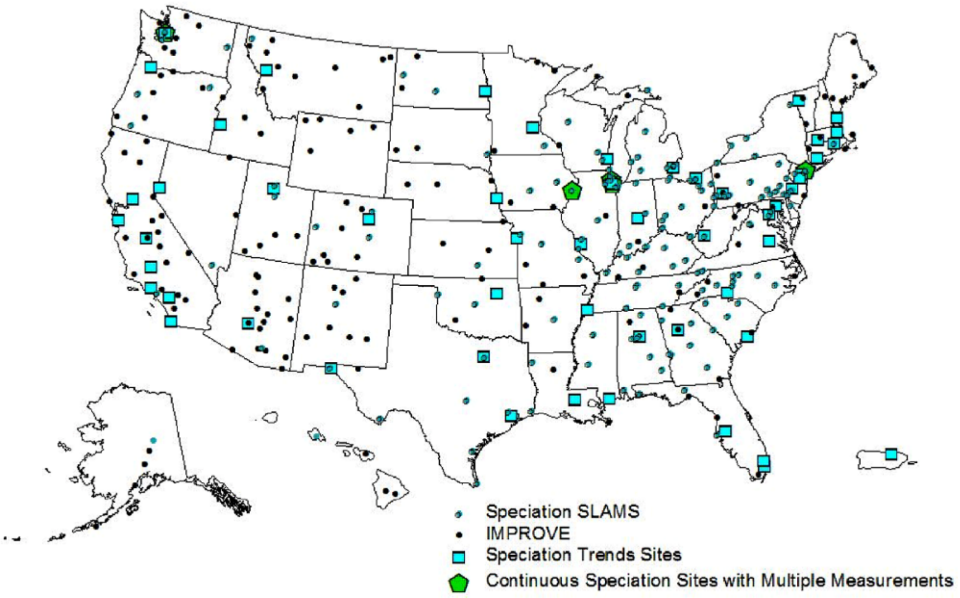


Figure 2-50. Locations of chemical speciation sites delineated by program type.

The speciation networks typically collect a 24-h sample once every 3 or 6 days. CASTNET provides weekly averaged measurements of major ions including SO_4^{2-}, NO_3^-, calcium (Ca^{2+}), sodium (Na^+), potassium (K^+), NH_4^+, and magnesium (Mg^{2+}) integrated over all aerosol sizes by means of open-face filter packs. Daily, 24–h speciated samples often requested by health effects researchers is limited to fewer than five sites in the U.S. and Canada. Similarly, a small and variable number of sites, fewer than 10 most years, provide near-continuous speciation data, usually limited to some combination of pSO_4, pNO_3, and EC and OC. In addition, the 22 NATTS sites include aetholometers measuring semi-continuous light absorption, often used as a surrogate for EC.

The EPA PM Supersites Program (Wittig, 2006, 92821) provided highly time-resolved aerosol measurements at 8 cities in the U.S. for a mix of time periods between 1999 and 2004. Depending on location and time period, a number of different instrument configurations were deployed ranging from additional spatial coverage of standard speciation sites to systems capturing near-continuous size-distributed chemical composition profiles.

The SEARCH program, funded since 1998 and EPRI and Southern Company, has provided continuous, semi-continuous and integrated data on a wide variety of species from eight highly instrumented paired research sites in the Southeastern U.S. in Alabama, Florida, Georgia and Mississippi (see descriptions in Hansen (2003). At present, the suite of measurements made at all sites includes: (1) 24-hr $PM_{2.5}$ filter samples, analyzed for mass, ions, (SO_4, NO_3, NH_4^+), OC, EC, and elements as measured by XRF; 2) two 24-h coarse mass ions, and XRF elements; 3) 24-h gaseous NH_3 as collected with an annular denuder for continuous (minute-to-hourly) $PM_{2.5}$ mass, OC, EC, NH_4^+, NO_3^- and SO_4^{2-}; 4) light-scattering and light absorption; 5) continuous O_3, NO_2, NO_Y, NO_3^-, CO, and SO_2; 6) continuous 10-m meteorological parameters: wind speed, wind direction, temperature, relative humidity, solar radiation, barometric pressure, and precipitation.

Precipitation-based Networks

Precipitation chemistry is the primary link between atmospheric and terrestrial and aquatic systems. The NADP (http://nadp.sws.uiuc.edu/) oversees a network of more than 250 sites (see Figure 2-51) where most of the major ions key to aquatic chemistry addressing acidification and eutrophication effects are measured. The NADP includes the Mercury Deposition Network (MDN) of ~90 sites and 7 Atmospheric Integrated Research Monitoring Network (AIRMoN) sites providing greater temporal resolution.

The joint Canadian and U.S. Integrated Atmospheric Deposition Network (IADN) (http://www.msc-smc.ec.gc.ca/iadn/index_e.html) includes a mix of master and satellite stations across the Great Lakes where both precipitation and ambient air are sampled for a range of toxics compounds. The IADN emphasizes many of the more persistent organic compounds including polychlorinated biphenyl compounds, pesticides, dioxins, and toxic metals such as lead (Pb), cadmium (Cd), arsenic (As), and selenium (Se).

2.9.2. Intensive Field Campaigns

Intensive field campaigns of relatively short duration supplement routine longer term monitoring networks by enhancing spatial, temporal, and compositional distribution of atmospheric species to better elucidate physical/chemical processes relevant to the fate, transport and removal of secondarily formed gases and aerosols. Typically, these campaigns utilize some combination of aircraft studies, high time resolved instrumentation and advanced analytical methods (in-situ and laboratory) all complementing routine ground based measurements, which usually do not address reactive gaseous species, aerosol size distributions, organic chemistry characterization and vertically stratified data.

There has been a long history of intensive field campaigns starting with the Regional Air Pollution Study (RAPS) in the 1970s which formed the basis evaluating the early photochemical gridded Eulerian airshed models used in acid deposition and O_3 assessments. Landmark campaigns in the U.S. through the 1980s and 1990s such as the Southern California Air Quality Study (SCAQS) (Lawson, 1990), the San Joaquin Valley Air Quality Study (SJAQS)/Atmospheric Utility Signatures, Predictions, and Experiments (AUSPEX) (Roth, 1988) and the Southern Oxidant Study (SOS) (Cowling and Furiness, 2000) were reviewed as part of the 2000 NARSTO O_3 assessment (Wittig, in press). Over the last decade there have been a series of field campaigns focusing on characterization of surface level aerosols through the PM Supersites program (Solomon et al., 2007). While the early campaigns focused on urban environments, the Eulerian Model Evaluation Field Study (EMEFS) and SOS during the early 1990s shifted focus toward regional spatial scales consistent with the dominant air pollution concerns (acid rain and ozone) of the time. In addition to addressing urban areas of concern such as Houston, TX, and Los Angeles, CA, more recent campaigns have extended spatial scales beyond regional studies to address oceanic transport and a variety of air pollution issues across the Northern Hemisphere, recognizing the importance of far ranging source regions and continental scale atmospheric processes. Some of these campaigns include local and regional studies for the northeast and southeast U.S., portions of Texas, and central and southern California; intercontinental studies including those for transport across Atlantic, Pacific, and Indian Ocean areas. A variety of federal and state entities have served as lead agencies for these studies. Table 2-15 provides a listing of studies conducted since the mid-1990s with well-known campaigns as far back as the 1960s identified in footnotes.

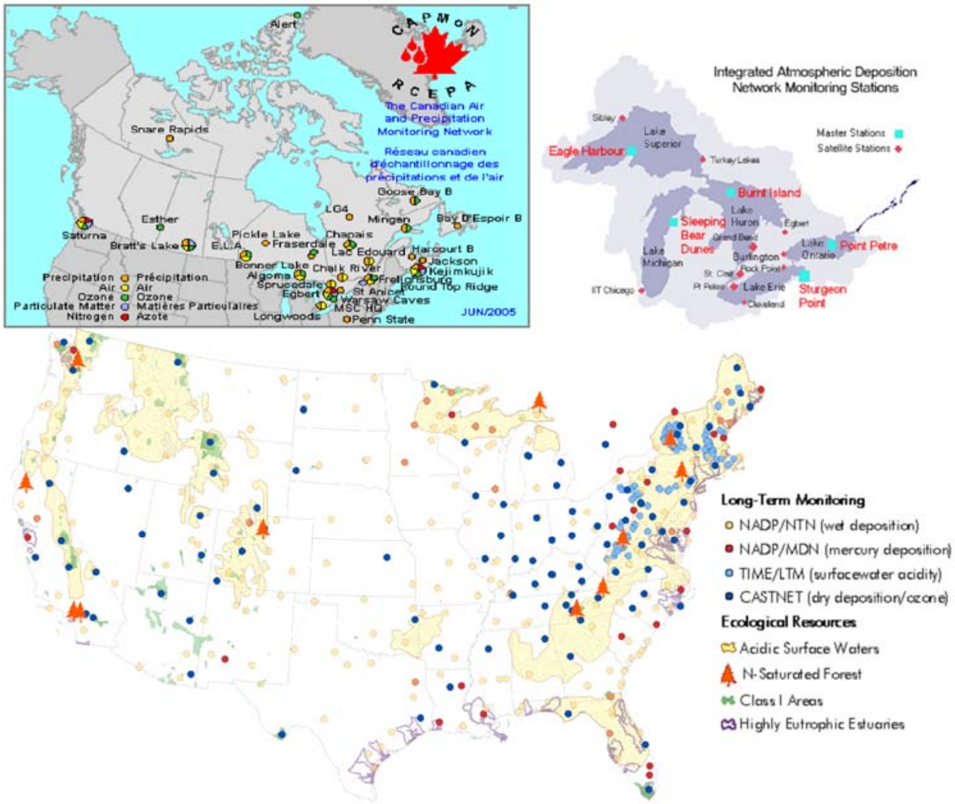


Figure 2-51. Routinely operating North American precipitation and surface water networks. Upper left, Canadian Air and Precipitation Monitoring Network (CAPMON); Upper right, Integrated Atmospheric Monitoring Deposition Network (IADN); Bottom, National Atmospheric Deposition Monitoring Program (NADP) with Time/LTM surface chemistry sites.

Table 2-15. Air monitoring networks/campaigns for non-routine special intensive studies.

Lead Agency[1]	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data	Notes
Texas	17	2006	O_3, NO_X, NO_Y, SO_2, haze, visibility, CO, VOC, solar radiation, surface meteorology, upper air	http://www.utexas.edu/research/ceer/texaqsII/PDF/12-12-04_Projected_SurfaceSites_tbl.pdf	Researchers from universities, state and federal agencies, private industry, and local governments are joining forces to conduct a major field study to address air quality issues in the eastern half of Texas. The study, planned for a period extending from Apr 2005 through Oct 2006, will examine regional ozone formation, transport of ozone and ozone precursors, meteorological and chemical modeling, issues related to ozone formation by highly reactive emissions, and particulate matter formation. It is anticipated that the information from the study will be the scientific basis used for developing State Implementation Plans (SIPs) for ozone (with concentrations averaged over 8 h), regional haze, and, if necessary, for fine particulate matter (particulate matter less than 2.5 microns in diameter, $PM_{2.5}$.
NOAA	1 ship, 2 aircraft	2006	O_3, NO, NO_2, NO_Y, VOCs, CO_2, CO, SO_2, HNO_3, NH_3, other reactive pollutants, aerosols, meteorological parameters and upper air	http://esrl.noaa.gov/csd/2006/	For TexAQS 2006, the NOAA air quality component will investigate, through airborne and sea-based measurements, the sources, and processes that are responsible for photochemical pollution and regional haze during the summertime in Texas. The focus of the study will be the transport of ozone and ozone precursors within the state and the impact of the long-range transport of ozone or its precursors.
NOAA	3 aircraft	2006	O_3, NO, NO_2, NO_Y, VOCs, CO_2, CO, SO_2, HNO_3, NH_3, other reactive pollutants, aerosols, meteorological parameters, altitude — NOAA aircraft	http://cloud1.arc.nasa.gov/intex-b/	The export of air pollutants from urban to regional and global environments is a major concern because of wide-ranging potential consequences for human health, cultivated and natural ecosystems, visibility degradation, weather modification, changes in radiative forcing, and tropospheric oxidizing capacity. During the spring of 2006 a highly integrated atmospheric field experiment was performed over and around North America. The Megacity Initiative: Local and Global Research Observations (MILAGRO), http://www.eol.ucar.edu/projects/milagro/ , resulted through a highly coordinated collaboration between NSF (through MIRAGE-Mex), DOE (through MAX-Mex), NASA (through INTEX-B) and a variety of research institution in the U.S. and Mexico and involved ground and air borne activities centered on Mexico City, Mexico during March 2006. MILAGRO goals were greatly facilitated and enhanced by a number of concurrent and coordinated national and international field campaigns and global satellite observations.

[1] EPA— Environmental Protection Agency; NASA — National Aeronautics and Space Administration; NOAA — National Oceanic and Atmospheric Administration; NPS — National Park Service\NSF — National Science Foundation; UCSD — University of California San Diego (Scripts Institution of Oceanography)

[2] This study is part of the Central California Air Quality Studies (CCAQS) which comprise the California Regional Particulate Air Quality Study (CRPAQS) and the Central California Ozone Study (CCOS). CCAQS is a multi-year effort of meteorological and air quality monitoring, emission inventory development, data analysis, and air quality simulation modeling. Prior studies in California included: Southern California Ozone Study (SCOS97) — 1997; Integrated Monitoring Study (IMS95) — 1995; San Joaquin Valley Air Quality Study (SJVAQS) — 1990; SARMAP Ozone Study — 1990; Southern California Air Quality Study (SCAQS) — 1987.

[3] Historically, there have been many other field studies in the 1960s - 1990s that are not reflected in this Table that involve both fixed monitoring sites and aircraft; well known examples include Regional Air Pollution Study (RAPS), Large Power Plant Effluent Study (LAPPES), Northeast Corridor Regional Modeling Program (NECRMP), Northeast Regional Oxidant Study (NEROS), Persistent Elevated Pollutant Episode (PEPE), and Lake Michigan Ozone Study (LMOS).

A synthesis of key findings and lessons learned from major field campaigns conducted over the last two decades would elevate exposure of these programs to a wider audience potentially generating support to enhance and sustain atmospheric process and model evaluation studies which are important complements to routine ground based and satellite observation platforms. While the NARSTO database (http://eosweb.larc.nasa.gov/PRODOCS/narsto/Table_narsto.html) provides access to raw data for various field campaigns, coverage of campaigns beyond North America must be acquired from other sources. The National Aeronautics and Space Agency (NASA)'s Atmospheric Data Science Center (http://eosweb.larc.nasa.gov/) also provides access to some of the more recent field campaigns. These web services would benefit potential users by providing intermediate descriptions of the scopes (locations, time frames, measurement systems and models) of these campaigns, including key objectives and finding.

2.9.3. Satellite-Based Air Quality Observing Systems

An extensive array of satellite-based systems (see Table 2-16 and Table 2-17) with the capability of measuring atmospheric column total species has been established by U.S. and European Satellite programs lead by NASA and the National Oceanic and Atmospheric Administration (NOAA) in the U.S. and the European Space Agency (ESA). A suite of satellites including Aqua, Aura, CALIPSO, OCO, Glory, as well as NOAA-17, NOAA-18 and NPOESS, have either been launched since about the year 2000 or have other near-term proposed launch dates. Collectively, the remote sensing techniques for measuring columns and/or profiles of aerosols (AOD), O_3, CO, CO_2, CH_4, SO_2, NO_2, chlorinated fluorocarbon compounds (CFCs), other pollutants, and atmospheric parameters such as temperature and H_2O content. Most of these satellites have a near-polar orbit allowing for two passes per day over a given location. When taken together, a group of six satellites (Aqua, Aura, CALIPSO, OCO, as well as CloudSat and PARASOL) coined the A-Train is being configured to fly in a formation that crosses the equator a few minutes apart at around 1330 local time to give a comprehensive picture of earth weather, climate, and atmospheric conditions.

Satellite imagery offers the potential to cover broad spatial areas; however, an understanding of their spatial, temporal and measurement limitations is necessary to determine how these systems complement ground based networks and support air quality management assessments.

Table 2-16. Satellite-based air quality observing systems.[1,4]

Instrument	Satellite Platform[3]	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
OLS (Operational Linescan System)	DMSP satellites	DOD	1962?	Identify fires and smoke plume	Polar Imagery only	http://www.af.mil/factsheets/factsheet.asp?fsID=94
BUV (Backscatter Ultraviolet Spectrometer)	Nimbus 4	NASA	1970–1980	O_3, CO_2, SO_2	Sun synchronous	http://nssdc.gsfc.nasa.gov/database/MasterCatalog?sc=1970-025A
SBUV (Solar Backscatter Ultraviolet Spectrometer)	Nimbus 7	NASA	1978–1993	O_3, SO_2	Polar	http://jwocky.gsfc.nasa.gov/n7toms/nimbus7tech.html
TOMS (Total Ozone Mapping Spectrometer)	Nimbus 7 Meteor 3 Earth-Probe	NASA	1978–1993 1991–1994 1996	O_3, SO_2, Aerosols	Polar ~100 km	http://toms.gsfc.nasa.gov/fltmodel/spacecr.html
LIMS (Limb Infrared Monitor of the Stratosphere	Nimbus 7	NASA	1978–1979	O_3, HNO_3, NO_2,	Polar	http://lims.gats-inc.com/about_lims.html
ATMOS (Atmospheric Trace Molecule Spectroscopy)	Spacelab 3 ATLAS — 1,2,3	NASA	1985, 1992, 1993, 1994	O_3, $CFCl_3$, CF_2Cl_2, $ClONO_2$, HCl, HF, CO, CH_4, HCN, HNO_3, NO, NO_2, N_2O_5, Aerosols		http://remus.jpl.nasa.gov/atmos/sl3.html
CLAES (Cryogenic Limb Array Etalon Spectrometer)	UARS	NASA	1991–1993	O_3, $CFCl_3$, CF_2Cl_2 $ClONO_2$, CH_4, HNO_3, NO, NO_2, N_2O, N_2O_5, Aerosols		http://umpgal.gsfc.nasa.gov/

Instrument	Satellite Platform[3]	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
HALOE (Halogen Occultation Experiment)	UARS	NASA	1991–2005	O_3, HCl, HF, CH_4, NO, NO_2, Aerosols		http://umpgal.gsfc.nasa.gov/
ISAMS (Improved Stratospheric and Mesospheric Sounder)	UARS	NASA	1991–1992	O_3, CO, CH_4, NO_2, N_2O, N_2O_5 Aerosols		http://umpgal.gsfc.nasa.gov/
MLS (Microwave Limb Sounder)	UARS	NASA	1991–1999	O_3, ClO, CH_3CN, HNO_3, SO_2		http://umpgal.gsfc.nasa.gov/
GOES Imager (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Fire products for WF_ABBA (imagery) and GASP (aerosol optical depth)	Geostationary	http://www.nesdis.noaa.gov/
GOES Sounder (Geostationary Operational Environmental Satellites)	GOES-10 GOES-12	NOAA	1994	Total column O_3	Geostationary	http://cimss.ssec.wisc.edu/goes/goesmain.html#sndrinfo
AVHRR (Advanced Very High Resolution Radiometer)	NOAA-15 NOAA-16 NOAA-172	NOAA	1998	Aerosol optical depth, particle size information and vegetation/ drought index products related to air quality through fires	Polar 4 km	http://noaasis.noaa.gov/NOAASIS/ml/avhrr.html
SBUV/2 (Solar Backscattered Ultraviolet Radiometer Model 2)	NOAA-16 NOAA-172	NOAA	2000	Total and profile O_3 from surface to top of atmosphere in ~5 km thick Umkehr layers	Polar	http://www2.ncdc.noaa.gov/docs/podug/html/c4/sec4–4.htm
MOPITT (Measurement of Pollution in the Troposphere)	EOS Terra	NASA	1999	CO, CH_4	Polar 22 × 22 km^2	http://www.eos.ucar.edu/mopitt/
MISR (Multi-angle Imaging SpectroRadiomenter)	EOS Terra	NASA	1999	Aerosol properties and plume height information near the vicinity of fires	Polar ~1 km	http://www-misr.jpl.nasa.gov/mission/introduction/welcome.html
MODIS (Moderate Resolution Imaging Spectroradiometer)	EOS Terra EOS Aqua	NASA	1999 2002	O_3, aerosol optical depth, particle size information, fine particle fraction, and forest fires	Polar 1 km	http://modarch.gsfc.nasa.gov/index.php
AIRS (Atmospheric Infrared Sounder)	EOS Aqua	NASA	2002	Total column ozone, surface temperature, temperature and moisture vertical profiles, (plus under development are CO and CO_2 total column, O_3 vertical distribution, and CH_4 distribution)	Polar 50 km	http://www-airs.jpl.nasa.gov/
HIRDLS (High Resolution Dynamics Limb Sounder)	EOS Aura	NASA	2004	O_3, $CFCl_3$, CF_2Cl_2, $ClONO_2$, CH_4, HNO_3, NO_2, N_2O, N_2O_5,	Aerosols	Polar http://aura.gsfc.nasa.gov/index.html
MLS (Microwave Limb Sounder)	EOS Aura	NASA	2004	O_3, BrO, ClO, HOCl, HCl, CO, HCN, CH_3CN, HNO_3, N_2O, OH, HO_2, SO_2	Polar	http://aura.gsfc.nasa.gov/index.html
OMI (Ozone Monitoring Instrument)	EOS Aura	NASA	2004	O_3, BrO, OClO, HCHO, NO_2, SO_2 and aerosol	Polar	12 × 24 km^2 http://aura.gsfc.nasa.gov/index.html
TES (Total Emission Spectrometer)	EOS Aura	NASA	2004	O_3, NO_Y, CO, SO_2, CH_4	Polar 26 × 42 km	http://aura.gsfc.nasa.gov/index.html
CALIPSO (Cloud-Aerosol Lidar & Infrared Pathfinder Satellite Observations)	CALIPSO	NASA	2005	Aerosol optical depth, backscatter, extinction	Polar 0.3 × 0.3 km^2	http://www-calipso.larc.nasa.gov/about/
OMPS	Ozone Mapping and Profiling Suite NPOESS - Preparatory Project	NOAA	2006	Total column and vertical profile ozone data	Polar	http://www.ipo.noaa.gov/Projects/npp.html

Instrument	Satellite Platform[3]	Lead Federal Agency	Initiated	Measurement Parameters	Orbit & Horizontal Resolution	Location of Information and/or Data
VIIRS (Visible Infrared Imaging Radiometer Suite)	NPOESS - Preparatory Project	NOAA	2006	Aerosol optical depth	Polar	http://www.ipo.noaa.gov/Projects/npp.html
Orbiting Carbon Observatory	OCO	NASA	2008	CO_2	Polar	http://oco.jpl.nasa.gov/
APS & TIM (Aerosol Polarimetry Sensor & Total Irradiance Monitor)	Glory	NASA	2008	Black carbon soot, other aerosols, total solar irradiance, cloud images Sun- synchronous, circular	Low Earth Orbit	http://glory.gsfc.nasa.gov/

[1] Non-U.S. satellite systems are not included in table at this time.

[2] As of 3/15/06 the operational satellite platforms may need to include NOAA-18.

[3] CALIPSO — Cloud-Aerosol Lidar & Infrared Pathfinder Satellite Observations
DMSP— Defense Meteorological Satellite Program
EOS — Earth Observing System
GOES — Geostationary Operational Environmental Satellites
NOAA — National Oceanic and Atmospheric Administration|
NPOESS — National Polar-orbiting Operational Environmental Satellite System
OCO — Orbiting Carbon Observatory
UARS — Upper Atmosphere Research Satellite

[4] See the following table for additional information on NASA satellites, instrument systems, pollutants measured, and data availability:

Table 2-17. Key atmospheric chemistry and dynamics data sets at the NASA Goddard DAAC.

Missions	Nimbus 4		Nimbus 7		Nimbus 7 Meteor 3 ADEOS 1 Earth-Probe	Nimbus 7		Spacelab 3, ATLAS 1, 2, 3	UARS		ERS-2	Terra Aqua		Aqua		Aura
Instruments	BUV	SBUV	TOMS	LIMS	ATMOS	CLAES	HALOE	SAMS	MLS	GOME	MODIS	AIRS	OMI	HIRDLS	MLS	TES*
Data Period	Apr '70–May '77	Nov '78–May '93	Nov '78–Present	Oct '78–May '79	'85, '92, '93, '94	Oct '91–May '93	Oct '91–Present	Sep '91–Jul '92	Sep '91–Jul '99	April '95–Present	Mar '00–Present	Sep '02–Present	Jul '04–Present	Jul '04–Present	Jul '04-Present	Jul '04–Present
Spectral Region	255–380 nm	255–340 nm	309–360 312–380 nm	6.2–15 µm	2.98–15 µm	3.5–12.7 µm	2.43–10.25 µm	4.6–16.6 µm	63, 183, 205 GHz	240–790 nm	0.4–14 µm	0.4–1.1, 3.74–15.4 µm	270–500 nm	6.12–17.76 µm	118, 190, 240, 640 GHz, 2.5 THz	3.2–15.4 µm
Bands	13	13	6	6	16	9	8	8	3	3072	36	2382	1560	22	5	12
O_3	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●	●
BrO										●			●		●	
$CFCl_3$					●	●								●		
CF_2Cl_2					●	●								●		
ClO									●						●	
OClO										●			●			
ClONO2					●	●								●		
HOCl															●	
HCl					●		●								●	
HF					●		●									
HCHO										●			●			
CO					●			●				●			●	●
CH_4					●	●	●	●				●		●		●
CH_3CN									●							
HCN					●										●	

Missions	Nimbus 4		Nimbus 7		Nimbus 7 Meteor 3 ADEOS 1 Earth-Probe	Nimbus 7		Spacelab 3, ATLAS 1, 2, 3	UARS		ERS-2	Terra Aqua		Aqua		Aura
HNO_3				●	●	●			●					●	●	●
NO					●	●	●									
NO_2				●	●	●	●	●		●			●	●		●
N_2O					●	●		●						●	●	
N_2O_5					●	●		●						●		
OH															●	
H_2O/ Humidity				●	●	●	●	●	●	●	●	●		●	●	●
SO_2	●	●	●						●	●			●		●	
Aerosols			●		●	●	●	●			●		●	●		
Cloud	●	●	●								●	●	●	●		
Temperature				●		●	●	●	●		●	●		●	●	●
Geopotential Height				●					●			●		●	●	
Reflectance	●	●	●								●	●	●			

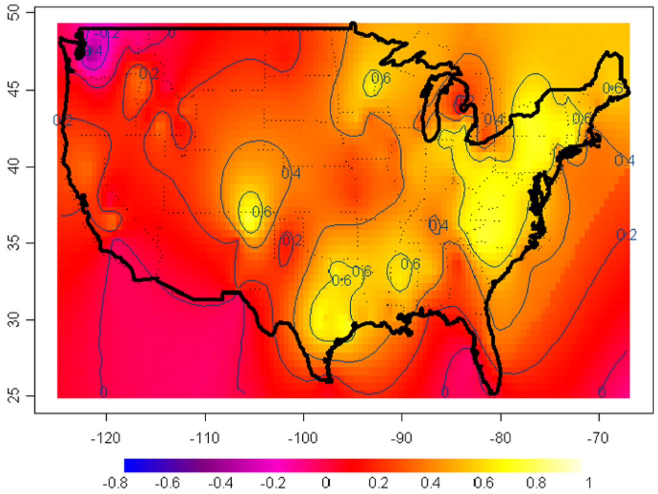
Please note that the Table above does not contain parameters from all sensors and products. Also available from the GES DAAC are many more Atmospheric and Earth Sciences data products from AIRS, AMSU-A, HSB, MODIS, SeaWiFS, OCTS, CZCS, TRMM (PR, TMI, VIRS), TOVS Pathfinder, Data Assimilation Model (GEOS-1, GEOS-DAS, CPC/ACDB), UARS (HRDI, WINDII, SOLSTICE, SUSIM, PEM), SORCE, several Field Campaigns, and Interdisciplinary data sets consisting of 70 geophysical Earth Sciences parameters. TOMS & SBUV reprocessed data (version-8) are now available on DVD-ROM. The MLS and OMI-Aura products & Visualization tools are now available from GES DISC.

Source: Aura instrument 'TES' is archived at the NASA Langley Atmospheric Sciences Data Center (http://eosweb.larc.nasa.gov/) http://disc.gsfc.nasa.gov/.

2.9.3.1. Satellite Coverages

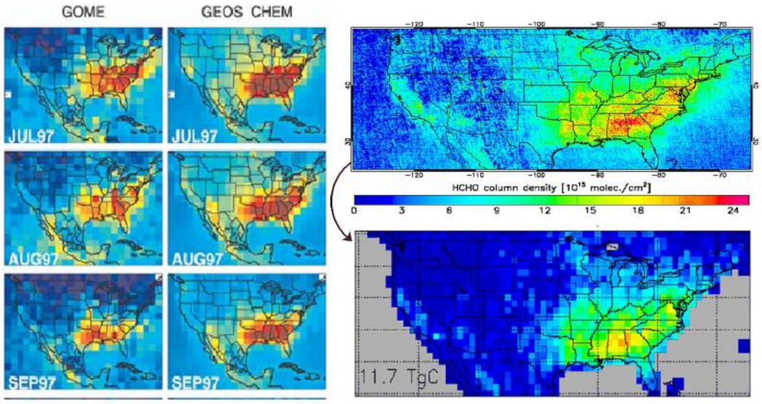
The near polar orbiting tracks of most satellites performing trace gas measurements provides wide spatial coverage of reasonable horizontal (10–50 km) resolution, but delivers only twice-daily snapshots of a particular species. Consequently, temporal patterns of pollutants as well as a time-integrated measure of pollutant concentrations cannot be delineated explicitly through satellite measurements alone. The geostationary satellite platforms such as the GOES systems of NOAA do provide near-continuous coverage of physical parameters for weather tracking and forecasting purposes. There are proposed campaigns within NASA and across partnership Federal agencies to deploy geostationary platforms with measurement capabilities for trace gases and aerosols to enhance space based characterization of tropospheric air quality (Fishman, 1987).

Polar orbiting satellites typically provide horizontal spatial resolution between 10 and 100 km, depending on the angle of a particular swath segment. Spatial resolution less than 10 km is possible with geostationary platforms. Characterization of elevated pollutants delivered by satellite systems complements of our ground based in-situ measurement networks – especially considering that a considerable fraction of pollutant mass resides well above Earth's surface. With few exceptions, satellite data typically represents a total atmospheric column estimate. For certain, important trace gases (e.g., NO_2, SO_2, CH_2O) and aerosols, the majority of mass resides in the boundary layer of the lower troposphere, enabling associations linking column data to surface concentrations or emissions fields. For example, reasonable correlations, especially in the Eastern U.S., have been developed between concentrations from ground level $PM_{2.5}$ stations and aerosol optical depths (AOD) from NASA's Moderate Resolution Imaging Spectroradiometer (MODIS) aboard the Aqua and Terra satellites (Engel-Cox, 2004); see the example in Figure 2-52. The Infusing Satellite Data into Environmental Applications (IDEA; http://idea.ssec.wisc.edu/) site provides daily displays and interpretations of MODIS and surface air quality data. The Cloud-Aerosol Lidar and Infrared Pathfinder Satellite Observation (CALIPSO) satellite (discussed below) provides some ability to resolve aerosol vertical gradients.



Source: Engel-Cox et al. (Engel-Cox, 2004).

Figure 2-52. Correlation surfaces between MODIS AOD and hourly $PM_{2.5}$ surface sites from April-September 2002.



Source: Abbot et al. (2003) and Palmer et al. (2006)

Figure 2-53. Comparisons between GEOSchem global model and GOME derived formaldehyde fields (left); Summer 2006 OMI column HCHO and translation to isoprene emission estimates (right).

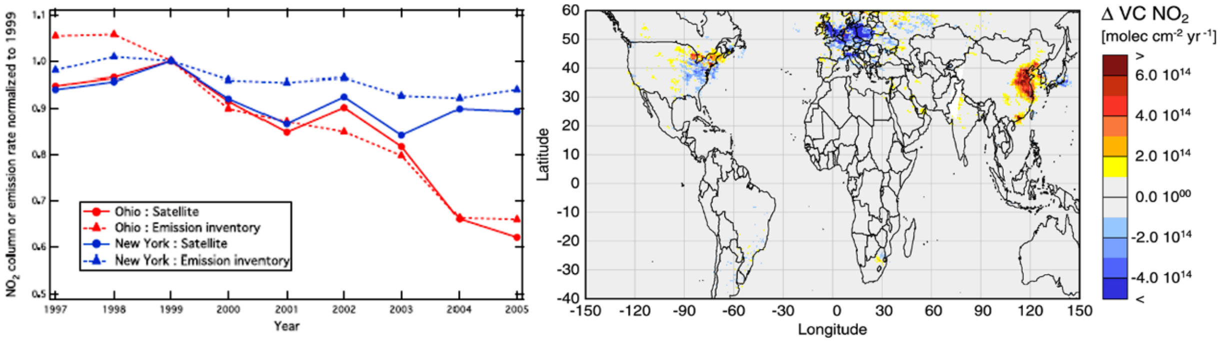
2.9.3.2. Measurement Issues

Most satellite air quality observations are based on spectroscopic techniques typically using reflected solar radiation as a broad source of UV through IR electromagnetic radiation (LIDAR aboard CALIPSO does utilize an active laser as the radiation source). While the science of satellite based measurements of trace gases and aerosols is relatively mature, interferences related to surface reflections, cloud attenuation and overlapping spectra of nearby species require adequate filtering and accounting for in processing remote signals. For example, aerosol events episodes associated with clouds often are screened out in developing in applications involving AOD characterizations through MODIS. Correlations between AOD and surface aerosols generally are better in the eastern U.S. relative to the West because due to excessive surface light scattering from relatively barren land surfaces.

Use of satellite data in air quality management assessments. Satellite data, particularly fire and smoke plume observations and GOES meteorological data, support various air quality forecasting efforts servicing public health advisories. Forecasting is driven by characterizing the environment in current and immediate-future time frames, on the order of 1 to 3 days. Air quality assessments require greater confidence in a systems response behavior to longer term, and usually much greater, changes in emissions, land use and meteorology; which requires greater confidence in formulation of numerous physical and chemical processes. Despite these differences, research and application products originally catalyzed by forecasting objectives generally overlap well with retrospective air quality assessment needs, the focus of this discussion.

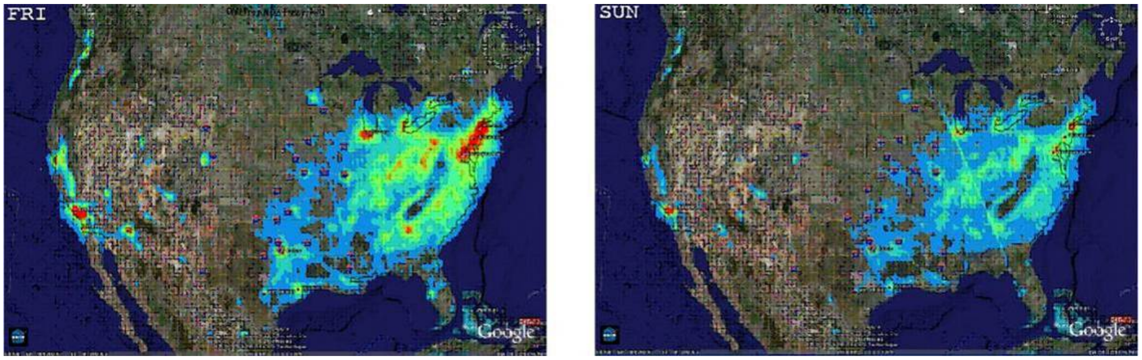
Launched in 2004, NASA's Aura satellite mission (http://www.nasa.gov/mission_pages/aura/spacecraft/index.html) deploys sensors potentially capable of measuring all criteria gases, CH_4, CH_2O, HNO_3, N_2O, H_2O vapor, OH and HO_2 and AOD – a multiple pollutant space based complement to the NCore multiple pollutant ground based network and intensive field campaigns. NASA's Orbiting Carbon Observatory (OCO), scheduled to be launched in 2008, will be dedicated to tracking CO_2 levels which currently are captured on the Aqua based Atmospheric Infrared Sounder (AIRS) instrument. The Aqua, Terra, Aura and OCO all are part of NASA's Earth Observation System (EOS).

Satellite data for CO, NO_2, and CH_2O as shown in Figure 2-53, as an indicator for biogenic isoprene, have been used for improving emission inventories (Fu, 2006; Martin, 2006; Martin, 2003). As longer-term records are developed, satellite imagery offers another means of checking progress of major emission strategy plans as well as illustrating emissions growth in developing parts (East Asia) of the world as shown in Figure 2-54 and Figure 2-55.



Source: Kim et al. (2006) and Richter et al. (2005).

Figure 2-54. Superimposed eastern U.S. emission and combined GOME and SCIAMACHY NO$_2$ 1997-2002 trends (left); GOME NO$_2$ trends from 1995–2002 (right). Clear evidence of reductions in Midwest U.S. and European NO$_X$ emissions, and increased NO$_X$ generated in eastern Asia.



Source: Husar (2005; http://capiton.wustl.edu/CAPITA/)

Figure 2-55. 2004 OMI NO$_2$ column images aggregated for all Fridays (left) and Sundays (right) indicating weekend/weekday patterns associated with reduced Sunday emissions.

2.9.4. European Air Monitoring Networks

Extensive air monitoring networks have also been implemented in Europe. In addition to the programs discussed above, many European-based programs are served by centralized organization structures linked to international efforts such as Convention on Long Range Transport of Air Pollution (LRTAP) (http://www.unece.org/env/lrtap/) and the underlying technical assessment body, the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP). The Global Atmospheric Watch (GAW) program (http://www.wmo.int/pages/prog/arep/gaw/gaw_home_en.html) under the World Meteorological Organization (WMO) provides quality assurance guidelines and data access to an important body of air quality measurements relevant to assessing intercontinental pollution transport and climate forcing phenomena. The Norwegian Institute for Air Research (NILU) (http://www.nilu.no/index.cfm?ac=topics&folder_id=4572&lan_id=3), maintains a database for much of the European based networks. These programs are noted not only as resources for large spatial scale environmental assessments, but also as examples of coordination and data harmonization that could be extended or replicated for North American purposes. The MOZAIC aircraft atmospheric chemistry vertical profile measurements illustrate the close linkage between European observation systems and air quality modeling and process formulation studies. European-based efforts in deposition monitoring relevant to sensitive ecosystems preceded efforts in North America and continue to lead the International community in coordinated efforts in sustaining science based measurement programs.

Table 2-18 includes combined contributions from all countries ranging from a few sites to tens of sites per country. Measurements for a variety of air pollutants are addressed including O_3, heavy metals, persistent organic pollutants (POPs), PM, VOCs, and deposition from acidifying and eutrophying compounds.

Table 2-18. International and European air monitoring programs.

Network	Lead Agency	Number of Sites	Initiated	Measurement Parameters	Location of Information and/or Data
EMEP – Co-operative Programmed for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (encompasses networks for ~37 European countries and organizations)	UNECE	270	1977	Acidifying / Eutrophying Compounds (precipitation): SO_4^{2-}, NO_3, NH_4, trace elements, pH, acidity (air): SO_2, NO_2, HNO_3, NH_3, PM_{10}, $PM_{2.5}$, major ions O_3 Heavy Metals precipitation, major ions, $PM_{2.5}$, PM_{10}, Hg, wet deposition POPs precipitation, air, deposition Particulate Matter $PM_{2.5}$, PM_{10}, EC, OC, TC, BC VOC HCs, Carbonyls	http://www.nilu.no/projects/ccc/emepdata.html
EUROTRAC—The European Experiment on the Transport and Transformation of Environmentally Relevant Trace Constituents over Europe	International Executive Committee (European Countries)	???	1986	EUROTRAC programs performed analyses utilizing data from existing or specially designed monitoring networks in order to: 1. elucidate the chemistry and transport of ozone and other photo-oxidants in the troposphere, e.g., TOR—30 O_3 stations and ALPTRAC—15 snow-monitoring sites 2. identify processes leading to the formation of acidity in the atmosphere, particularly those involving aerosols and clouds. 3. understand uptake and release of atmospheric trace substances by the biosphere.	http://www.gsf.de/eurotrac/index_what_is.html
EUROTRAC-2 — The EUREKA project on the transport and chemical transformation of trace constituents in the troposphere over Europe; second phase. Subprojects: – AEROSOL – BIATEX-2 – CAPMAN – CMD – EXPORT-E2 – GENEMIS – GLOREAM – LOOP – MEPOP – PROCLOUD – SATURN – TOR-2 – TRAP45 – TROPOSAT	International Scientific Secretariat (European Countries and EU)	???	1996	EUROTRAC-2 programs performed analyses utilizing data from existing monitoring networks in order to: support the further development of abatement strategies within Europe by providing an improved scientific basis for the quantification of source-receptor relationships for photo-oxidants and acidifying substances.	http://www.gsf.de/eurotrac/index_what_is.html

2.9.5. Ambient Concentrations of Relevant N Compounds

2.9.5.1. NO and NO_2

Species concentrations described in this section were taken from two types of networks described in Section 2.9 above: (1) the mostly urban networks designed and maintained for NAAQS attainment demonstrations; and (2) the mostly rural and remote networks designed and operated to comply with a range of requirements for protection of landscapes and views.

Figure 2-56 shows the distribution of monitoring sites for NO_2 across the U.S. Data for ambient NO_2 are not collected or collected at very few sites over large areas of the U.S. Few cities have more than two monitors and several large cities, including Seattle, WA, have none. Note that the number of NO_2 monitors has been decreasing in the U.S. as ambient average concentrations have fallen to a few tenths of the level of the NAAQS. There were, for example, 375 NO_2 monitors identified in mid-2006, but only 280 in November 2007.

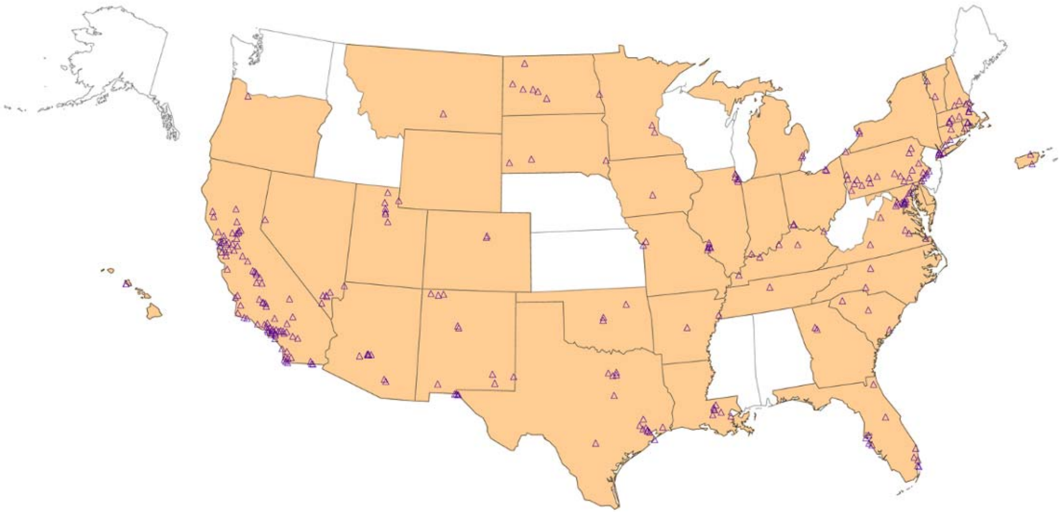


Figure 2-56. Location of ambient-level NO_2 monitors for NAAQS compliance in 2007. Shaded states have NO_2 monitors; unshaded states have none.

Criteria for siting ambient monitors for NAAQS pollutants are given in the SLAMS / NAMS / PAMS Network Review Guidance (EPA, 1998). As might be expected, criteria for siting monitors differ by pollutant. NO_2 monitors are meant to be representative of several scales: middle, or several city blocks, 300 to 500 m; neighborhood, or 0.5 to 4 km; and urban, or 4 to 50 km. Middle- and neighborhood-scale monitors are used to determine highest concentrations and source effects, while neighborhood- and urban-scale monitors are used for monitoring population exposures. As can be seen, there is considerable overlap between monitoring objectives and scales of representativeness. The distance of neighborhood- and urban-scale monitor inlets from roadways increases with traffic volume and can vary from 10 to 250 m away from roadways as traffic volume increases. Where the distance of an inlet to a road is shorter than the value in this range for the indicated traffic volume on that road, that monitor is classified as middle scale. Vertically, the inlets to NO_2 monitors can be set at a height from 2 to 15 m.

Figure 2-57 shows box plots of ambient concentrations of NO_2 measured at all monitoring sites located within MSAs or urbanized areas in the U.S. from 2003 through 2005. As can be seen, mean NO_2 concentrations are ~15 ppb for averaging periods ranging from a day to a year, with an interquartile range (IQR) of 10 to 25 ppb. However, the average of the daily 1–h max NO_2 concentration over this 3−year period is ~30 ppb. These values are about twice as high as the 24–h avg. The highest maximum hourly concentration (~200 ppb) found during the period of 2003 to 2005 was more than a factor of ten greater than the overall mean 24–h concentrations. The ratio of the 99th percentile concentration to the mean ranges from 2.1 for the 1–year avgs to 3.5 for the 1–h avgs.

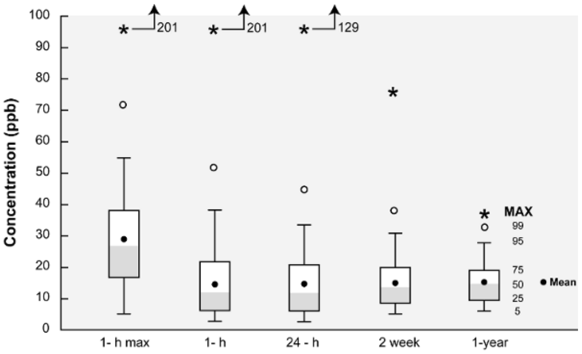


Figure 2-57. Ambient concentrations of NO_2 measured at all monitoring sites located within Metropolitan Statistical Areas in the U.S. from 2003 through 2005. * max; • mean

Because ambient NO_2 monitoring data are so sparse across the U.S. and are particularly so in rural areas, it would not be appropriate to use these data in constructing a map of NO_2 concentrations across the continental U.S. The short τ of NO_2 with respect to conversion to NO_Z species and the concentrated nature of NO_2 emissions result in steep gradients and low concentrations away from major sources that are not adequately captured by the existing monitoring networks. Model predictions might be more useful for showing large-scale features in the distribution of NO_2 and could be used in conjunction with the values shown in Figure 2-57 to provide a more complete picture of the variability of NO_2 across the U.S. Monthly avg NO_2 concentrations for July and January 2002 calculated using EPA's CMAQ model are shown in Figure 2-58. (A description of the capabilities of CMAQ and other three-dimensional CTMs is given in Section 2.8) The high variation in NO_2 concentrations of at least a factor of 10 is apparent in these model estimates. As expected, the highest NO_2 concentrations are seen in large urban regions, such as the Northeast Corridor, and lowest values are found in sparsely populated regions located mainly in the West. NO_2 concentrations tend to be higher in January than in July.

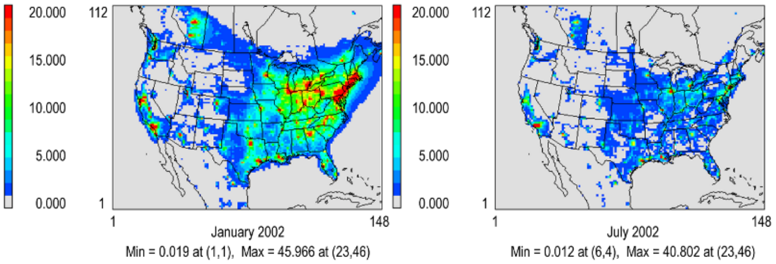


Figure 2-58. Monthly average NO_2 concentrations for January 2002 (left panel) and July 2002 (right panel) calculated by CMAQ (36 X 36 km horizontal resolution).

Trends in NO_2 concentrations across the U.S. from 1990 to 2006 are shown in Figure 2-59. The white line shows the mean values and the upper and lower borders of the shaded areas represent the 10th and 90th percentile values. Information on trends at individual, local air monitoring sites can be found at www.epa.gov/airtrends/nitrogen.html.

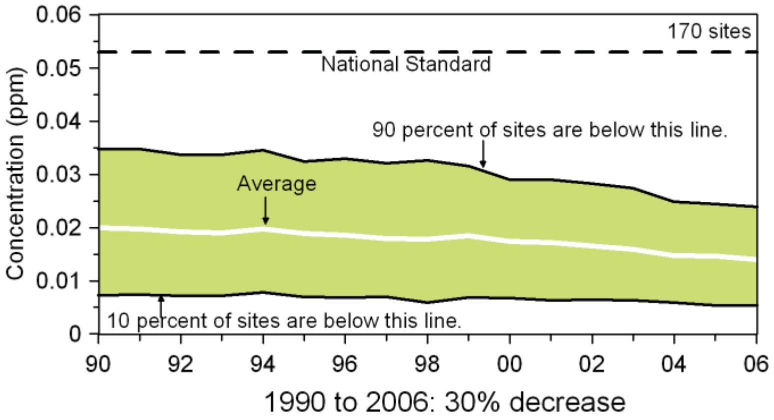


Figure 2-59. Nationwide trend in NO_2 concentrations. The white line shows the mean values, and the upper and lower borders of the green (shaded) areas represent the 10th and 90th percentile values. The current NAAQS of 0.53 ppm is shown with the dotted line. Information on trends at local air monitoring sites can be found at www.epa.gov/airtrends/nitrogen.html.

Concentrations were substantially higher during earlier years in selected locations and contributed in those years to the "brown clouds" observed in many cities. Residents in Chattanooga, TN, for example, were exposed more than 30 years ago to high levels of NO_2 from a munitions plant (Shy, 1980). Annual mean NO_2 concentrations there declined from ~102 ppb in 1968 to ~51 ppb in 1972. There was a strike at the munitions plant in 1973 and levels declined to ~32 ppb. With the implementation of control strategies, values dropped further. In 1988, the annual mean NO_2 concentration varied from ~20 ppb in Dallas, TX and Minneapolis, MN to 61 ppb in Los Angeles, CA. However, New York City, with the second-highest annual mean concentration in the U.S. in 1988, the mean NO_2 concentration was 41 ppb.

In contrast to most urban areas in the U.S., in other countries, NO_2 concentrations have increased. For example, annual mean NO_2 concentrations in central London increased during the 1980s from ~25 ppb in 1978 to ~40 ppb in 1989 at the background measurement site and from ~35 to ~45 ppb at the roadside site. Corresponding NO concentrations increased from ~20 ppb to ~40 ppb at the background site and from ~125 to ~185 ppb at the roadside site (Elsom, 2002d. Increased use of motor vehicles may have contributed to much of these increases in NO_2 levels.

The month-to-month variability in 24–h avg NO_2 concentrations at two sites in Atlanta, GA, is shown in Figure 2-60. (Similar plots of variability at other individual sites in selected urban areas are shown in Figure 2-61 through Figure 2-68; these cities were chosen to represent regions with large populations and, hence, large emissions from on-road vehicles and combustion for energy production, the two largest sources of NO and NO_2.)

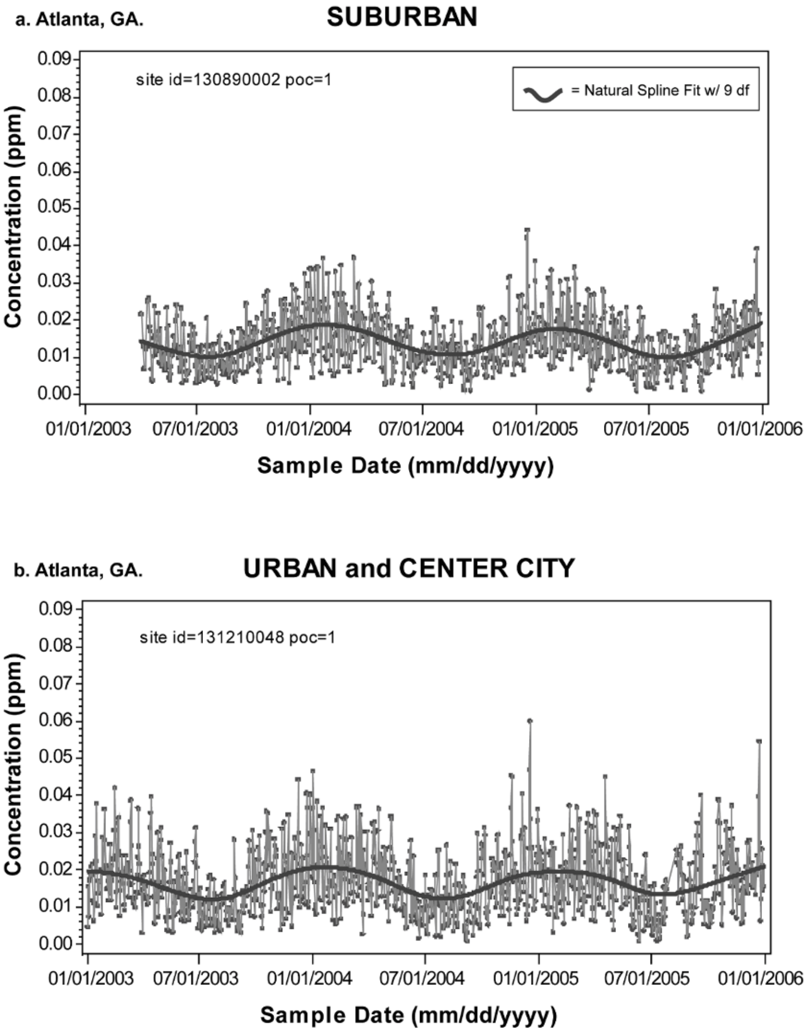
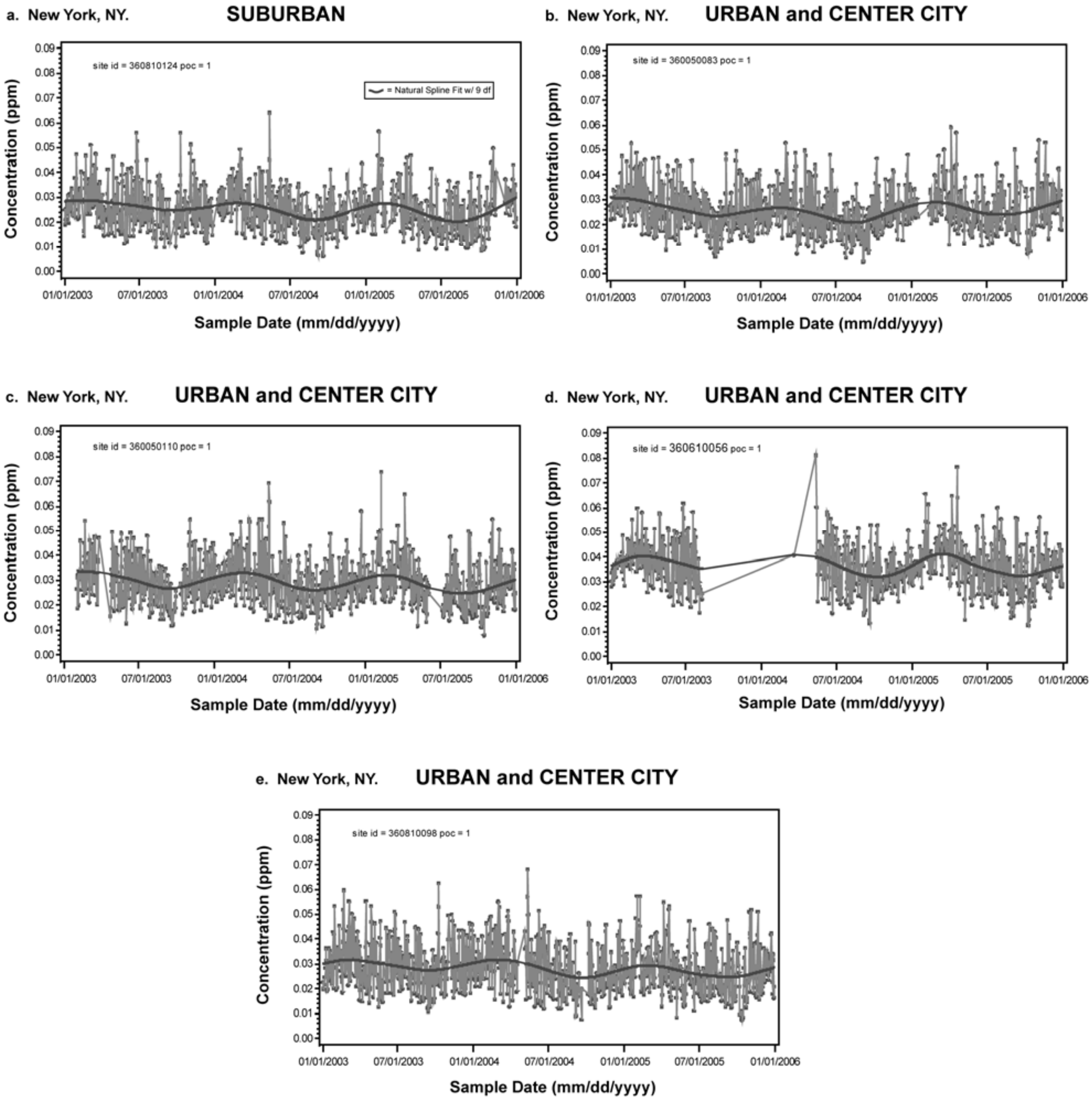


Figure 2-60. Time series of 24–h avg NO_2 concentrations at individual sites in Atlanta, GA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).



Source: U.S. EPA AQS, 2007

Figure 2-61. Time series of 24-h avg NO_2 concentrations at individual sites in New York City from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

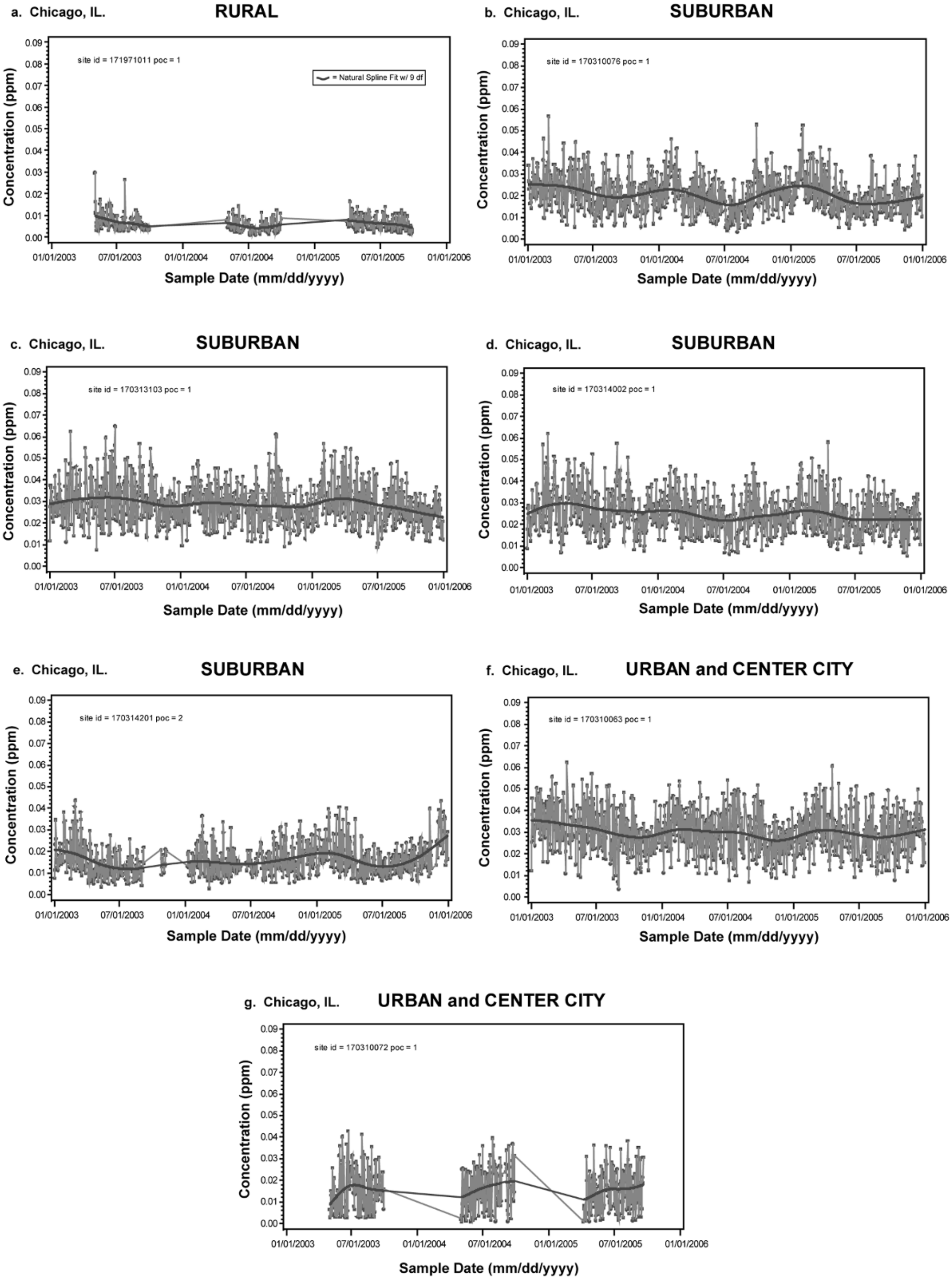
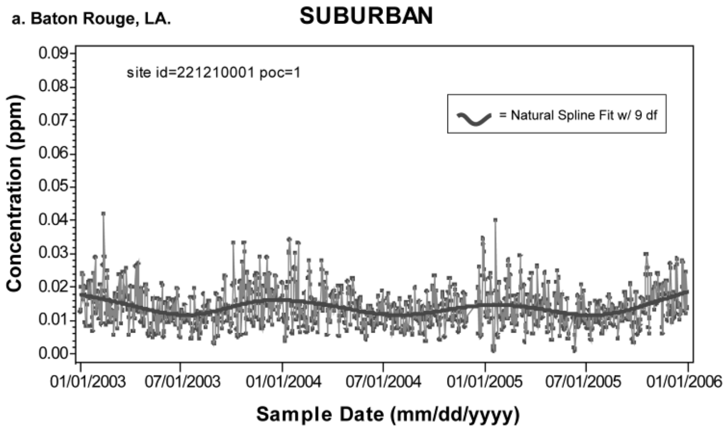


Figure 2-62. Time series of 24–h avg NO_2 concentrations at individual sites in Chicago, IL from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).



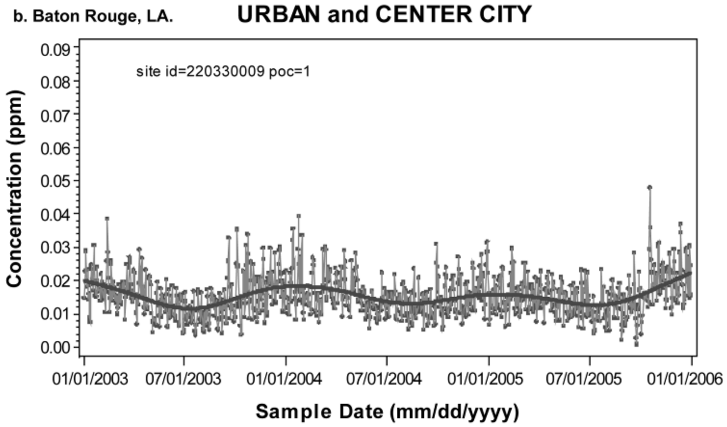


Figure 2-63. Time series of 24–h avg NO_2 concentrations at individual sites in Baton Rouge, LA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

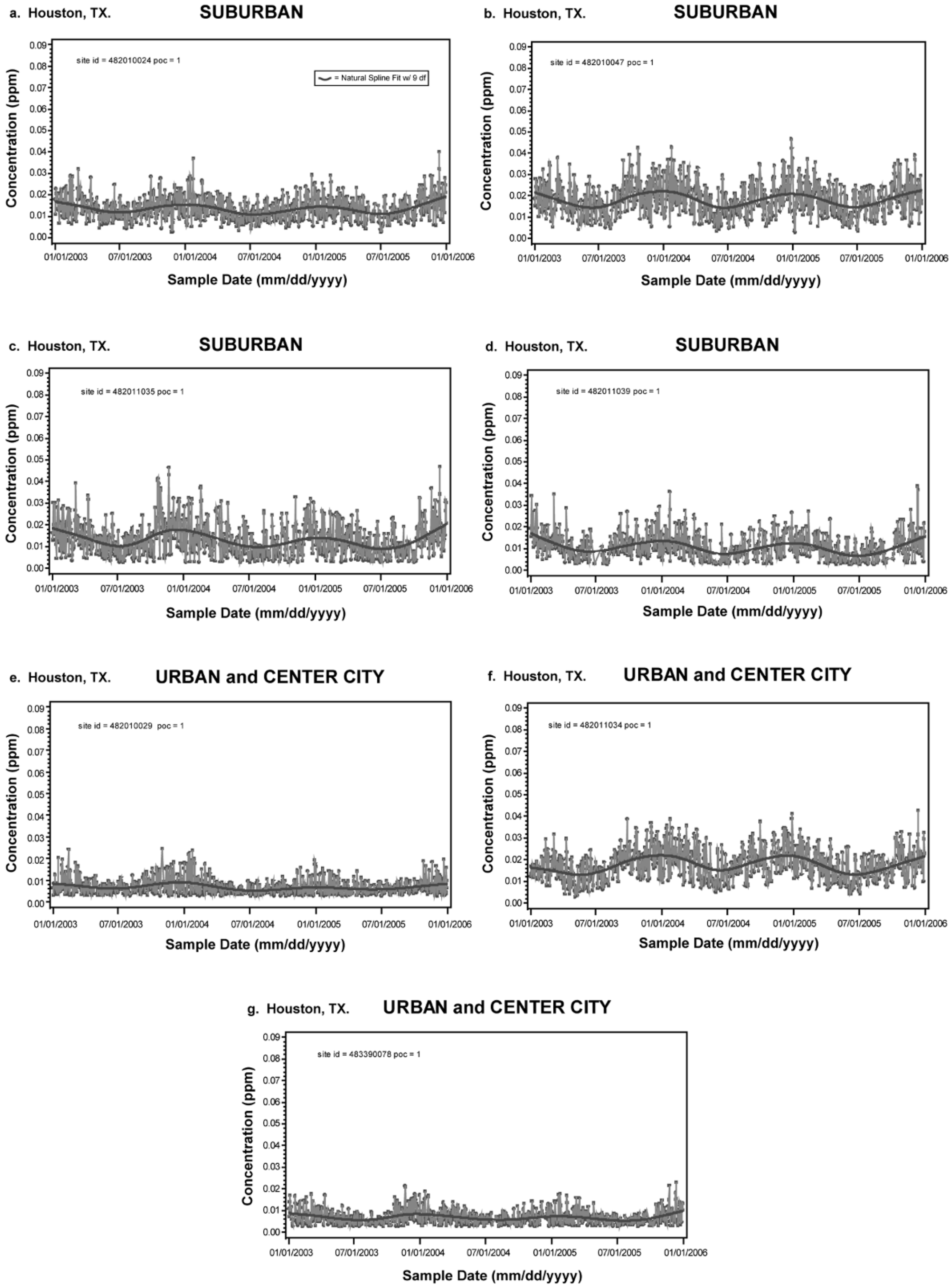


Figure 2-64. Time series of 24–h avg NO_2 concentrations at individual sites in Houston, TX from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

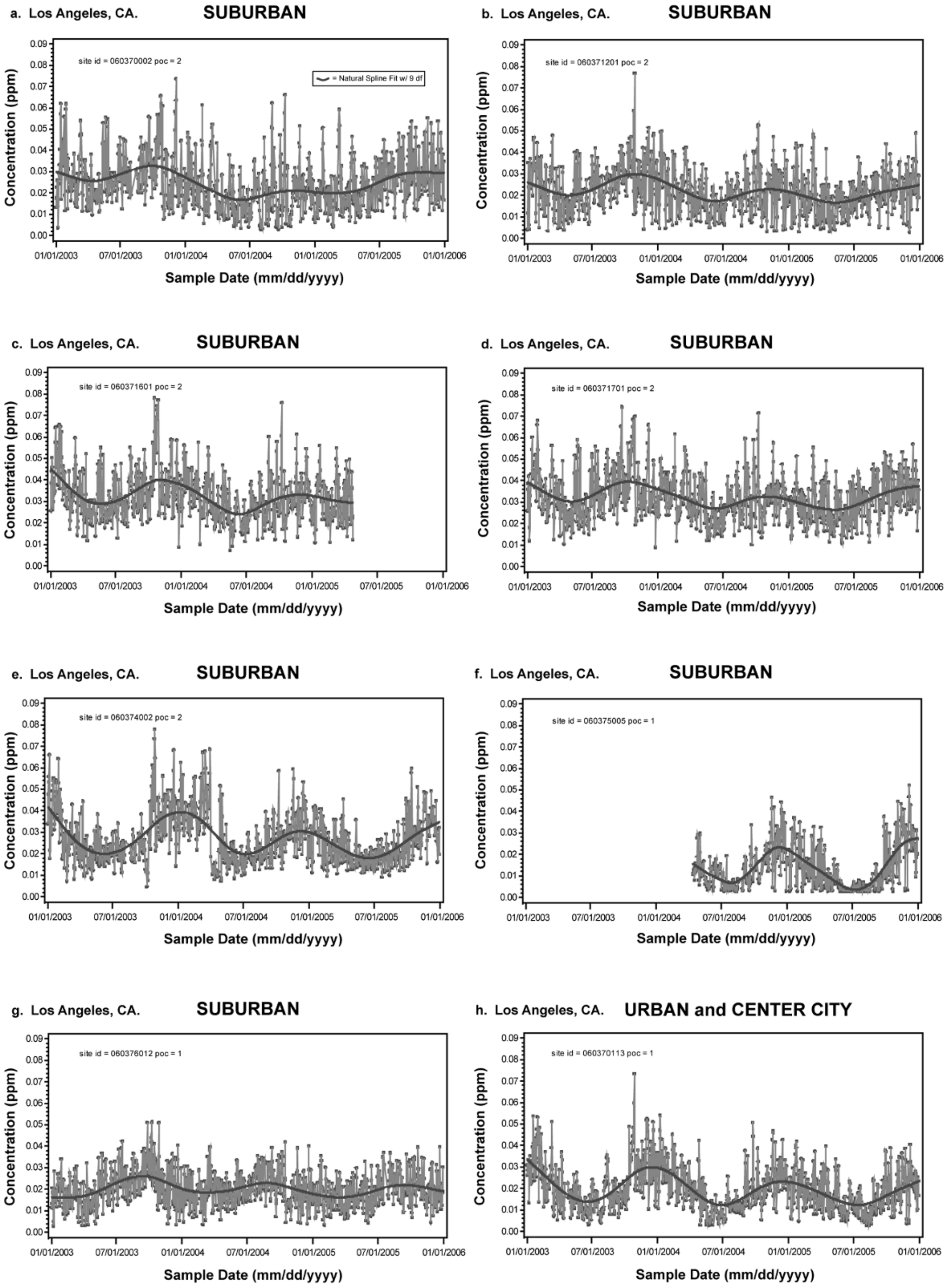


Figure 2-65. Time series of 24–h avg NO_2 concentrations at individual sites in Los Angeles, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

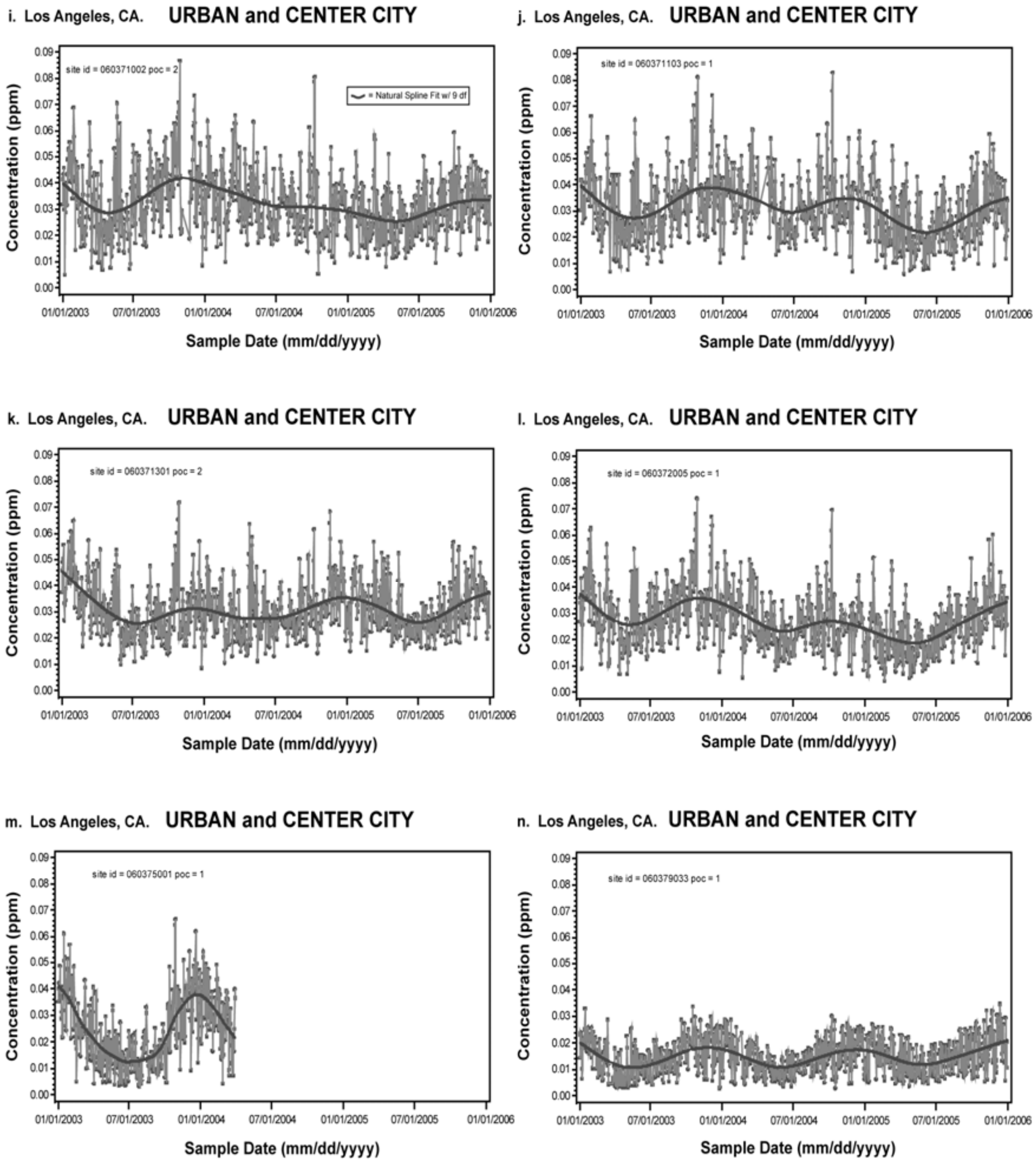


Figure 2-66. Time series of 24–h avg NO_2 concentrations at individual sites in Los Angeles, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

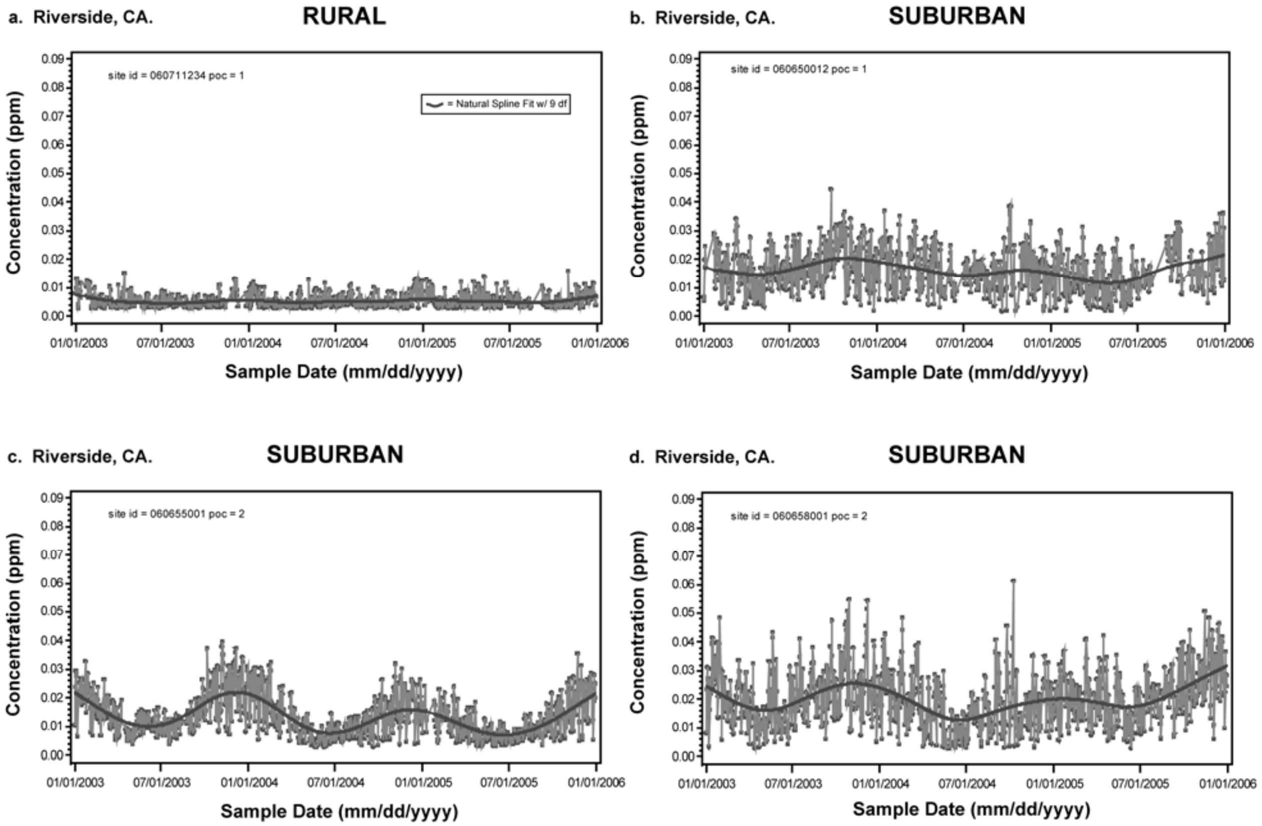
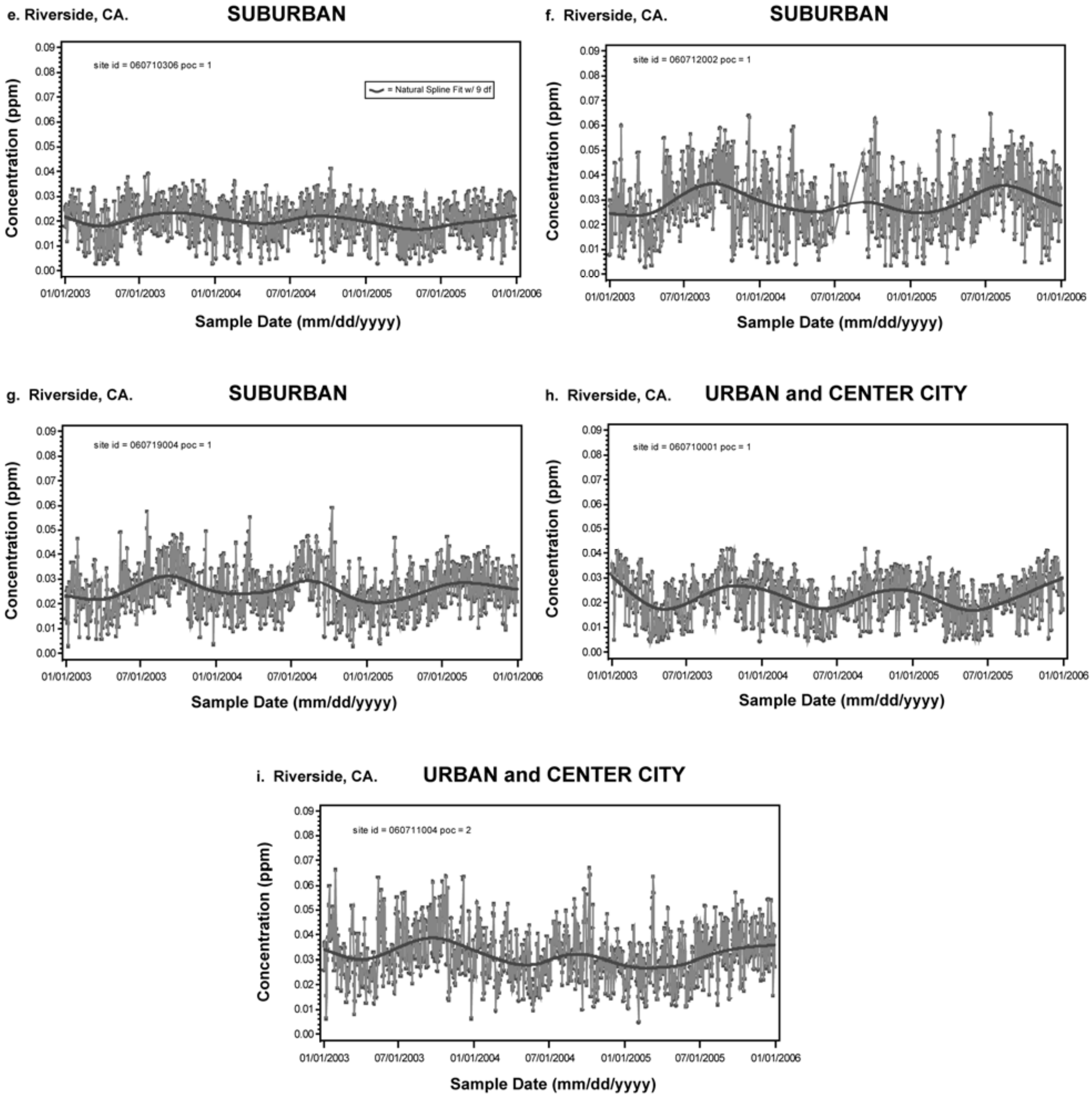


Figure 2-67. Time series of 24–h avg NO_2 concentrations at individual sites in Riverside, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).



Source: EPA (2003)

Figure 2-68. Time series of 24–h avg NO_2 concentrations at individual sites in Riverside, CA from 2003 through 2005. A natural spline function (with 9 degrees of freedom) was fit and overlaid to the data (dark solid line).

Strong seasonal variability exists in NO_2 concentrations in the data shown above. Higher concentrations are found during winter, consistent with the generally lower PBL depths in winter. Lower concentrations are found during summer, consistent with PBL depths and increased rates of photochemical oxidation of NO_2 to NO_Z. Note also the day-to-day variability in NO_2 concentration, which also tends to be larger during the winter. There appears to be a somewhat regular pattern for the other southern cities examined with their winter maxima and summer minima.

Monthly maxima tend to be found from late winter to early spring in Chicago, IL, and New York, NY, with minima occurring from summer through the fall. However, in Los Angeles and Riverside, CA, monthly maxima tend to occur from autumn through early winter, with minima occurring from spring through early summer. Mean and peak NO_2 concentrations during winter can be up to a factor of two greater than those during the summer at sites in Los Angeles.

The diurnal variability in NO_2 concentrations at the same two sites in the Atlanta metropolitan area shown in Figure 2-60 is illustrated in Figure 2-69. As can be seen from these figures, NO_2 typically exhibits daily maxima during the morning rush hours, although they can occur at other times of day. In addition, there are differences between weekdays and weekends. At both Atlanta sites, NO_2 concentrations are generally lower and the diurnal cycles more compressed on weekends than on weekdays. The diurnal variability of NO_2 at these sites is typical of that observed at other urban sites. Monitor siting plays a role in determining diurnal variability in the sense that monitors located farther from traffic will measure lower concentrations and show a flatter overall distribution of data compared to monitors located closer to traffic.

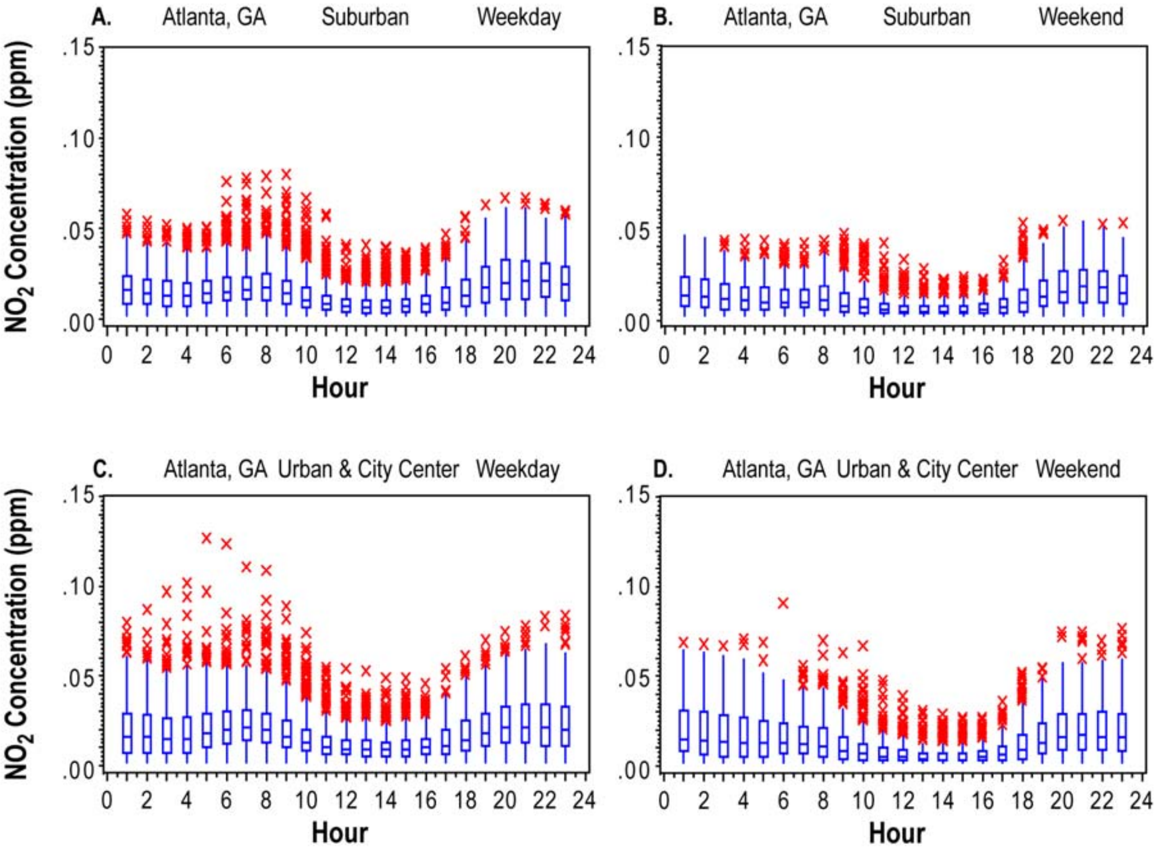


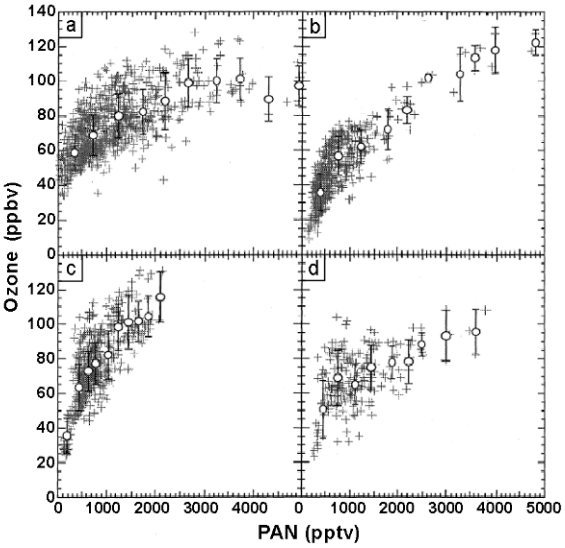
Figure 2-69. Mean hourly NO_2 concentrations on weekdays and weekends measured at two sites in Atlanta, GA. A and B refer to a suburban site, and C and D refer to a site classified as urban and city center.

2.9.5.2. NO_Y and NO_Z

Data for individual NO_Y species are much less abundant than for either oxides of nitrogen or for total NO_Y. Data for several NO_Y species are collected typically only as part of research field studies, e.g., the Southern Oxidant Study (SOS), Texas Air Quality Study (TexAQS I and TexAQS II) in the U.S. As a result, this information is simply not available for a large number of areas in the U.S.

PANs

At warm temperatures, the concentration of PAN forms a photochemical steady state with its radical precursors on a timescale of roughly 30 min. This steady state value increases with the ambient concentration of O_3 (Sillman, 1990). O_3 and PAN may show different seasonal cycles, because they are affected differently by temperature. Ambient O_3 increases with temperature, driven in part by the photochemistry of PAN. The atmospheric τ of PAN decreases rapidly with increasing temperature due to thermal decomposition. Based on the above, the ratio of O_3 to PAN is expected to show seasonal changes, with highest ratios in summer, although there is no evidence from measurements. Measured ambient concentrations show a strong nonlinear association between PAN and O_3 (Pippin, 2001; Roberts, 1998); see Figure 2-70. Moreover, uncertainty in the relationship between O_3 and PAN grows as the level of PAN increases.

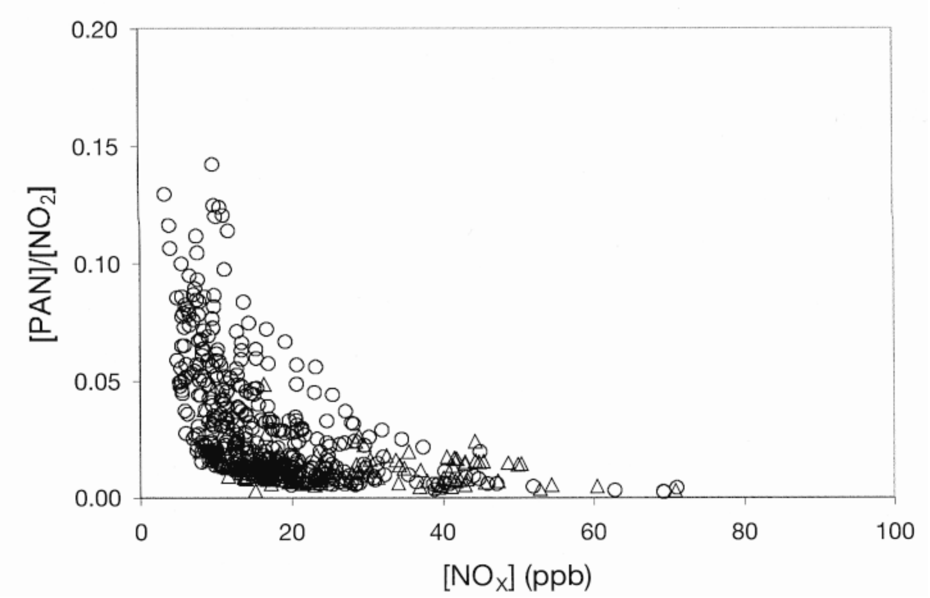


Source: Roberts et al. (1998)

Figure 2-70. Measured O_3 (ppb) versus PAN (pptv by volume) in Tennessee, including (a) aircraft measurements, and (b, c, and d) suburban sites near Nashville.

Measurements and models show that PANs in the U.S. includes major contributions from both anthropogenic and biogenic VOC precursors (Horowitz et al., 1998(Roberts, 1998). Measurements in Nashville during the 1999 summertime Southern Oxidants Study (SOS) showed PPN and MPAN amounting to 14% and 25% of PANs, respectively (Roberts, 2002). Measurements during the TexAQS 2000 study in Houston indicated PAN concentrations of up to 6.5 ppb (Roberts, 2003). PAN measurements in southern California during the SCOS97–NARSTO study indicated peak concentrations of 5–10 ppb, which can be contrasted to values of 60–70 ppb measured back in 1960 (Grosjean, 2003). Vertical profiles measured from aircraft over the U.S. and off the Pacific coasts typically show PAN concentrations above the boundary layer of only a few hundred ppt, although there are significant enhancements associated with long-range transport of pollution plumes from Asia (Kotchenruther, 2001; Roberts, 2004).

Observed ratios of PAN to NO_2 as a function of NO_X at a site at Silwood Park, Ascot, Berkshire, UK are shown in Figure 2-71 United Kingdom Air Quality Expert Group (U.K. Air Quality Expert Group, 2004). As can be seen there is a very strong inverse relation between the ratio and the NO_X concentration, indicating photochemical oxidation of NO_X has occurred in aged air masses and that PAN can make a significant contribution to measurements of NO_2 especially at low levels of NO_2. It should be noted that these ratios will likely differ from those found in the U.S. because of differences in the composition of precursor emissions, the higher solar zenith angles found in the UK compared to the U.S., and different climactic conditions. Nevertheless, these results indicate the potential importance of interference from these compounds in measurements of NO_2.



Source: U.K. Air Quality Expert Group (2004).

Figure 2-71. Ratios of PAN to NO_2 observed at Silwood Park, Ascot, Berkshire, U.K. from July 24 to August 12, 1999. Each data point represents a measurement avgd over 30 minutes.

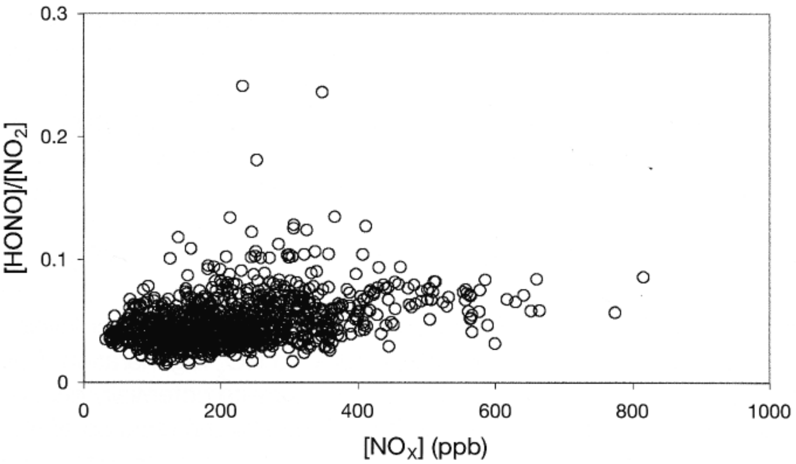
HNO_2

Measurements of HNO_2 in urban areas are extremely limited; however, data from Stutz et al. (2004) and Wang and Lu (2006) indicate that levels of HNO_2 are <1 ppb even under heavily polluted conditions, with the highest levels found during the night and just after dawn and the lowest values found in the afternoon. However, data collected in the U.K. (U.K. Air Quality Expert Group, 2004; Lammel, 1996) and in the U.S. (Kirchstetter, 1996) indicate that HNO_2-to-NO_X ratios could be of the order of ~5% in motor vehicle emissions. These results indicate that HNO_2 levels in traffic could be comparable to those of NO_2. Several field studies conducted at ground level (Hayden, 2003, near Boulder CO; Williams, 1987) and aircraft flights (Singh, 2007, over Eastern North America), have found much higher NO_Z concentrations than NO_X concentrations in relatively unpolluted rural air.

Measurements of HNO_2 in urban areas are very limited; however, data from Stutz et al., (2004) and Wang and Lu, (Wang, 2006) indicate that HNO_2 concentrations are < 1 ppb even under heavily polluted conditions (with the highest levels found during the night and just after dawn and lowest values found in the afternoon). Several field studies such as Hayden et al. (2003) in rural Quebec, Williams et al. (Williams, 1987) near Boulder, CO, and Singh et al. (Singh, 2007) in aircraft flights over eastern North America have also found much higher levels of NO_Z compounds than NO_X in relatively unpolluted rural air.

Calculations with CMAQ for the mid-Atlantic region in a domain from Virginia to southern New Jersey showed that the highest HNO_3 and $RONO_2$ concentrations occur during mid-afternoon, consistent with their formation by photochemical processes also producing O_3. Model simulations of an O_3 episode in July 2002 made for the Maryland State O_3 Implementation Plan (SIP) showed episode averages of the ratio of the further-oxidized N species like HNO_3 to NO_2 ranging from 0.26 to 3.6 in rural Virginia, with the highest ratios in rural areas and lowest ratios in urban centers nearer the sources of fresh NO_X emissions.

The ratio of HNO_2 to NO_2 as a function of NO_X measured at a curbside site in a street canyon in London, UK is shown in Figure 2-72, where HNO_2 is labeled HONO. The ratio is highly variable, ranging from about 0.01 to 0.1, with a mean ~0.05. As NO_2 constitutes several percent of motor vehicle emissions of NO_X, the above implies that emissions of HNO_2 represent a few tenths of a percent of mobile NO_X emissions. A similar range of ratios have been observed at other urban sites in the United Kingdom (Lammel, 1996).



Source: UK AQEG (2004).

Figure 2-72. Ratios of HNO_2 to NO_2 observed in a street canyon (Marylebone Road) in London, U.K. from 11 a.m. to midnight during October 1999. Data points reflect 15–min average concentrations of HONO and NO_2.

HNO_3 and NO_3

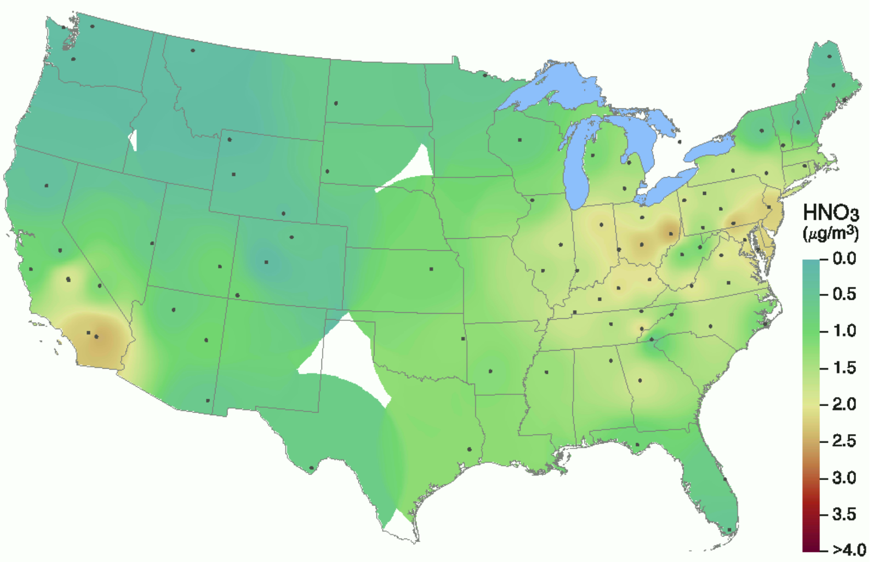
Data for concentrations of HNO_3 and NO_3 in urban areas in the U.S. are sparse. The most geospatially intensive set of data for any HNO_3 were taken as part of the Children's Health Study for which gas-phase HNO_3 was measured at 12 sites in southern California from 1994 through 2001 (Alcorn, 2004). Two week avg concentrations ranged from <1 ppb to >10 ppb, with the highest HNO_3 concentrations and highest ratio of HNO_3 to NO_2, ~0.2, was found downwind from central Los Angeles in the San Bernardino during summer, as one would expect for this more oxidized N product.

HNO_3 data have also been reported from the SEARCH network of four pairs (eight total sites) of urban and rural sites in the southeastern U.S using increasingly sophisticated methods since 1998; see Zhang et al. (Zhang, 2006). Concentrations of HNO_3 in this area have ranged from <1 ppb to >10 ppb.

Maps of ambient concentrations from CASTNET data for rural and remote areas are available below. The CASTNET ambient concentration maps were produced with ArcInfo using an inverse distance weighting (IDW) interpolation technique. Using IDW, the surface is most influenced by the nearest point values and less so by more distant points. CASTNET sites within 400 km of each grid point were used in the computation. As noted above, thin data coverage complicates interpretation of these maps and renders them most useful as heuristic guides to large areas of possible differences. Strict quantitative values should not be imputed to areas away from the measurement sites.

Ranges of years in the chart represent 3−year averages. For example, 2004–2006 is the average concentration of 2004, 2005 and 2006, as calculated from gridded output for each of the years. The three annual grids from the 3-year period were averaged to derive the mean concentration of the 3-year period. Only sites meeting completeness criteria for at least two of the three years of the averaging period were included.

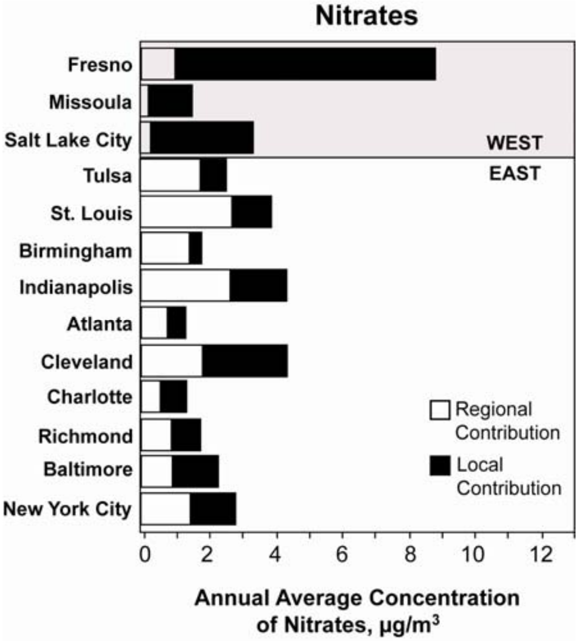
Figure 2-73 shows annual avg concentrations for gas-phase HNO_3 from CASTNet for the years 2004 through 2006. (White areas on the maps are areas where monitoring sites are absent and no information is available.) Because HNO_3 is produced mostly as a secondary product from emitted NO the regions of higher concentrations HNO_3 are geographically similar to those of high concentration NO and NO_2, the northeast corridor and southern California.



Source: CASTNET, USEPA/CAMD 7/30/07

Figure 2-73. Annual average gas-phase HNO_3 concentrations, 2004–2006.

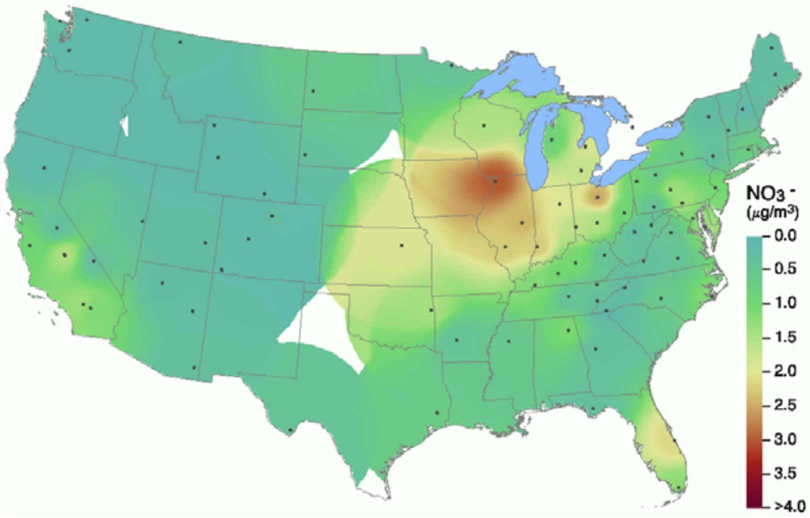
Because they have the same precursor reactants in NO and NO_2, elevated O_3 concentrations are often associated with elevated HNO_3 concentrations. However, HNO_3 can be produced in significant quantities in winter, even when O_3 concentrations are low. The ratio between O_3 and HNO_3 also shows great variation in air pollution events, with NO_X-saturated environments having much lower ratios of O_3 to HNO_3 (Ryerson, 2001). pNO_3 is formed primarily by the combination of NO_3 supplied by HNO_3 with NH_3, and may be limited by the availability of either reactant. NO_3 is expected to correlate loosely with O_3, whereas NH_3 is not expected to correlate with O_3. 2003 annual avg concentrations of pNO_3 from U.S. EPA's STN (CSN) at several locations are shown in Figure 2-74 along with estimated of the fraction contributed locally. (A concentration of 1 $\mu g/m^3$ reported here corresponds to ~0.40 ppb NO_3^-.)



Source: EPA (2004).

Figure 2-74. Concentrations of particulate NO_3 measures as part of the EPA's speciation network. 1 µg/m^3 ~0.40 ppb equivalent gas phase concentration for NO_3^-. (Note: Regional concentrations are derived from the rural IMPROVE monitoring network, http://vista.cira.colostate.edu/improve.

Thus, annual average pNO_3 can account for several ppb of NO_Y, with the higher values in the West. There is a strong seasonal variation, which is especially pronounced in western areas where there is extensive wood burning in the winter resulting in a larger fractional contribution of local sources. Areas in the East where there are topographic barriers might be expected to show higher fractional contributions from local sources than other eastern areas that are influenced by regionally dispersed sources. Figure 2-76 shows a map of annual avg NO_3 concentrations in the years 2004 to 2006 produced from CASTNet measurements of ambient concentrations. This maps indicates at least qualitatively that maximum NO_3 concentrations are found in areas of maximum NO and NO_2 emissions.



Source: CASTNET, USEPA/CAMD 7/30/07

Figure 2-75. Annual average gas-phase NO_3 concentrations, 2004–2006.

However, depending on the acidity of the particles, which in turn depends strongly on their SO_4^{2-} and NH_4^+ contents, higher pNO_3 concentrations could be found in coarse mode particles $PM_{10\text{-}2.5}$ than in $PM_{2.5}$ samples. The average pNO_3 content of $PM_{2.5}$ and PM_{10} is typically ~1% in the eastern U.S.; and 15.7% and 4.5% in the western U.S. (EPA, 1996). These values suggest that most of the pNO_3 was in the $PM_{2.5}$ size fraction in the studies conducted in the western U.S., but pNO_3 in the studies in the eastern U.S. was mainly in the $PM_{10\text{-}2.5}$ size fraction.

2.9.5.3. Nitro-PAHs

Nitro-PAHs are widespread and found even in high altitude, relatively unpolluted environments (Schauer, 2004) but there are differences in composition and concentration profiles both within and between sites (rural vs. urban) as well as between and within urban areas (Albinet, 2006; Soderstrom, 2005; Naumova, 2003, 89234; Naumova, 2002), with some differences in relative abundances of nitro- and oxo-PAHs also reported. Source attribution has remained largely qualitative with respect to concentrations or mutagenicity (Eide, 2002). The spatial and temporal concentration pattern for the nitro-PAHs may differ from that of the parent compounds because concentrations of the latter are dominated by direct emission from local combustion sources. These emissions results in higher concentrations during atmospheric conditions more typical of wintertime when mixing heights tend to be low. The concentrations of secondary nitro-PAHs are elevated under conditions that favor hydroxyl and NO_3 radical formation, i.e., during conditions more typical of summertime, and are enhanced downwind of areas of high emission density of parent PAHs and show diurnal variation (Fraser, 1998; Reisen, 2005; Kameda, 2004). Nitro-napthalene concentrations in Los Angeles, CA varied between about 0.15 to almost

0.30 ng/m^3 compared to 760 to 1500 ng/m^3 for napthalene. Corresponding values for Riverside, CA were 0.012 to more than 0.30 ng/m^3 for nitro-napthalene and 100 to 500 ng/m^3 for napthalene. Nitro-pyrene concentrations in LA varied between approximately 0.020 to 0.060 ng/m^3 compared to 3.3 to 6.9 ng/m^3 pyrene, whereas corresponding values for Riverside were 0.012 to 0.025 ng/m^3 and 0.9 to 2.7 ng/m^3.

2.9.5.4. NH_3

Section 2.7.1.5 above established that a successful real-time continuous monitoring technique for ambient NH_3 has not been identified; and, of at least equal importance, Section 2.4 above described the severely limiting unknowns related to NH_3 emissions on national and local scales. With these important lacunae, estimates of NH_3 concentrations at any scale for the U.S. must be constructed and interpreted with caution. It is possible, for example, to rank NH_3 concentrations by land use types from the few special field campaigns where it was measured as Walker et al. (Walker, 2004) did for agricultural, non-agricultural, and urban types; see Table 2-19. This table shows the enormous range in NH_3 concentrations by season and land use type, from a low of 0.02 µg/m^3 in summer over alpine tundra on Niwot Ridge, CO, (Rattray and Sievering, 2001) to 11.0 µg/m^3 over fertilized lands in Wekerom in the central Netherlands (Buijsman, 1998).

A preliminary draft U.S. national-scale, county-level NH_3 map was created by the U.S. EPA using emissions data from the widely-used Carnegie Mellon University (CMU) NH_3 emissions model, version 3 (see, Pinder, 2007) for a description and application information) and an empirical relationship between emissions and ambient concentration derived from field measurements over five different land use types in North Carolina covering the range of expected NH_3 emissions densities. In the CMU emissions model used for this analysis, fertilized soils were included but NH_3 emissions from natural (non-fertilized soils) was not because of overwhelmingly large uncertainties in their emissions factors. Emissions from mobile sources are included in this analysis, although uncertainties in those values are also large. And emissions from a small number of counties having very low emissions rates was set to missing because their extremely low values invalidated determination of densities in those counties. The CMU-derived county-level NH_3 emissions map is show in Figure 2-76. Differences in the techniques for estimating NH_3 emissions and the very large uncertainties in NH_3 emissions factors and totals complicate direct, fine-scale comparisons to other NH_3 emissions maps. However, both the magnitude and areal extent of the emissions map here compare very favorably to the U.S. EPA NEI database NH_3 emissions map shown in Section 2.4 above.

Table 2-19. Ambient NH_3 concentrations summarized by study.

Concentration (μgm³)	Land Use	Comment
3.0	Agricultural	Low NH_3 emissions
11.0	Agricultural	Moderate NH_3 emissions [a]
10.48	Agricultural	Fall [b]
0.65-1.2	Agricultural	Spring [c]
0.26	Agricultural	Winter [c]
0.34	Non-agricultural	High elevation, summer and fall [d]
0.02	Non-agricultural	High elevation, summer [e]
0.62-1.47	Non-agricultural	High elevation, summer [f]
0.29	Non-agricultural	High elevation, summer [g]
0.22	Non-agricultural	Coastal, summer [g]
0.21	Non-agricultural	Forest, summer [g]
0.16	Non-agricultural	Forest [h]
0.21	Non-agricultural	Wetland, summer [g]
0.23	Non-agricultural	Wetland, summer [g]
0.63	Non-agricultural	Desert, summer [g]
4.75	Non-agricultural	Grassland, summer [g]
0.38-1.49	Urban	Pittsburgh, PA; summer [i]
0.63-0.72	Urban	Research Triangle Park, NC; fall [j]
1.18	Urban	Vinton, VA; summer [k]

[a] Buijsman et al. (1998).

[b] McCulloch et al. (1998).

[c] Pryor et al. (2001).

[d] Tarnay et al. (2001).

[e] Rattray and Sievering (2001)

[f] Aneja et al. (1998).

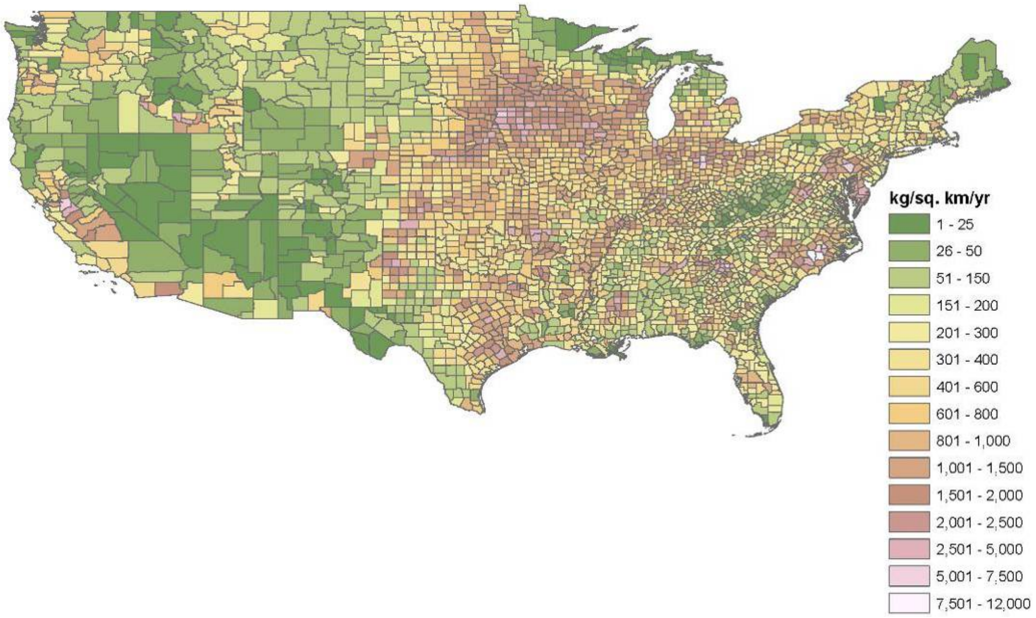
[g] Langford et al (1992).

[h] Lefer et al. (1999)

[I] McCurdy et al. (1999).

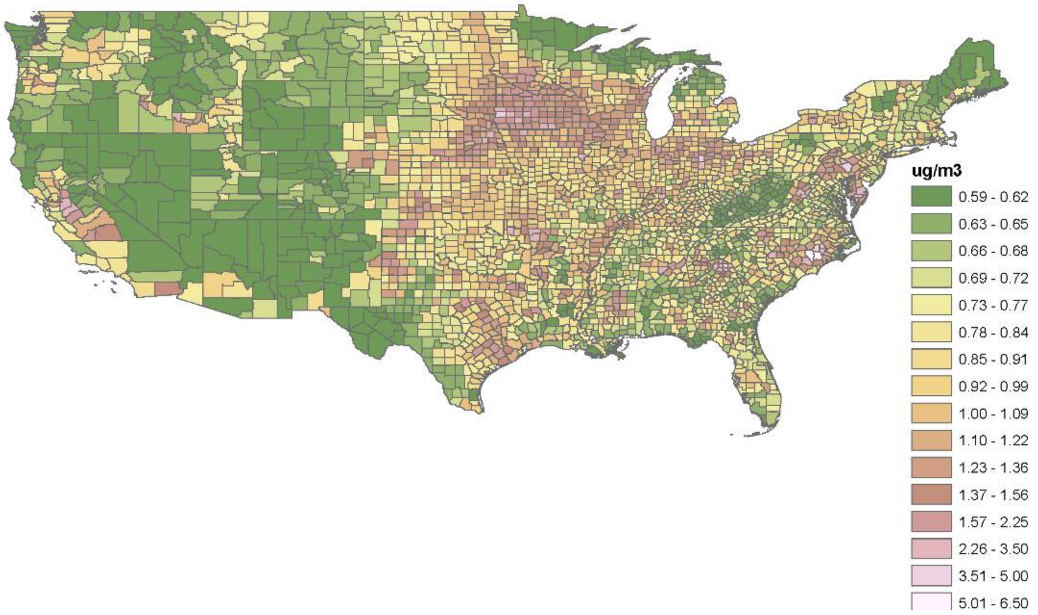
[j] Sickles et al. (1990).

[k] Leaderer et al. (1999).



Source: J. Walker, USEPA/ORD/NRMRL

Figure 2-76. County-scale NH_3 emissions densities from the CMU inventory model.



Source: J. Walker, USEPA/ORD/NRMRL

Figure 2-77. Estimated county-scale ambient NH_3 concentrations.

2.9.5.5. NH_4NO_3

The IMPROVE network is the premier source of data about the spatial and temporal patterns of rural and remote pNO_3 in the U.S. Data about urban pNO_3 and other particles comes primarily from the collection of networks now termed the Chemical Speciation Network (CSN), which includes the U.S. EPA Speciation Trends Network (STN) and others (Jayanty, 2003). Although IMPROVE began and still functions primarily to characterize visibility impairments in protected areas, the network has been expanded several times since its inception to include coverage of remote areas in central and western states of the U.S. to better understand regional components of particulate pollution. Except where noted, information in this section was derived form the IMPROVE IV Report (DeBell, 2006) with data displays created with data and tools available at http://vista.cira.colostate.edu/views/. Much of these data and conclusions are also to appear in Pitchford et al., 2008.

The IMPROVE Network monitors the major fine particle components pSO_4, NO_3, crustal, EC and OC, and coarse mass concentration computed as the concentration difference PM_{10} minus $PM_{2.5}$. An implicit assumption is that most of the pNO_3 is present as NH_4NO_3 in the $PM_{2.5}$ size range. One component of the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study, conducted at Big Bend National Park, TX, in the summer and fall of 1999, entailed use of detailed measurements of aerosol chemical composition, size distribution, water growth, and optical properties to characterize the aerosol and assess the relationships among aerosol physical, chemical, and optical properties (Schichtel, et al., 2004). Fine pNO_3 accounted for <5% of the mass concentration in these samples and was present mostly as $NaNO_3$. Approximately 67% of the pNO_3, again inferred to be $NaNO_3$, was found in the coarse mode where it comprised ~8% of the mass concentration.

A year-long special study of coarse particle speciation was conducted at nine IMPROVE remote area monitoring sites during 2003 and 2004 to provide additional information about the geographic and seasonal variations in coarse particle composition; see Malm, et al. 2007. The same sampling and analytical methodologies procedures were used for the PM_{10} samples as are routinely used on the IMPROVE $PM_{2.5}$ samples. The IMPROVE coarse particle speciation study did not include NH_4^+ analysis, so pNO_3 was assumed again to be NH_4NO_3. As expected crustal minerals were the largest contributors to coarse mass overall at ~60%, and organic particles contributed significantly at ~25% of coarse mass. On average, pNO_3 was the third largest contributor to coarse mass at ~8% on average for the nine monitoring sites. The sites with the highest coarse pNO_3 concentrations were the two in California (San Gorgonio, $0.74\mu g/m^3$ and Sequoia, $0.69\mu g/m^3$) where fine pNO_3 were also high on average ($2.66\mu g/m^3$ and $2.14\mu g/m^3$ respectively). Brigantine, a coastal site in NJ had the highest fraction of total coarse pNO_3 at 36%. The authors speculated that Brigantine's pNO_3 was likely $NaNO_3$, the result of HNO_3 reactions with sea-salt NaCl. The nine-site average fraction of total coarse pNO_3 was 26%.

Figure 2-78 shows maps of remote NH_4NO_3 for two years selected to demonstrate the additional information available after expansion of the IMPROVE network into the central U.S. The locations of monitoring sites supplying the data shown as color contours are shown as dot on the maps. Concentration contour maps generally carry the caution that their isolines are provided merely to guide visual similarities among sites reporting similar values, and should not be read to suggest any quantitative spatial interpolation where sites do not exist. These plots, showing the so-called Midwest pNO_3 “bulge” illustrate why that caution is always warranted.

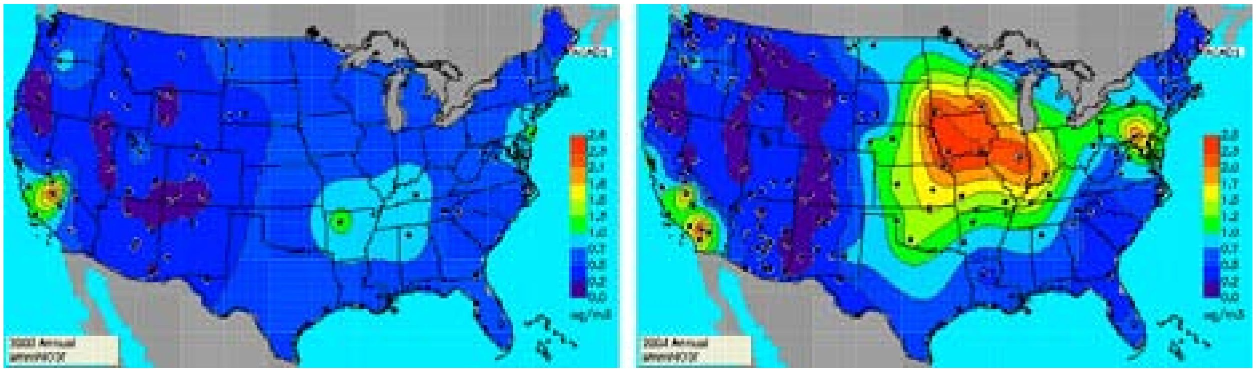


Figure 2-78. IMPROVE network measured annual averaged ammonium NO_3 concentration for 2000 (left) and for 2004 (right). (maps produced by VIEWS)

Prior to 2001 no IMPROVE or any other remote-area aerosol speciation monitoring sites exited in the central states between northern MN and MI to the north and AK and KY to the south. The lack of monitoring over such a large region in the center of the country hid the largest regional distribution of particulate matter dominated by NH_4NO_3, previously thought to be a phenomenon isolated to CA. However, with fewer than 6 years of complete data for this region, insufficient information exists to test for long-term trends.

Combining IMPROVE and CSN data makes possible comparison of urban pNO_3 to surrounding remote-area regional values. These are shown as paired color contour maps for IMPROVE and IMPROVE plus CSN in Figure 2-79. EPA (2004b) used the pairing of IMPROVE and CSN monitoring sites at 13 selected areas to separate local and regional contributions to the major contributors of $PM_{2.5}$, as shown for pNO_3 in Figure 2-80.

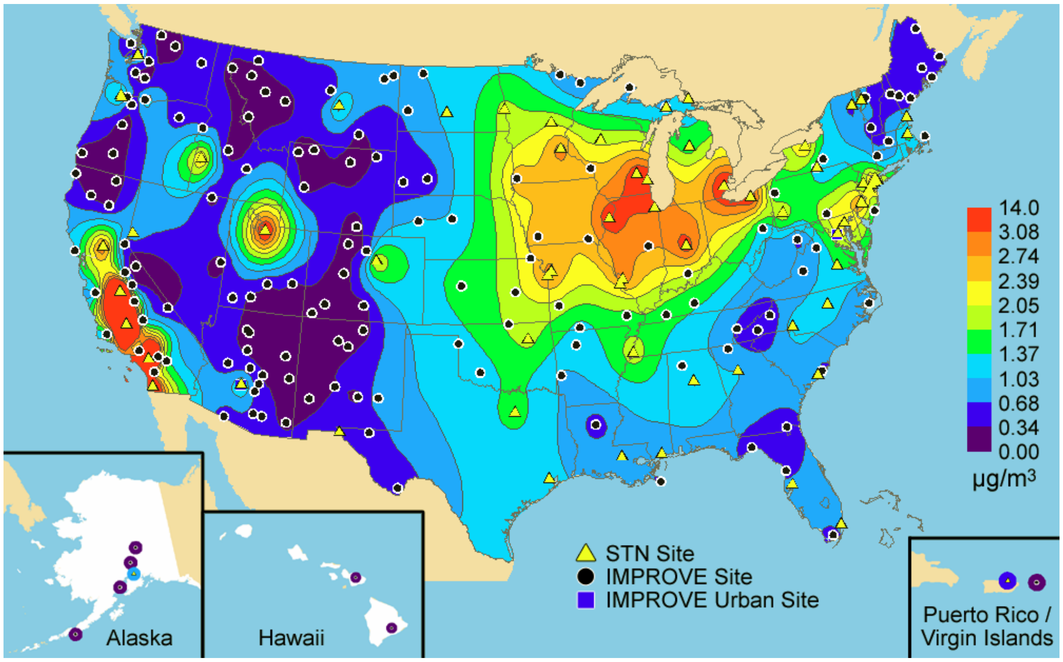
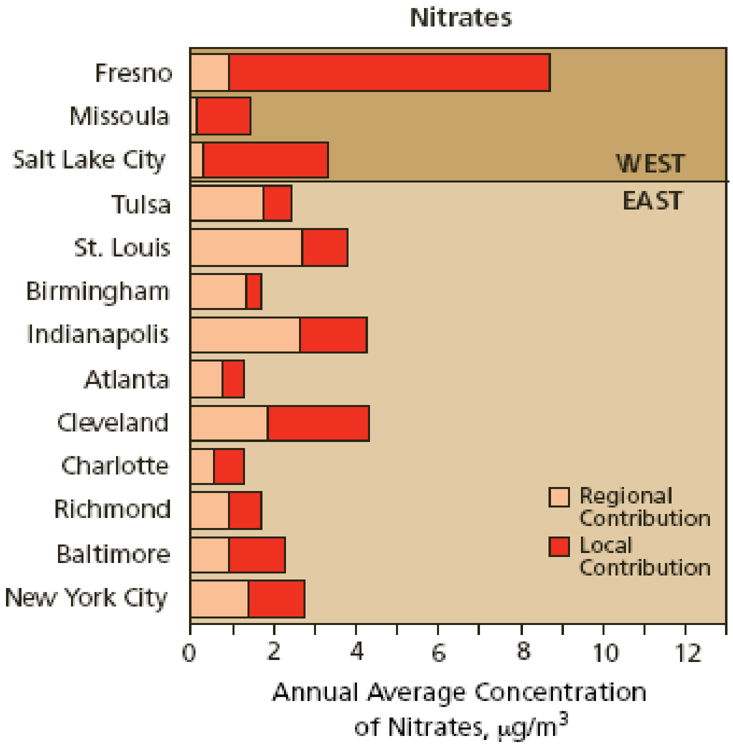


Figure 2-79. IMPROVE and CSN (labeled STN) monitored mean ammonium nitrate concentrations for 2000 through 2004.



Source: EPA, 2004b.

Figure 2-80. Regional and local contributions to annual average $PM_{2.5}$ by pNO_3 for select urban areas based on paired IMPROVE and CSN monitoring sites.

Urban pNO_3 concentrations in Western states are in general more than a factor of 2 greater than the remote-area regional concentrations. For the Central Valley of California and Los Angeles areas, the urban excess NH_4NO_3 exceed regional concentrations by amounts ranging from 2µg/m^3 to 12µg/m^3. In the region of the recently identified Midwest pNO_3 bulge, the urban concentrations were less than twice the background concentrations for an annual urban excess of about 1µg/m^3. Northeast and southeast of the Midwest NO_3 bulge, annual urban pNO_3 were ~1µg/m^3 or less above the remote-area regional concentrations, with warmer southern locations tending to have smaller concentrations of both regional and urban excess pNO_3.

Holland et al. (1999) developed NO_X emissions trends from 1989 to 1995 and compared them to corresponding trends in total N (pNO_3 + gas-phase HNO_3) for the states in the U.S. between LA and MN and East of that line based on data from 34 rural CASTNet dry deposition monitoring sites. They reported a decrease in total N median values of ~8% associated with a decrease of 5.4% in non-biogenic NO_X emissions. Because of the form of total N assumed in this analysis, it is not possible to determine whether this change is larger for HNO_3 or pNO_3. For situations with limited gas-phase NH_3 or with elevated temperatures, it may be assumed that the trend in total N is principally in HNO_3 with no net change in pNO_3. Where NH_3 concentrations are substantially in excess of those required to neutralize pSO_4 and where temperatures are lower, this trend may be assumed to be reversed.

Potential causes of the Midwest pNO_3 bulge can be examined through comparison of the pNO_3 areal extent to that of NO_X and NH_3 emissions. Figure 88 shows a map of the annual average pNO_3 concentrations (top) with a map of NH_3 emissions (bottom). The spatial extent of NH_3 emissions in the Midwest is strikingly similar to that of pNO_3 concentrations, each having regional maxima centered on Iowa. NO and NO_2 emissions are high over a broad region of the country associated with the larger population densities and greater numbers of fossil fueled EGUs to the east of the Midwest pNO_3 bulge. While both NH_3 and HNO_3 are needed to form NH_4NO_3, the maps suggest the Midwest NO_3 bulge is due primarily to the abundance of free NH_3, defined as the amount beyond that required to neutralize the acidic pSO_4. By contrast, the region East of the Midwest NO_3 bulge might be expected to have excess HNO_3 given greater emissions of NO and NO_2, but apparently has a deficiency of free NH_3. The few eastern monitoring sites with locally high pNO_3 (near southern PA) are located within a small region of high density animal agricultural sites identified as a high NH_3 emissions region in Figure 88. Note that California's South Coast and Central Valley have both high NH_3 and NO and NO_2 emissions, explaining its own high pNO_3 concentration.

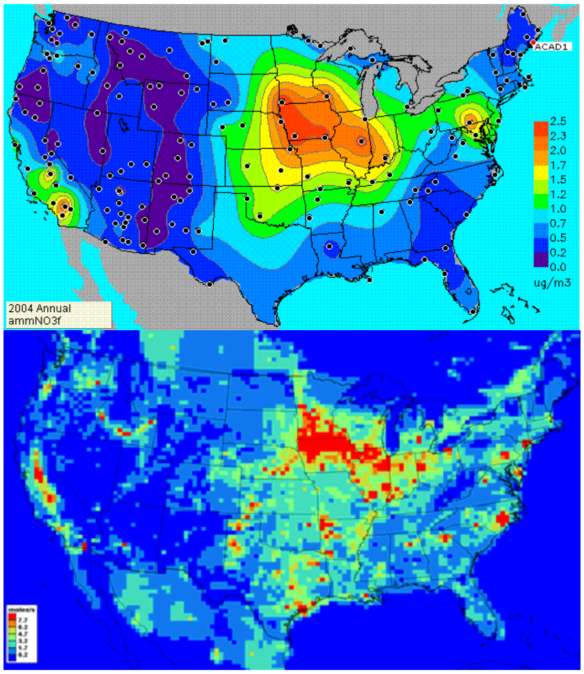


Figure 2-81. Maps of spatial patterns for average annual particulate NO_3 measurements (top), and for NH_3 emissions for April 2002 from the WRAP emissions inventory (bottom).

Importantly, although the Midwest pNO_3 bulge was not apparent before measurements were made in its region, air quality modeling using national-scale emissions data predicted it as early as 1996 as done with CMAQ applications for the U.S. EPA Western Regional Air Partnership (http://www.wrapair.org). Figure 89 shows the CMAQ-predicted average pNO_3 concentration for the month of January 1996 (left panel) and the model-predicted sensitivities of pNO_3 to a 50% decrease in NH_3 emissions. Reductions in magnitude of ~3 $\mu g/m^3$ in the heart of the Midwest NO_3 bulge and in areal extent are predicted as a result of the NH_3 emissions decrease.

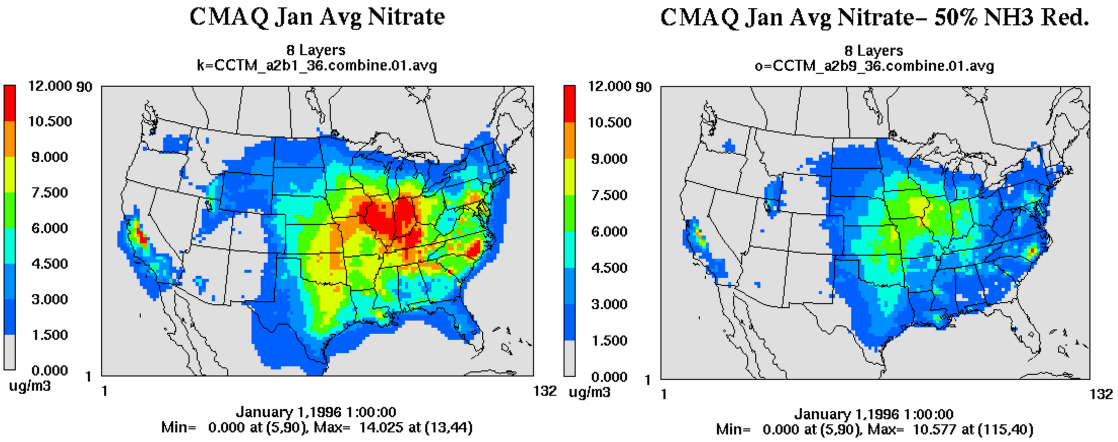


Figure 2-82. CMAQ simulation of January monthly averaged particulate NO_3 concentration using 1996 emissions (left), and for a 50% decrease in NH_3 emissions (right). Source: U.S. EPA / WRAP.

Several example monitoring locations distributed across the northern and southern portions of the Western U.S. have been selected to illustrate the attribution results from air quality simulation modeling by source region and source type for pNO_3. They include Olympic National Park (NP), WA; Yellowstone NP, WY; and Badlands NP, SD across the north, and San Gorgonio Wilderness (W), CA; Grand Canyon NP, AZ and Salt Creek W, NM across the south. Pie diagrams of pNO_3 attribution results by source region for each of these sites are shown in Figure 90. Based on these sites, 25% or less of the pNO_3 in remote areas of the Pacific coastal states is from outside of the U.S. (Pacific Offshore and Outside of the Domain). The Outside of the Domain values are derived by simulating the fate of the boundary condition concentrations, which for the WRAP air quality modeling were obtained using output from the GEOS-CHEM global air quality model (Fiore, 2003).

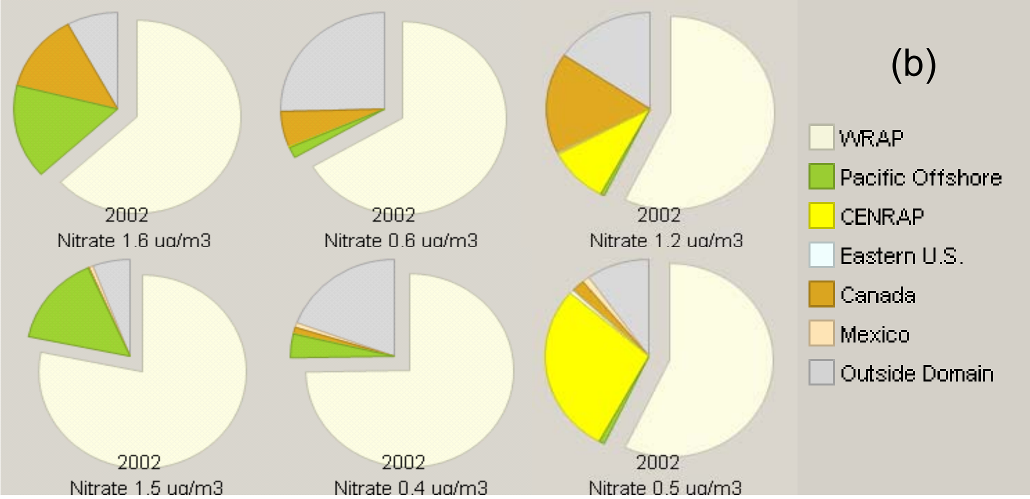


Figure 2-83. Particulate NO_3 source attribution by region using CAMx modeling for six western remote area monitoring sites. Top left to right Olympic NP, WA; Yellowstone NP, WY; Badlands NP, SD; bottom left to right San Gorgonio W, CA; Grand Canyon NP, AZ; and Salt Creek W, NM. WRAP includes ND, SD, WY, CO, NM and all states further west. CENRAP includes all states east of WRAP and west of the Mississippi River including MN. Eastern U.S. includes all states east of CENRAP. The Pacific Offshore extends 300km to the west of CA, OR, and WA. Outside Domain refers to the modeling domain, which extend hundreds of kilometer into the Pacific and Atlantic Oceans and from Hudson Bay Canada to just north of Mexico City.

By comparison, the pNO_3 is much more from domestic regional emission sources, with ~60 to ~80% being from emissions within the WRAP region. For the west coast sites ~25% of pNO_3 is from a combination of Pacific Offshore emissions (i.e. marine shipping) and Outside Domain regions. Canadian emissions are responsible for ~10 to 30% of pNO_3, but Mexican emissions do not contribute appreciably to pNO_3 for the three southern sites. Motor vehicles are the largest contributing $NO+NO_2$ source category responsible for pNO_3 for these six WRAP sites, with a combination of point, area and wildfire source categories also contributing from ~10 to 50% of the WRAP regional emissions.

2.9.6. Ambient Concentrations of Relevant S Compounds

2.9.6.1. SO_2 and SO_4^{2-} Near Urban Areas

SO_2 data collected from the SLAMS and National Air Monitoring Stations (NAMS) networks show that the decline in SO_2 emissions from EGUs has improved air quality. There has not been a single monitored exceedance of the SO_2 annual ambient air quality standard in the U.S. since 2000 (EPA, 2006b). EPA's trends data (www.epa.gov/airtrends) reveal that the national composite average SO_2 annual mean ambient concentration decreased by 48% from 1990 to 2005, with the largest single-year reduction coming in 1994–1995 (EPA, 2006b).

In 2007, there were ~500 SO_2 monitors reporting values to the EPA Air Quality System database (AQS). Trace level SO_2 monitoring is currently required at the approximately 75 proposed NCore sites, as noted in CFR 40 Part 58 Appendices C and D. Continued operation of existing State and Local Air Monitoring Sites (SLAMS) for SO_2 using FRM or FEM is required until discontinuation is approved by the EPA Regional Administrator. Where SLAMS SO_2 monitoring is required, at least one of the sites must be a maximum concentration site for that specific area.

Figures 91 through 96 illustrate the 2005 geospatial locations of monitors for SO_2, NO_2, CO, PM_{10}, $PM_{2.5}$, and O_3. These locations, sited in several cities in six states, were selected as relevant for SO_2 environmental effects to complement measurements from rural and remote CASTNet sites and to be near large sources of SO_2. For each state, map A of each figure shows locations of each monitor for all six pollutants; map B of each figure shows only the SO_2 monitor locations. Totals for each monitor type are included. These figures demonstrate the important point that not all SO_2 monitors in any Consolidated Metropolitan Statistical Area (CMSA) are co-located with monitors for other pollutants. Two examples are given below.

Table 2-20 lists the totals for all criteria air pollutant monitors (except Pb) in California, as well as the subset of these monitors in San Diego County. At each of the four sites where SO_2 was measured, NO_2, CO, PM_{10}, $PM_{2.5}$, and O_3 were also measured, with the exception of $PM_{2.5}$ at one site (AQS ID 060732007) in Otay Mesa, CA. Table 2-21 lists the totals for all criteria air pollutant monitors (except Pb) in Ohio, as well as the subset of in Cuyahoga County.

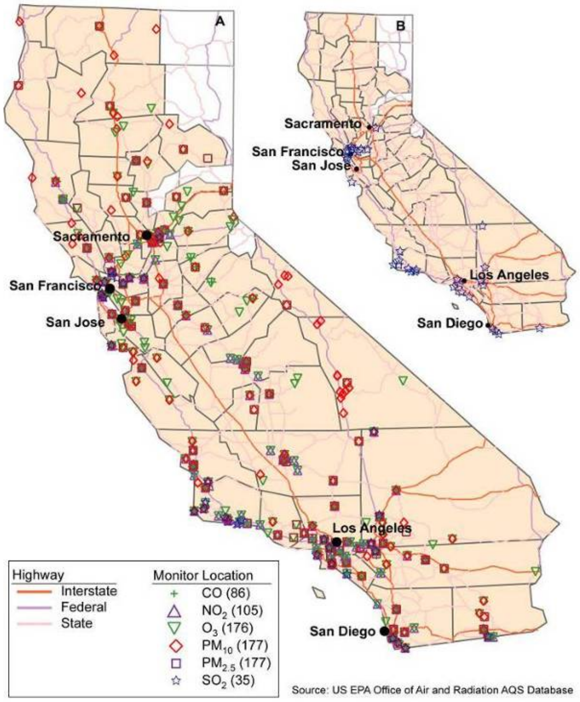
In Cuyahoga County, PM_{10} and $PM_{2.5}$ were measured at all four sites where SO_2 was also measured in 2005, but O_3 and CO were not measured at any of those four sites; NO_2 was only measured at one site (AQS ID 39050060) near Cleveland's city center and ~0.5 km from the intersection of Interstate Highways 77 and 90.

Table 2-20. Monitor counts for California and San Diego County, 2005.

	SO_2	NO_2	O_3	CO	PM_{10}	$PM_{2.5}$
California (all)	35	105	176	86	177	97
San Diego County	4	9	10	6	7	7

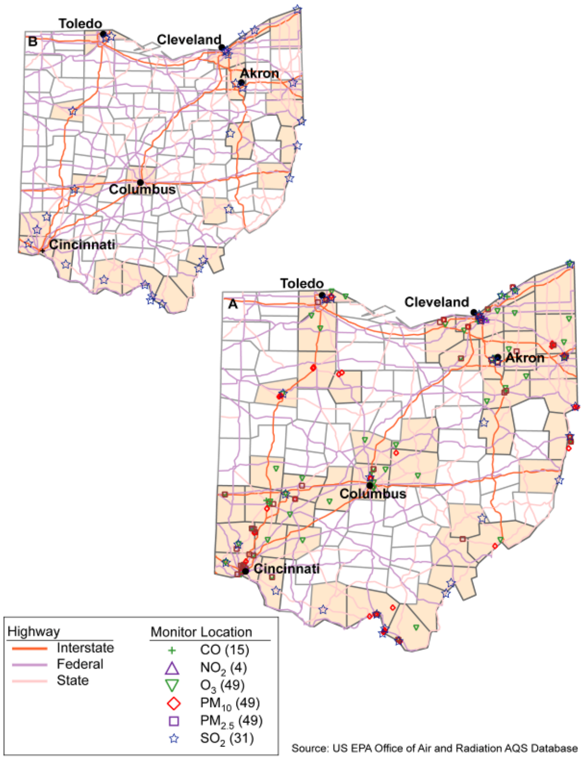
Table 2-21. Monitor counts for Ohio and Cuyahoga County, 2005.

	SO_2	NO_2	O_3	CO	PM_{10}	$PM_{2.5}$
Ohio (all)	31	4	49	15	49	49
Cuyahoga County	4	2	3	4	6	7



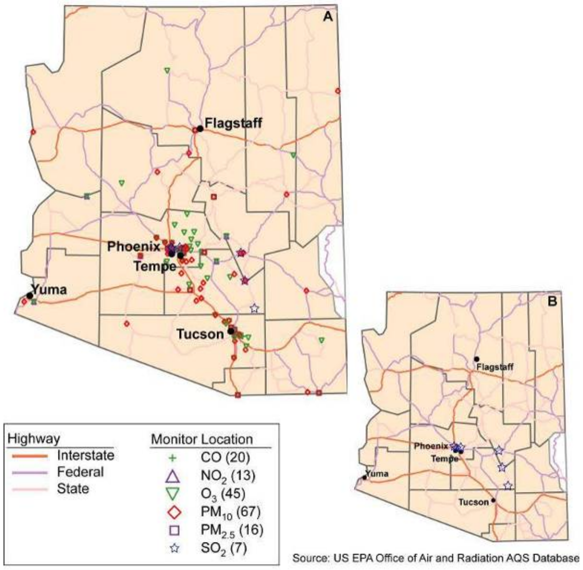
Source: US EPA Office of Air and Radiation AQS Database

Figure 2-84. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), California, 2005. Shaded counties have at least one monitor.



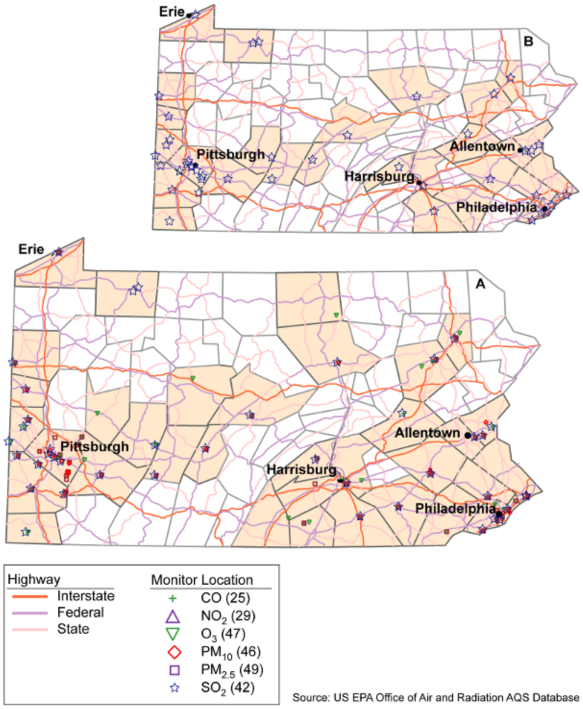
Source: US EPA Office of Air and Radiation AQS Database

Figure 2-85. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), Ohio, 2005. Shaded counties have at least one monitor.



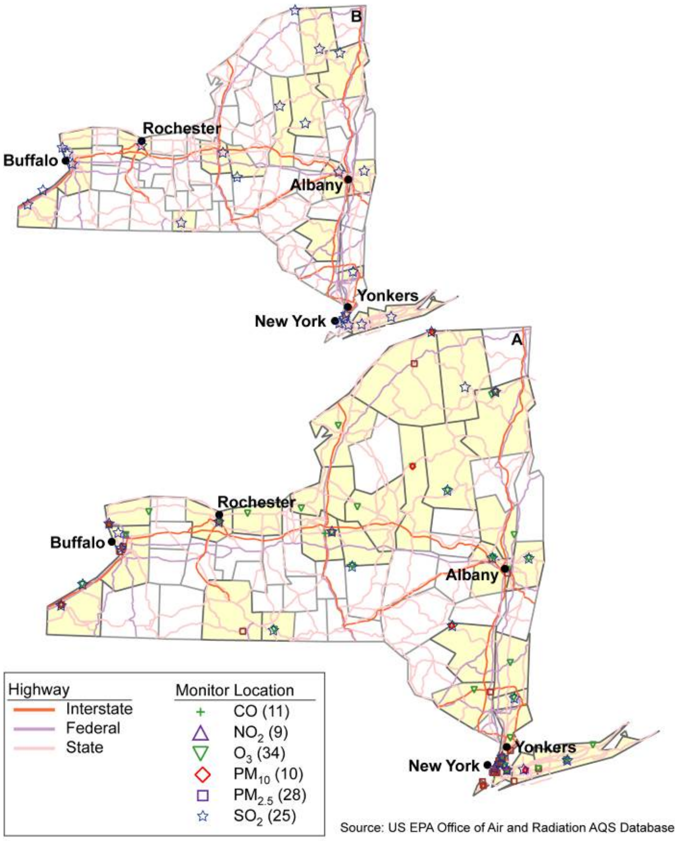
Source: US EPA Office of Air and Radiation AQS Database

Figure 2-86. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), Arizona, 2005. Shaded counties have at least one monitor.



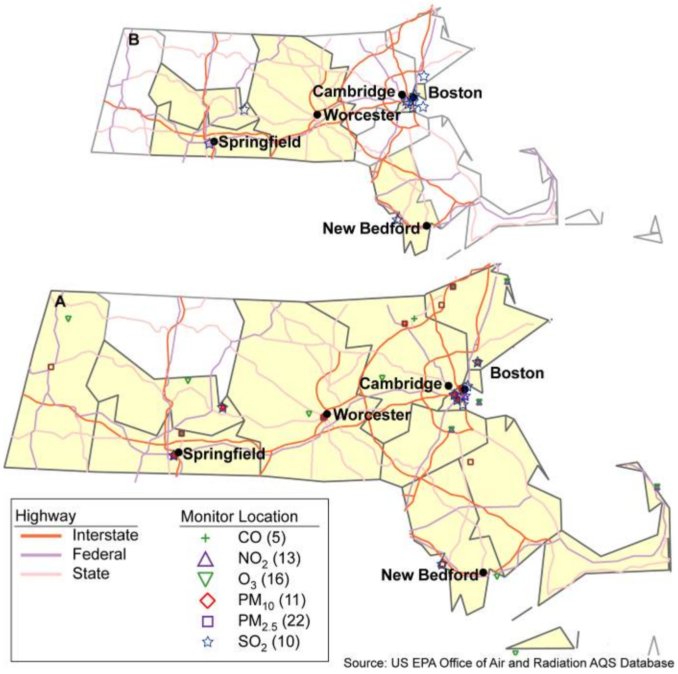
Source: US EPA Office of Air and Radiation AQS Database

Figure 2-87. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), Pennsylvania, 2005. Shaded counties have at least one monitor.



Source: US EPA Office of Air and Radiation AQS Database

Figure 2-88. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), New York, 2005. Shaded counties have at least one monitor.



Source: US EPA Office of Air and Radiation AQS Database

Figure 2-89. Criteria pollutant monitor locations (A) and SO_2 monitor locations (B), Massachusetts, 2005. Shaded counties have at least one monitor.

The regional distribution of SO_2 and SO_4^{2-} concentrations through the CONUS are shown in Table 2-22. In and around most individual CMSAs, the trends are also toward lower SO_2 levels. Table 2-22 shows that many annual and even 1–h mean concentrations for the years 2003 through 2005 were consistently at or below the operating LOD of ~3 ppb for the standard sensitivity UV fluorescence SO_2 monitors deployed in the regulatory networks; the aggregate mean value over all 3 years and all sites in and around the CMSAs was just above the LOD at ~4 ppb, and was identical to the 1–h and 24–h means.

Table 2-22. Regional distribution of SO_2 and SO_4^{2-} ambient concentrations, averaged for 2003−05.

Region	Concentration	
	SO_2 (ppb)	SO_4^{2-} (µg/m3)
Mid-Atlantic	3.3	4.5
Midwest	2.3	3.8
Northeast	1.2	2.5
Southeast	1.3	4.1

Table 2-23. Distributions of temporal averaging inside and outside CMSAs.

Averaging Time Monitor Locations	n	Mean	Percentiles											Max
			1	5	10	25	30	50	70	75	90	95	99	
1–h Max Concentration														
Inside CMSAs	332405	13	1	1	1	3	4	7	13	16	30	45	92	714
Outside CMSAs	53417	13	1	1	1	1	2	5	10	13	31	51	116	636
1–h Avg Concentration														
Inside CMSAs	7408145	4	1	1	1	1	1	2	4	5	10	15	34	714
Outside CMSAs	1197179	4	1	1	1	1	1	2	3	3	7	13	36	636
24–h Avg Concentration														
Inside CMSAs	327918	4	1	1	1	1	2	3	5	6	10	13	23	148
Outside CMSAs	52871	4	1	1	1	1	1	2	3	4	8	12	25	123
Annual Avg Concentration														
Inside CMSAs	898	4	1	1	1	1	2	4	5	6	8	10	12	15
Outside CMSAs	143	4	1	1	1	1	2	3	4	5	8	9	13	14
Aggregate 3−yr Avg Concentration, 2003−2005														
Inside CMSAs	283	4	1	1	1	2	3	3	5	5	8	10	12	14
Outside CMSAs	42	4	1	1	1	2	2	3	4	5	8	9	13	13

* Values are ppb

** CMSA = Consolidated Metropolitan Statistical Area

To be sure, the max 1–h concentration observed at some sites in and around some CMSAs still exceeded the mean by a large margin, with max 1–h values of > 600 ppb. However, the 50th percentile maximum value outside CMSAs, 5 ppb, was only slightly greater than the 1–h, 24–h, and annual mean value, 4 ppb. The 50th percentile maximum value inside CMSAs, 7 ppb, was 75% greater than these longer-term averages, reflecting heterogeneity in source strength and location. In addition, even with 1–h max values of > 600 ppb, the maximum annualized mean value for all CMSAs was still < 16 ppb, which is below the current annual primary SO_2 NAAQS.

The strong west-to-east increasing gradient in SO_2 emissions described above is well-replicated in the observed concentrations in individual CMSAs. For example, Table 2-23 shows the mean annual concentrations from 2003–2005 for the 12 CMSAs with four or more SO_2 regulatory monitors. Values ranged from a reported low of ~1 ppb in Riverside, CA and San Francisco, CA to a high of ~12 ppb in Pittsburgh, PA and Steubenville, OH, in the highest SO_2 source region.

The Pearson correlation coefficients (r) for multiple monitors in these CMSAs were generally very low for all cities, especially at the lower end of the observed concentration ranges, and even negative at the very lowest levels on the West Coast; see Table 2-24. This reflects strong heterogeneity in SO_2 ambient concentrations even within any one CMSA. At higher concentrations, the r values were also higher. In some CMSAs, this heterogeneity may result from meteorological effects, whereby a generally well-mixed subsiding air mass containing one or more SO_2 plumes with relatively high concentration would be more uniformly spread than faster-moving plumes with lower concentrations. However, instrument error may also play a role, because the highest r values, i.e., those > 0.7, correspond to the highest SO_2 concentrations, i.e., > 6 and > 10 ppb. Since the lowest SO_2 concentrations are at or below the operating LOD, and demonstrate the lowest correlation across monitors that share at least some air mass characteristics most of the year, the unbiased instrument error in this range may be confounding interpretation of any possible correlation. This could be because the same actual ambient value would be reported by different monitors (with different error profiles) in the CMSA as different values in this lowest concentration range.

To better characterize the extent and spatiotemporal variance of SO_2 concentrations within each of the CMSAs having four or more SO_2 monitors, the means, minima, and maxima were computed from daily mean data across all available monitors for each month for the years 2003 through 2005. Because many of these CMSAs with SO_2 monitors also reported SO_4^{2-}, it is possible to compute the degree of correlation between SO_2, the emitted species, and SO_4^{2-}, the most prominent oxidized product from SO_2. SO_4^{2-} values, however, while averaged over all available data at each site are generally available at their monitoring sites on a schedule of only 1 in 3 days or 1 in 6 days. Furthermore, SO_2 and SO_4^{2-} monitors are not all co-located throughout the CMSAs. For each of the five example CMSAs in Figure 2-11 through Figure 2-15, monthly aggregated values are depicted from daily means of: (a) the monthly mean, minimum, and maximum SO_2 concentrations; b) the monthly mean, minimum and maximum SO_4^{2-} concentrations; and (c) a scatterplot of SO_2 versus SO_4^{2-} concentrations.

Table 2-24. Range of mean annual SO_2 concentrations and Pearson correlation coefficients in urban areas having at least four regulatory monitors, 2003–2005.

CMSA	(# Monitors)	Mean SO_2 Concentration (ppb)	Pearson Correlation Coefficient
Philadelphia, PA		3.6 – 5.9	0.37 – 0.84
Washington, DC		3.2 – 6.5	0.30 – 0.68
Jacksonville, FL		1.7 – 3.4	−0.03 – 0.51
Tampa, FL		2.0 – 4.6	−0.02 – 0.18
Pittsburgh, PA		6.8 – 12	0.07 – 0.77
Steubenville, OH		8.6 – 14	0.11 – 0.88
Chicago, IL		2.4 – 6.7	0.04 – 0.45
Salt Lake City, UT		2.2 – 4.1	0.01 – 0.25
Phoenix, AZ		1.6 – 2.8	−0.01 – 0.48
San Francisco, CA		1.4 – 2.8	−0.03 – 0.60
Riverside, CA		1.3 – 3.2	−0.06 – 0.15
Los Angeles, CA		1.4 – 4.9	−0.16 – 0.31

Moving across the CONUS from highest to lowest SO_2 concentrations, first consider Steubenville, OH (Figure 97), where the area of highest SO_2 concentrations of all 12 CMSAs with more than four monitors, all monthly mean SO_2 concentrations (a) were substantially < 30 ppb, though max daily means in some months were often > 60 ppb, or even > 90 ppb. SO_4^{2-} data (b) at Steubenville were insufficient to make meaningful comparisons, though the 12 months of available SO_4^{2-} data suggest no correlation with SO_2 (c).

Next, consider Philadelphia, PA (Figure 98). SO_2 in Philadelphia, PA (a) is present at roughly one-half the monthly mean concentrations in Steubenville, OH, and demonstrates a strong seasonality with SO_2 concentrations peaking in winter. By contrast, SO_4^{2-} concentrations in Philadelphia peak in the three summer seasons, with pronounced wintertime minima. This seasonal anticorrelation still contains considerable monthly scatter, however.

Los Angeles, CA (Figure 99) presents a special case, since its size and power requirements place a larger number of SO_2 emitters near it than would otherwise be expected on the West Coast. Concentrations of SO_2 demonstrate weak seasonality in these 3 years, with summertime means of ~3 to 4 ppb, and maxima generally higher than wintertime ones, though the highest means and maxima occur during the winter of 2004–2005. SO_4^{2-} at Los Angeles shows stronger seasonality, most likely because the longer summer days of sunny weather allow for additional oxidation of SO_2 to SO_4^{2-} than would be available in winter. Weak seasonal effects in SO_2 likely explain the complete lack of correlation between SO_2 and SO_4^{2-} here.

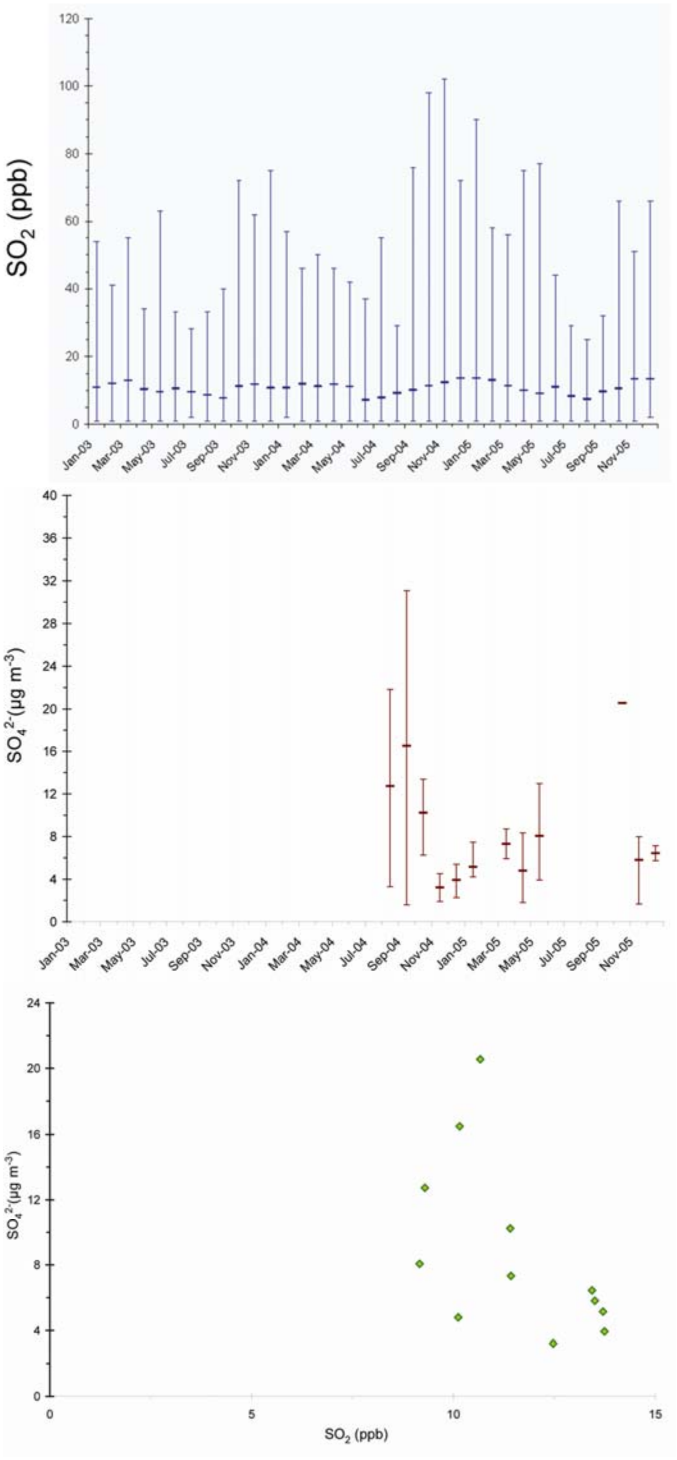


Figure 2-90. Steubenville, OH, 2003–2005. (a) Monthly mean, minimum, and maximum SO$_2$ concentrations. (b) Monthly mean, minimum, and maximum SO$_4^{2-}$ concentrations. (c) Monthly mean SO$_4^{2-}$ concentrations as a function of SO$_2$ concentrations.

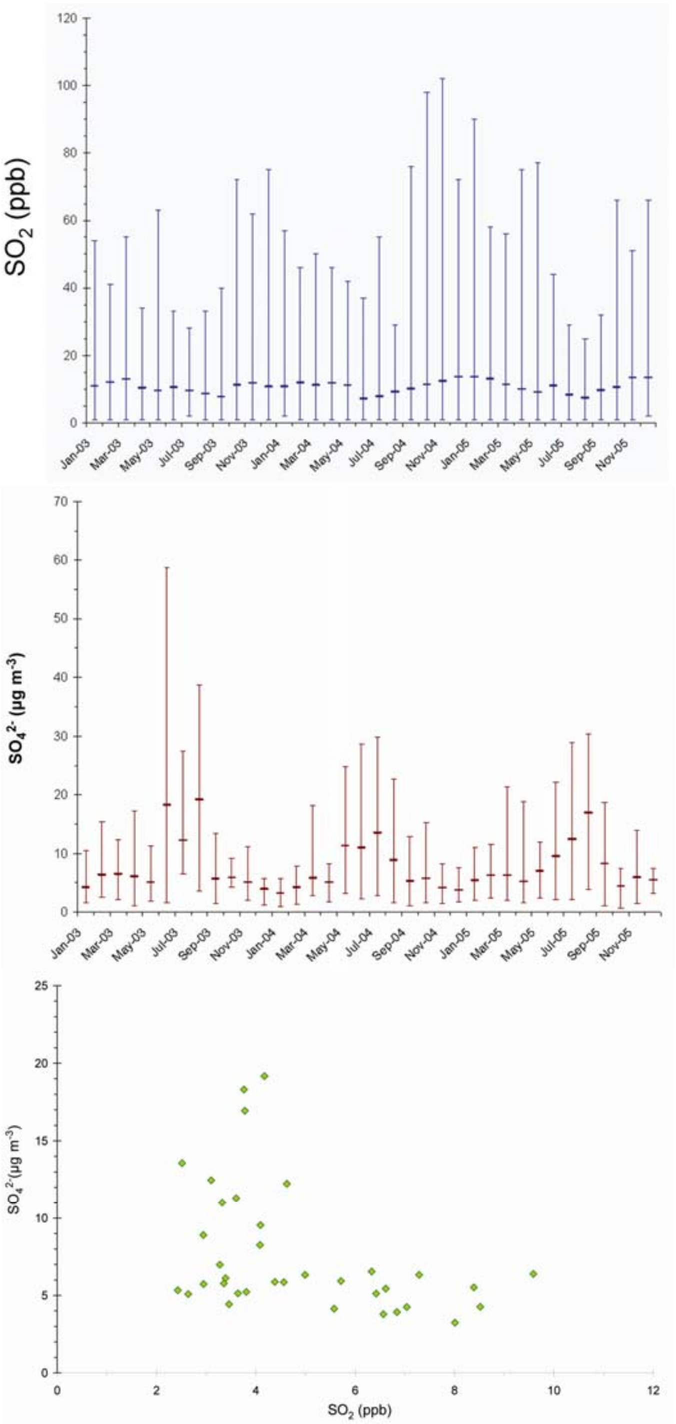


Figure 2-91. Philadelphia, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.

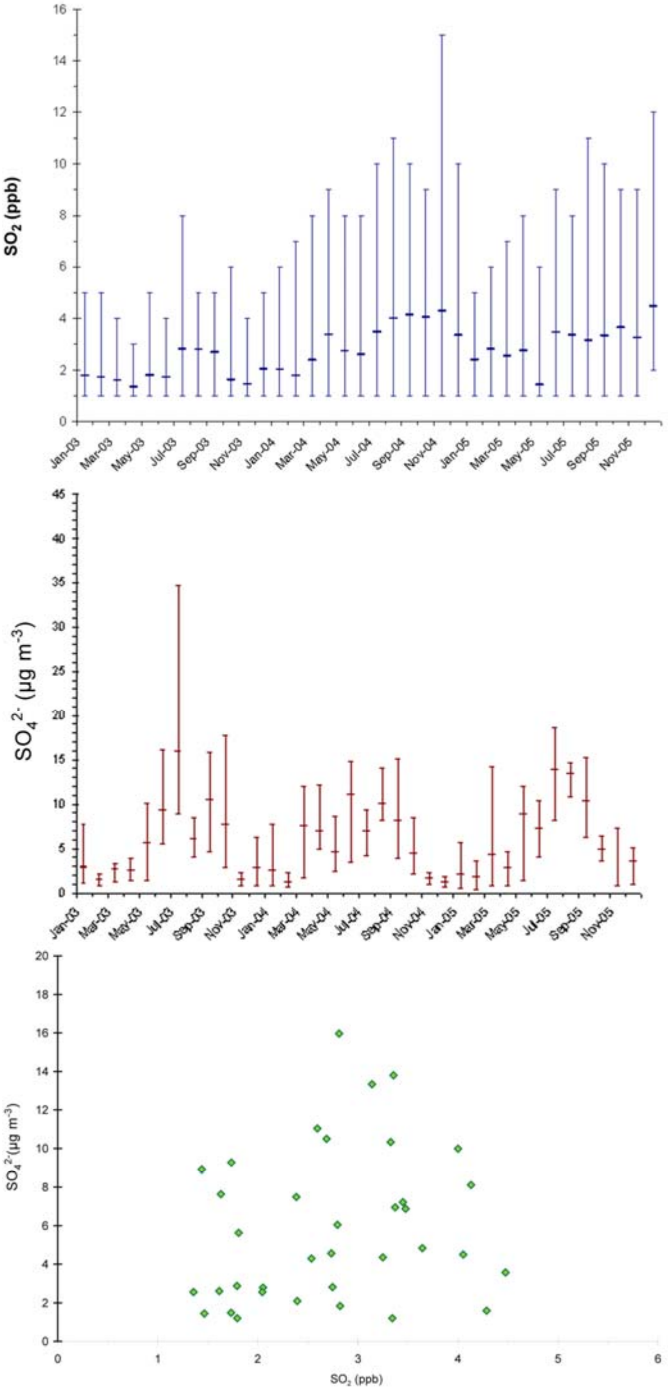


Figure 2-92. Los Angeles, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.

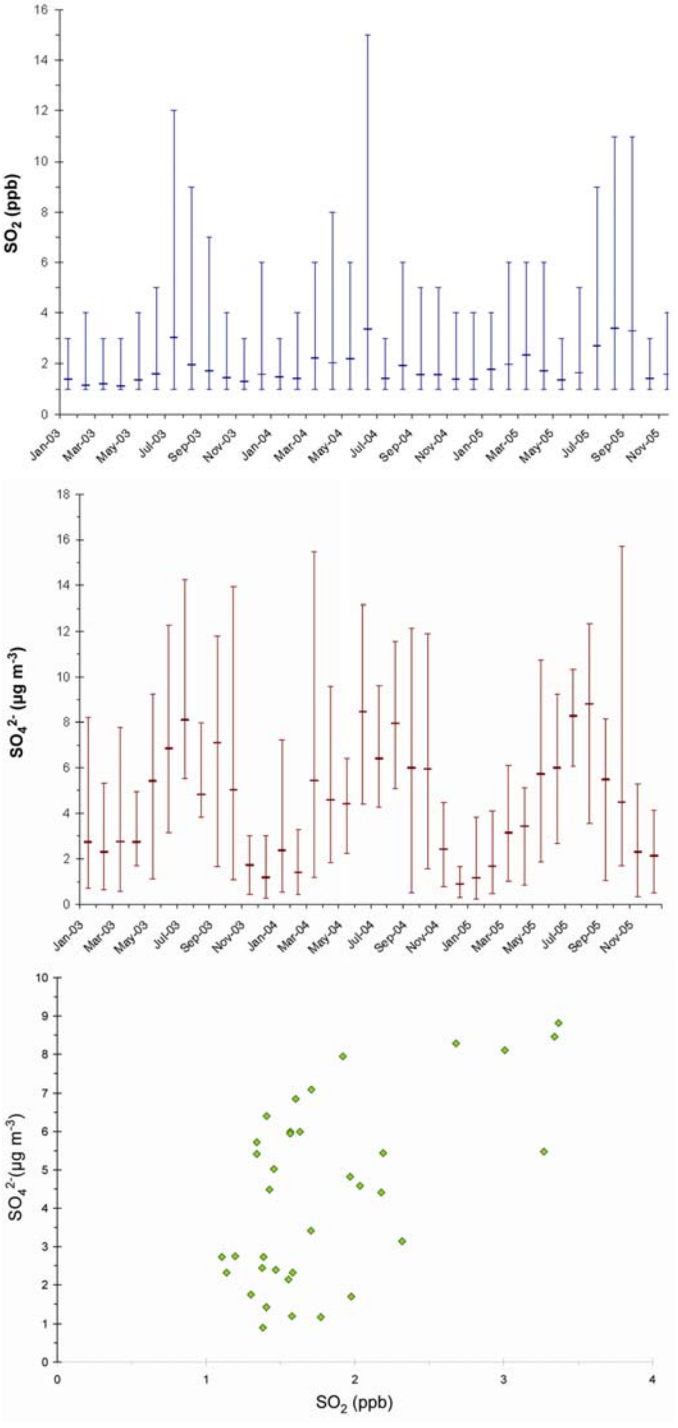


Figure 2-93. Riverside, CA, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.

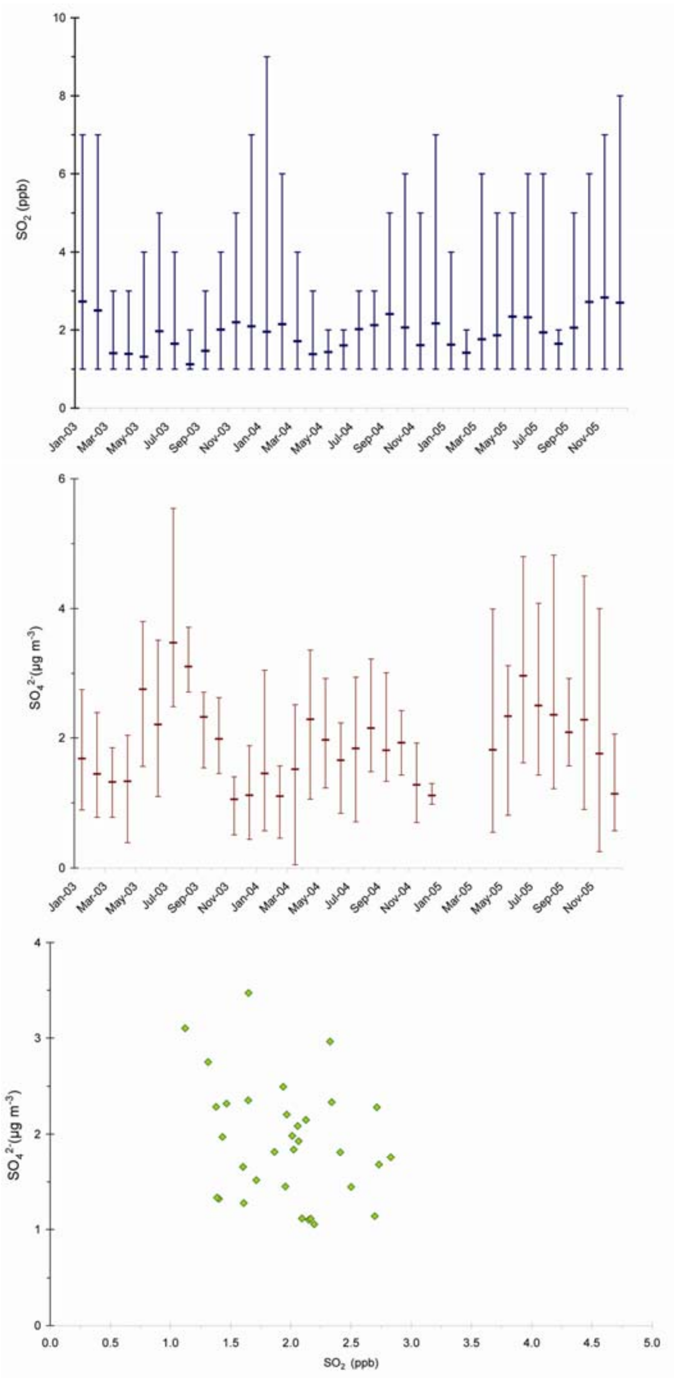


Figure 2-94. Phoenix, 2003–2005. (a) Monthly mean, minimum, and maximum SO_2 concentrations. (b) Monthly mean, minimum, and maximum SO_4^{2-} concentrations. (c) Monthly mean SO_4^{2-} concentrations as a function of SO_2 concentrations.

The Riverside, CA CMSA (Figure 100) presents the strongest example among the 12 examined for this study of correlation between SO_2 and SO_4^{2-}, though even here the R2 value is merely 0.3. Seasonal peaks are obvious in summertime for SO_2 and SO_4^{2-}, both at roughly one-half the ambient concentrations seen in Los Angeles. This is very likely due to Riverside's geographic location just downwind of the regionally large electric generating utility sources near Los Angeles and the prevailing westerly winds in summer. Again, as with Los Angeles, the summertime peaks in SO_4^{2-} are most likely due to the combination of peaking SO_2 and favorable meteorological conditions allowing more complete oxidation.

Phoenix, AZ was the CMSA with the lowest monthly mean SO_2 and SO_4^{2-} concentrations examined here (Figure 100). In Phoenix, nearly all monthly mean SO_2 values were at or below the regulatory monitors' operating LOD of ~3 ppb. SO_4^{2-} concentrations were equivalently low, roughly one-half the concentrations seen in Riverside, CA, for example. The monthly mean data show strong summertime peaks for even these very low-level SO_4^{2-} observations, which, at ~1 to 3 μg/m^3, were generally one-half of those in Philadelphia. This suggests some seasonality in SO_2, though anticorrelated with SO_4^{2-}; however, the trend is very weak, as the correlation scatterplot shows.

2.9.6.2. SO_2 and SO_4^{2-} in rural and remote areas

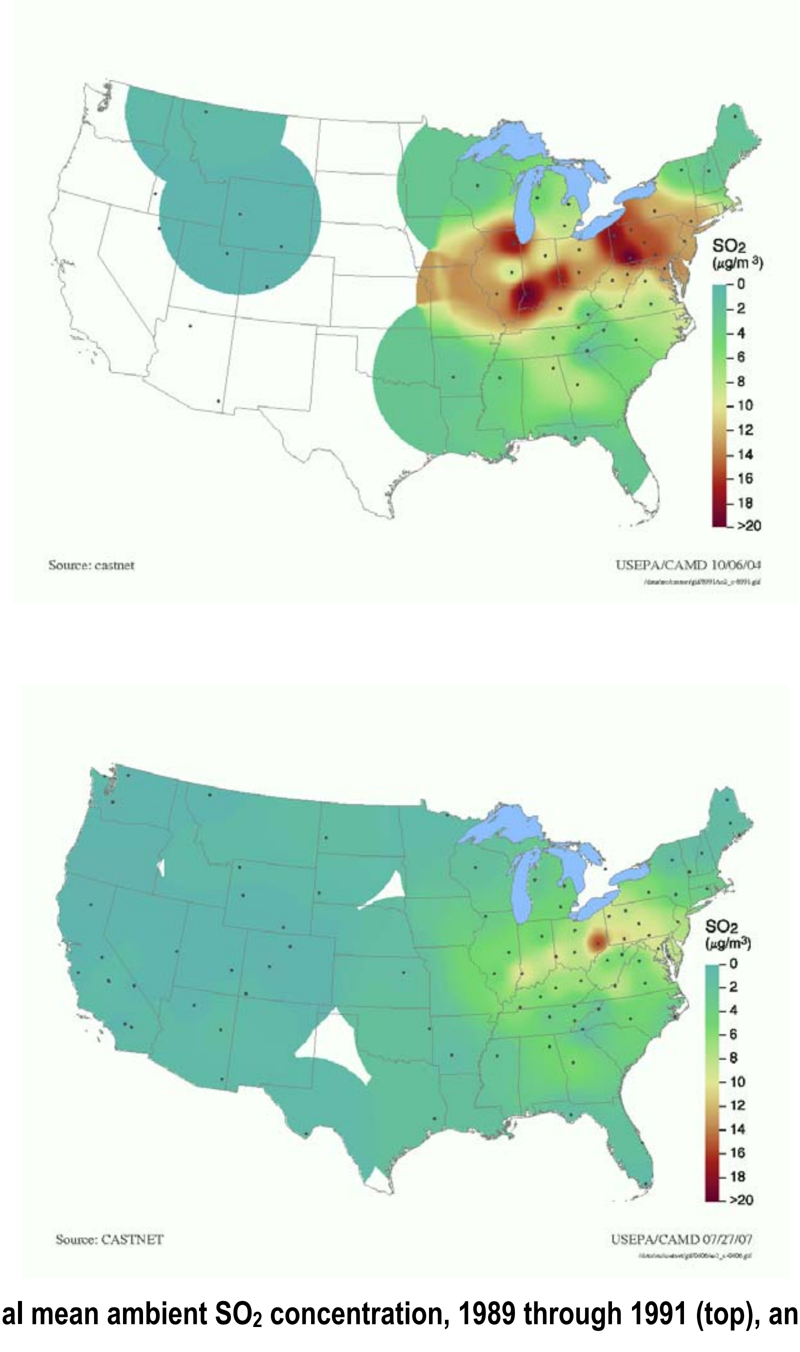
The mean annual concentrations of SO_2 and SO_4^{2-} from CASTNet's long-term monitoring sites can be compared using two 3−year periods, 1989–1991 and 2003−2005, shown in Figure 101 for SO_2 and Figure 102 for SO_4^{2-}.

From 1989 through 1991 the highest ambient mean concentrations of SO_2 and SO_4^{2-} were observed in western Pennsylvania and along the Ohio River Valley: > 20 μg/m3 (~8 ppb) SO_2 and > 15 μg/m^3 SO_4^{2-}. As with SO_2, in the years since the ARP controls were enacted, both the magnitude of SO_4^{2-} concentrations and their areal extent have been significantly reduced, with the largest decreases again along the Ohio River Valley.

The IMPROVE network monitors the major fine particle components including SO_4^{2-}, NO_3, crustal, elemental, and organic carbon plus coarse mass concentration defined as PM_{10} minus $PM_{2.5}$. An implicit assumption is that most of the pSO_4 is present as $(NH_4)_2SO_4$. Much of the information contained below is based on particulate elemental S used to infer the $(NH_4)_2SO_4$ levels. A discussion of IMPROVE S-to-pSO_4 history and trends is available (Eldred, 2001). As with data from IMPROVE used above for pNO_3, and except where noted, information in this section was derived form the IMPROVE IV Report (DeBell, 2006) with data displays created with data and tools available at http://vista.cira.colostate.edu/views/. Much of these data and conclusions are also to appear in Pitchford et al., 2008.

One component of the Big Bend Regional Aerosol and Visibility Observational (BRAVO) Study, conducted at Big Bend National Park, TX in the summer and fall of 1999, entailed use of detailed measurements of aerosol chemical composition, size distribution, water growth, and optical properties to characterize the aerosol and assess the relationship between aerosol physical, chemical, and optical properties. (Schichtel, et al., 2004). Fine-mode ammoniated pSO_4 during the BRAVO Study was ~50% of the fine particle mass concentration.

In contrasts to results seen for pNO_3, additional monitoring sites in the U.S. midwestern states produced no surprises for $(NH_4)_2SO_4$ or areal extent. Figure 103 shows highest $(NH_4)_2SO_4$ concentrations in the mid-Atlantic and upper southern U.S. states where annual concentrations ranged from ~3 µg/m^3 to ~6 µg/m^3. The $(NH_4)_2SO_4$ concentrations in most western U.S. states was <~1 µg/m^3.



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Source: CASTNET
USEPA/CAMD 07/27/07

Figure 2-95. Annual mean ambient SO_2 concentration, 1989 through 1991 (top), and 2003 through 2005 (bottom).

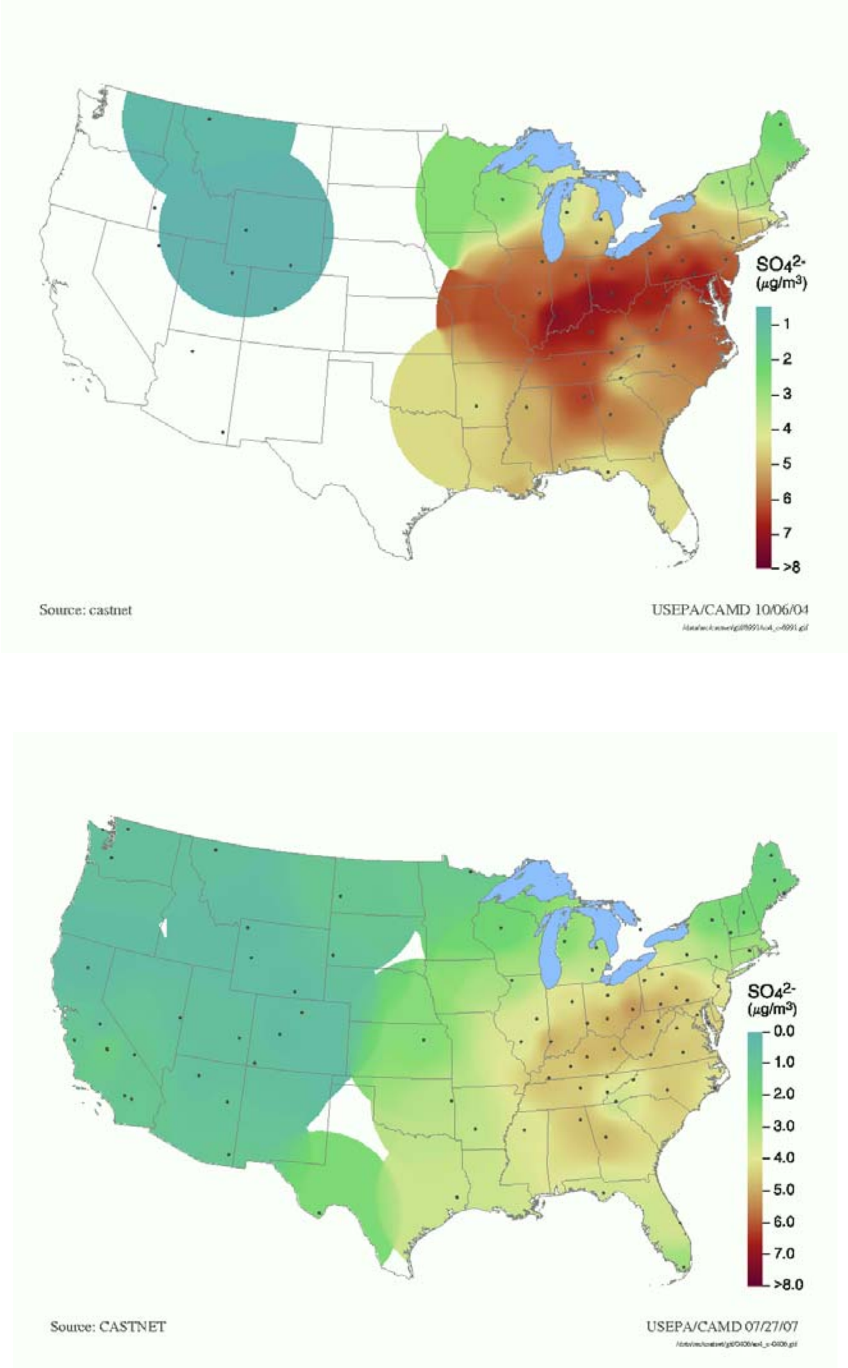


Figure 2-96. Annual mean ambient SO_4^{2-} concentration, 1989 through 1991 (top), and 2003 through 2005 (bottom).

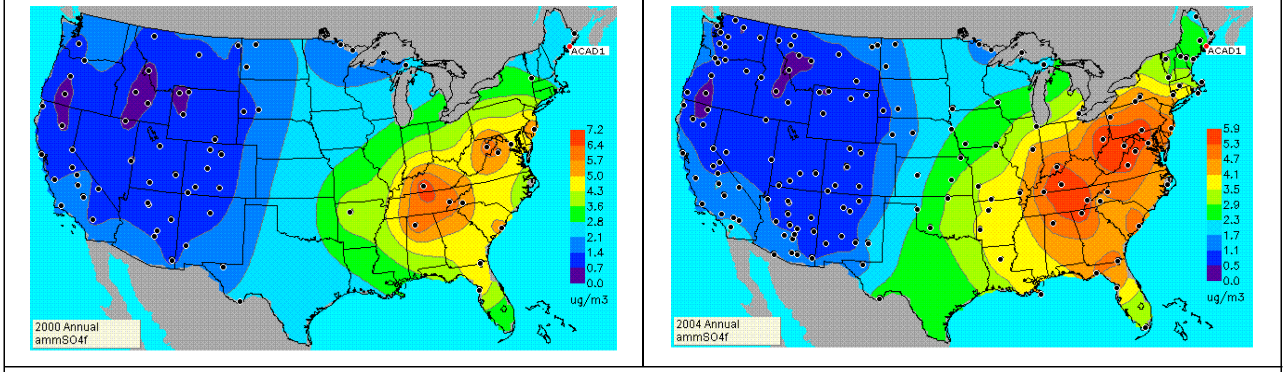


Figure 2-97. IMPROVE network measured annual averaged pSO_4 concentration for 2000 (top) and for 2004 (bottom). Note difference in scale.

Combining IMPROVE and CSN data makes possible comparison of urban pSO_4 to surrounding remote-area regional values. These are shown as paired color contours maps for IMPROVE and IMPROVE plus CSN in Figure 104. EPA (2004b) used the pairing of IMPROVE and CSN monitoring sites at 13 selected areas to separate local and regional contributions to the major contributors of $PM_{2.5}$, as shown for pSO_4 in Figure 105.

As shown in Figures 104 and 105, annual-averaged urban pSO_4 were in general not significantly greater than the regional values, with urban excess pSO_4 generally <~0.5 µg/m^3. Exceptions to the general case appear in Texas and Louisiana where urban excess pSO_4 were >1µg/m^3. Urban contributions were a larger fraction of the total pSO_4 in western U.S. states because the regional levels were much lower there than in eastern ones The modest additional pSO_4 associated with urban areas suggests that most pSO_4 is a regionally distributed pollutant, and that IMPROVE and CSN monitoring sites can be used together to enhance our ability to delineate pSO_4 spatial distributions. Note, for example, that the additional data from urban sites shown in Figure 105 extends to the north and south of the high pSO_4 loading shown in Figure 104 over Tennessee and Kentucky, as well as the high loadings over southern PA, eastern WV, and northern VA. The small area decrease in pSO_4 evident on these maps between the two eastern high concentrations regions may not be real, but cannot be verified without speciation monitoring sites in southern OH, KY, WV, and VA. U.S. EPA (2004b) estimates of the contribution of local sources to pSO_4 were made for the same cities included for pNO_3 shown above; see Figure 106. The east-west divide in both concentration and the regional contribution to pSO_4 is strongly apparent here.

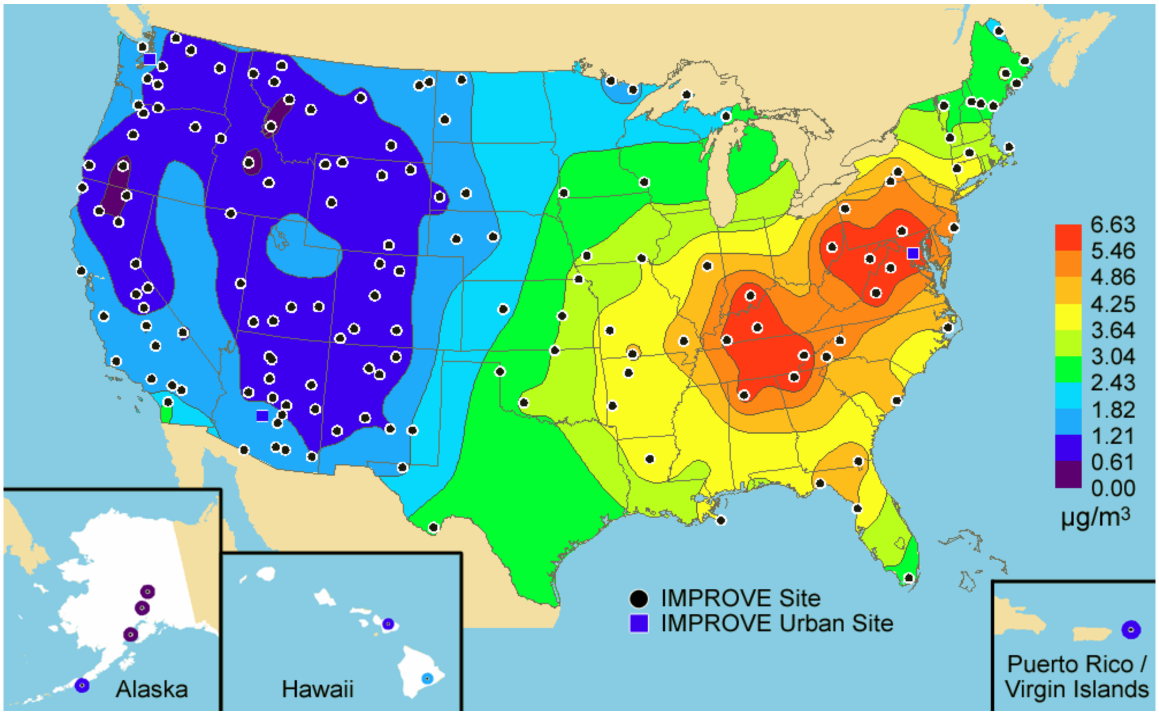


Figure 2-98. IMPROVE mean ammonium SO_4^{2-} concentrations for 2000 through 2004.

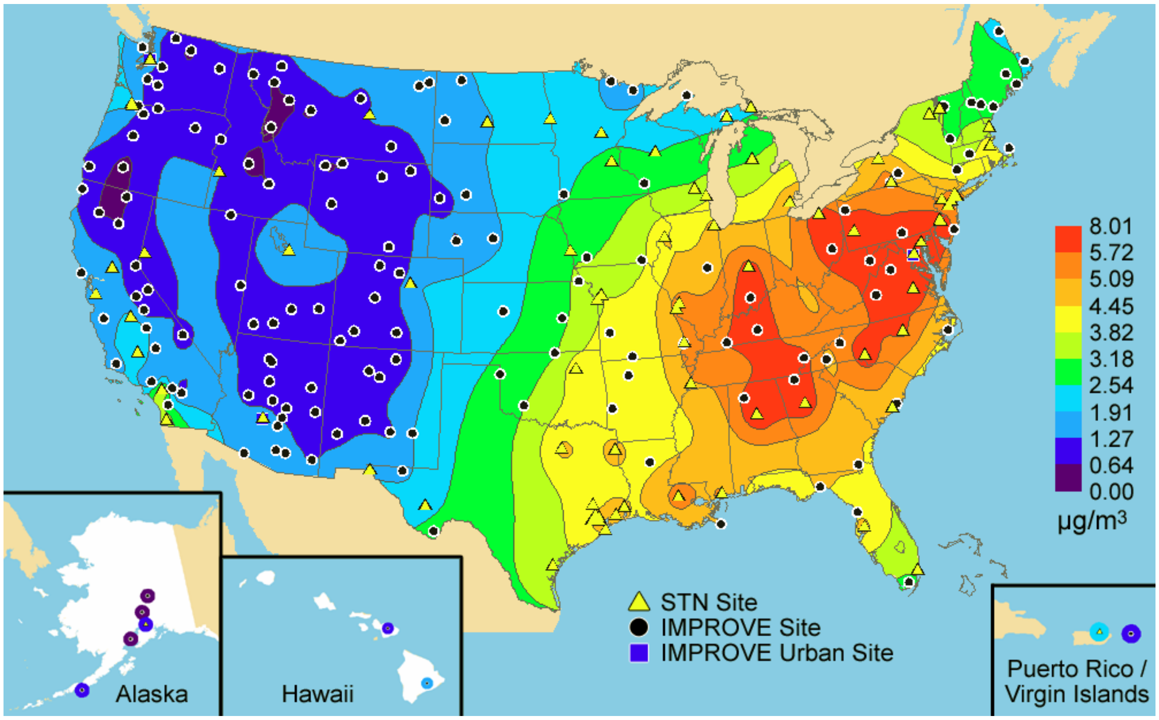
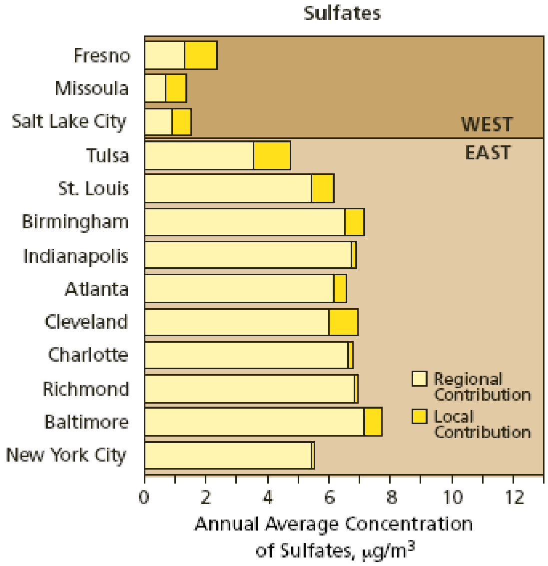


Figure 2-99. IMPROVE and CSN (labeled STN) monitored mean ammonium SO_4^{2-} concentrations for 2000 through 2004.



Source: From EPA, 2004b.

Figure 2-100. Regional and local contributions to annual average $PM_{2.5}$ by pSO_4 for select urban areas based on paired IMPROVE and CSN monitoring sites.

Source attribution of the pSO_4 contribution to haze at Big Bend NP, TX was a primary motivation for the BRAVO Study. Schichtel, et al. (2005) showed that during the four-month field monitoring study (July through October, 1999) SO_2 emissions sources in the U.S. and Mexico were responsible for ~55% and ~38% of the pSO_4 respectively. Among U.S. source regions, TX was responsible for ~16%, Eastern U.S. ~ 30%, and the Western U.S. ~9%. A large coal fired power plant, the Carbón facility in Mexico just south of Eagle Pass, TX was responsible for about ~19%, making it the largest single contributor.

Modeling for a three day pollution episode in September 1996 in the California South Coast Air Basin (SCAB) and for another episode in January 1996 in the Jan Joaquin Valley (SJV) by Ying and Kleeman (2006) has shown ~80% of pSO_4 for both regions are derived from upwind sources, with most of the remaining local contributions associated with diesel and high-sulfur fuel combustion. Kleeman, et al. (1999) using a combination of measurements and modeling showed that the upwind pSO_4 source region for the SCAB was over the Pacific Ocean, and this was confirmed by measurements on Santa Catalina Island. Moreover, these particles subsequently grew with accumulation of additional secondary aerosol material, principally NH_3NO_3 as they traversed the SCAB. The majority of the HNO_3 that forms pNO_3 in the SCAB is from diesel and gasoline combustion (~63%), while much of the NH_3 is from agricultural sources (~40%) and catalyst equipped gasoline combustion (~16%) and upwind sources (~18%). In the SJV most of the HNO_3 that forms pNO_3 is from upwind sources (~57%) with diesel and gasoline combustion contributing most of the rest (30%), while much of the NH_3 is from upwind sources (~39%) and a combination of area, soil and fertilizer sources (~52%).

Using a regression analysis to find the dependence of pSO_4 concentration measured over a three year period (2000–2002) at 84 western IMPROVE monitoring sites on the modeled transport trajectories to the sites for each sample period, Xu et al. (2006) were able to infer the source regions that supplied pSO_4 in the Western U.S. Among the source regions included in this analysis is the near-coastal Pacific Ocean (i.e. a 300 km zone off the coast of California, Oregon, and Washington states). Up to 50% of the pSO_4 measured at Southern California monitoring sites is associated with this source region. As shown in Figure 107 the zone of impact from this source region includes large regions of California, Arizona, and Nevada. The authors make the case that high S content fuel used in marine shipping and port emissions may be largely responsible. As a result, the Western Regional Air Partnership (WRAP) RPO emissions inventory was modified to include marine shipping and a Pacific Offshore source region was added to source attribution by air quality simulation modeling.

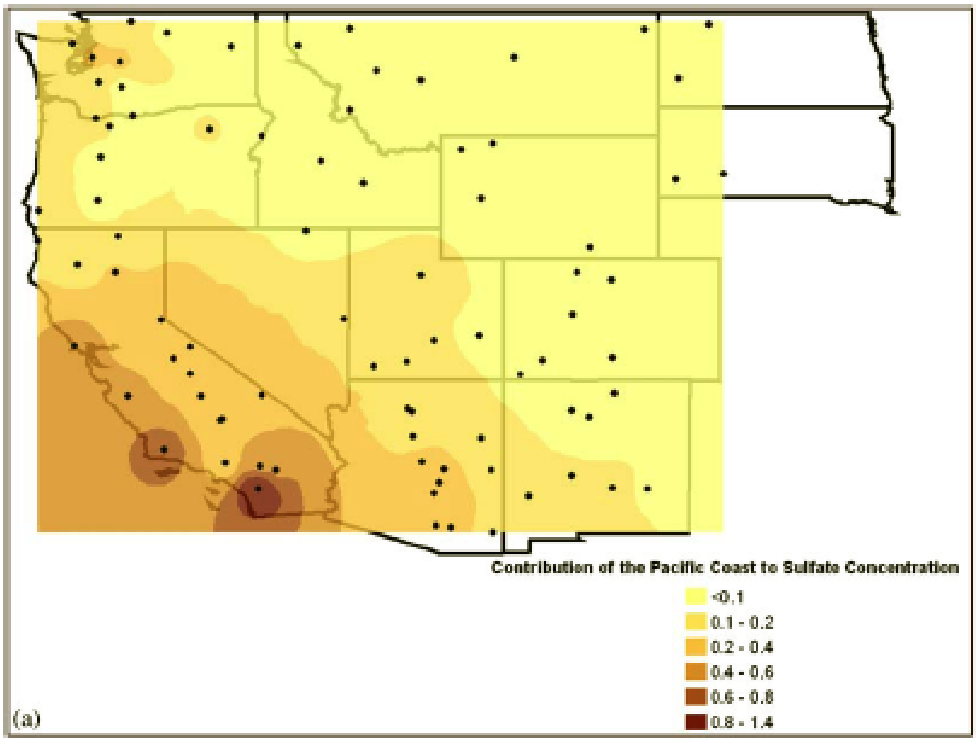


Figure 2-101. Contributions of the Pacific Coast area to the $(NH_4)_2SO_4$ (µg/m³) at 84 remote-area monitoring sites in Western U.S. based on trajectory regression (dots denote locations of the IMPROVE aerosol monitoring sites). From Xu, et al. (2006).

The SO_4^{2-} attribution results of the WRAP air quality modeling (available from http://wrapair.org) are largely in line with these empirical results, finding that the Pacific Offshore source region contributed somewhat smaller amounts than reported by Xu et al.,(2006) with concentrations at the peak impact site in California of ~45% compared to 50% by the regression analyses and even greater differences for more distant monitoring sites.

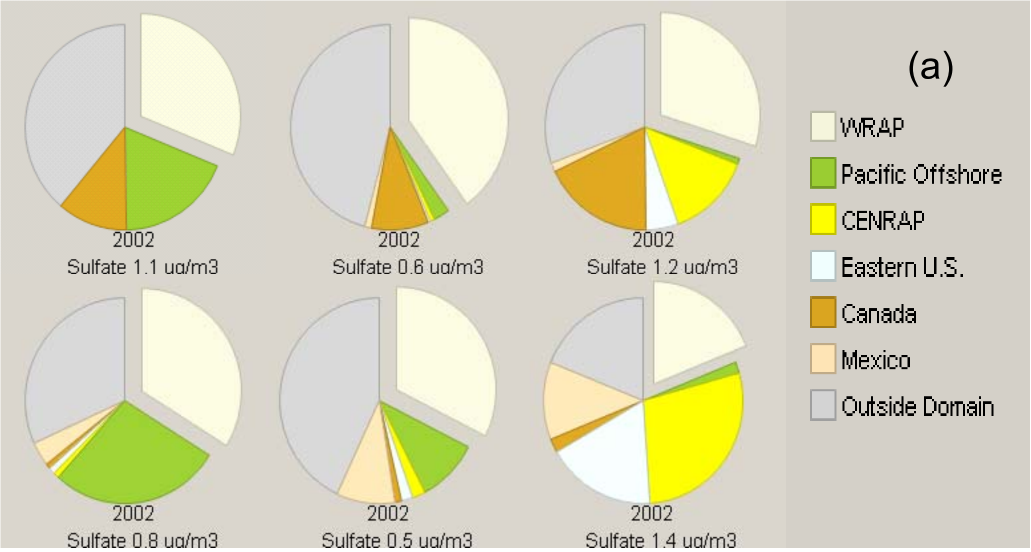
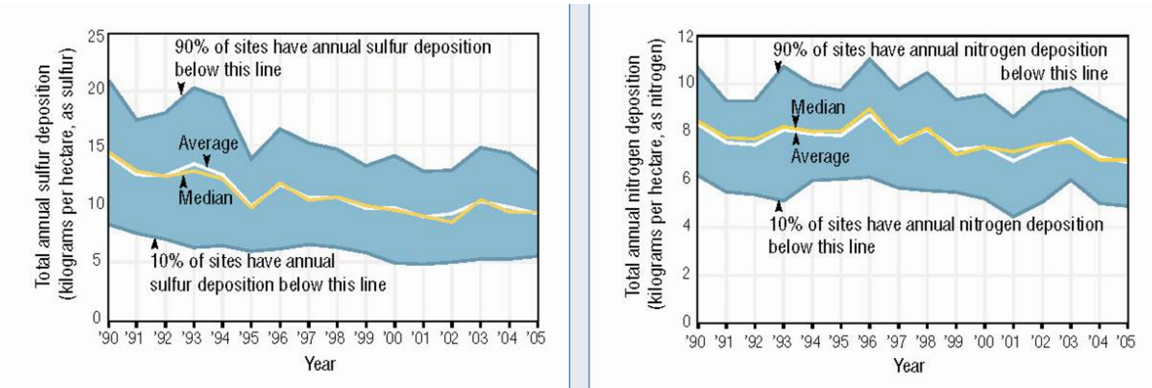


Figure 2-102. pSO_4 source attribution by region using CAMx modeling for six western remote area monitoring sites. Top left to right Olympic NP, WA; Yellowstone NP, WY; Badlands NP, SD; bottom left to right San Gorgonio W, CA; Grand Canyon NP, AZ; and Salt Creek W, NM. WRAP includes ND, SD, WY, CO, NM and all states further west. CENRAP includes all states east of WRAP and west of the Mississippi River including MN. Eastern U.S. includes all states east of CENRAP. The Pacific Offshore extends 300km to the west of CA, OR, and WA. Outside Domain refers to the modeling domain, which extend hundreds of kilometer into the Pacific and Atlantic Oceans and from Hudson Bay Canada to just north of Mexico City.

Several example monitoring locations distributed across the northern and southern portions of the Western U.S. have been selected to illustrate the attribution results from the WRAP air quality simulation modeling by source region and source type for pSO_4. They include Olympic National Park (NP), WA; Yellowstone NP, WY; and Badlands NP, SD across the north, and San Gorgonio Wilderness (W), CA; Grand Canyon NP, AZ and Salt Creek W, NM across the south. Pie diagrams of the pSO_4 attribution results by source region for each of these sites are shown in Figure 108. Based on these sites, >50% of the pSO_4 in remote areas of the Pacific coastal states is from outside of the U.S. (Pacific Offshore and Outside of the Domain). The Outside of the Domain values are derived by simulating the fate of the boundary condition concentrations, which for the WRAP air quality modeling were obtained using output from the GEOS-CHEM global air quality model (Fiore, 2003). The pSO_4 fraction from the region labeled Outside of Domain is approximately uniform throughout the western U.S. with site-to-site variation in the fraction mostly caused by the variations in the total SO_4^{2-} concentration. The more northerly sites have effects from Canadian emissions, while the southern sites have impacts from Mexican emissions. Half of the Salt Creek, NM, pSO_4 is from the domestic source emissions further to the east (CENRAP and Eastern U.S.), which also contribute about 20% to Badland pSO_4 concentrations. A breakout of the emission sources from within the WRAP region by source type (not shown) has most of the emissions from point sources, with the combination of motor vehicle, area and wildfire emissions contributing from a few percent at the furthest eastern sites to about half at San Gorgonio.

2.10. Deposition of N and S Species

As established in Sections 2.2 and 2.3 above, total emissions of NO_X and SO_X have decreased substantially in the last 35 years. Between 1970 and 2005, NO_X emissions fell from 26.9 million tons per year (Mt/yr) to 19 Mt/yr, and SO_2 emissions fell from 31.2 to 15 Mt/yr. These decreases in emissions led to correlative decreases in N and S concentrations, described just above in Section 2.9, and in atmospheric deposition of N and S species across the landscape; see the trends summarized in Figure 109. Importantly, however, these very recent decreases in deposition still leave current deposition amounts which are a factor of 2 greater than in pre-industrial times for NO_3 and NH_4, and a factor of 5 greater for SO_4^{2-}, according to modeling experiments by Luo et al. (2007).



[a]**Coverage:** 34 monitoring sites in the eastern United States.
Data source: *MACTEC Engineering and Consulting, Inc., 2006*

[a]**Coverage:** 34 monitoring sites in the eastern United States.
Data source: *MACTEC Engineering and Consulting, Inc., 2006*

Figure 2-103. Trends, 1990–2005 in S (left) and N (right) deposition for 34 sites in the eastern U.S.

Deposition maps were developed by CASTNET to show the composition of dry deposition for N and S. The maps are labeled with inferred total deposition at each site, and a pie chart showing the relative proportion of wet and dry deposition or the chemical components of the deposition. Wet deposition is estimated from the interpolated concentration as measured by the NADP multiplied by the measured rainfall at the site. Dry deposition is inferred from the measured ambient air concentrations of the chemical multiplied by the dry deposition rate obtained from an inferential model of linked resistances to derive species and location-dependent V_d. (See the CASTNET QAPP for more information on methods of computing their deposition totals). Note that NH_3 is not included in these total N estimates because it is not currently measured in these networks.

Data in this section are presented to show deposition across the landscape; finer-scale data and maps of sensitive and vulnerable regions and ecosystems are presented in other sections. Data presented in the maps and charts represent 3-yr averages. For example, "89–91" is the average total deposition of 1989, 1990, and 1991 for a given site. Only sites having valid total deposition for at least two of the three years are shown and in some instances, sites only met this criterion for one of the two reporting periods. Because of differences like these, direct site-by-site comparisons are not possible everywhere.

2.10.1. Nitrogen

For the years 2004–2006, mean N deposition was greatest in the Ohio River basin, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg/ha/yr, respectively; see Figure 110. Recent work by Elliott et al. (2007) using $\delta^{15}N$ to trace deposition totals and isolate them to point to mobile source type shows that for 33 NADP/NTN sites, in the East and Upper Midwest, spatial distributions $\delta^{15}N$ concentrations were strongly correlated with NO_X emissions from point sources, and that wet NO_3-deposition at the 33 sites considered was strongly associated with NO_X emissions from the surrounding point sources. N deposition is lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg/ha/yr, respectively. N deposition is generally much lower in the western U.S., where it is highest in urban areas in southern California and Denver, 4.8 and 3.3 kg ha/yr, respectively. It should be noted, however, that large portions of the U.S. west of the Mississippi River are poorly covered by the current deposition monitoring networks as the location icons on these maps make clear. Hence, the actual degree of heterogeneity and magnitude of real deposition in much of the West is largely unknown.

Because NO_X emissions decreased by ~25% between 1990 and 2005, recent N deposition is lower compared with average deposition for the years 1989 to 1991. For 1989 to 1991, several recording stations in the Ohio River basin reported average annual deposition rates in excess of 10 kg ha/yr. Data are lacking, however, for much of the central and western U.S. and little can be said for changes between the two reporting periods in these areas for the reasons given above. The greatest mass of N deposition primarily occurred as wet NO_3^- and NH_4^+, followed in importance by dry HNO_3, dry NH_4^+, and dry NO_3; see Figure 111. Although most deposition for both reporting periods occurred as wet deposition, there were some exceptions, including parts of California where N deposition was primarily dry.

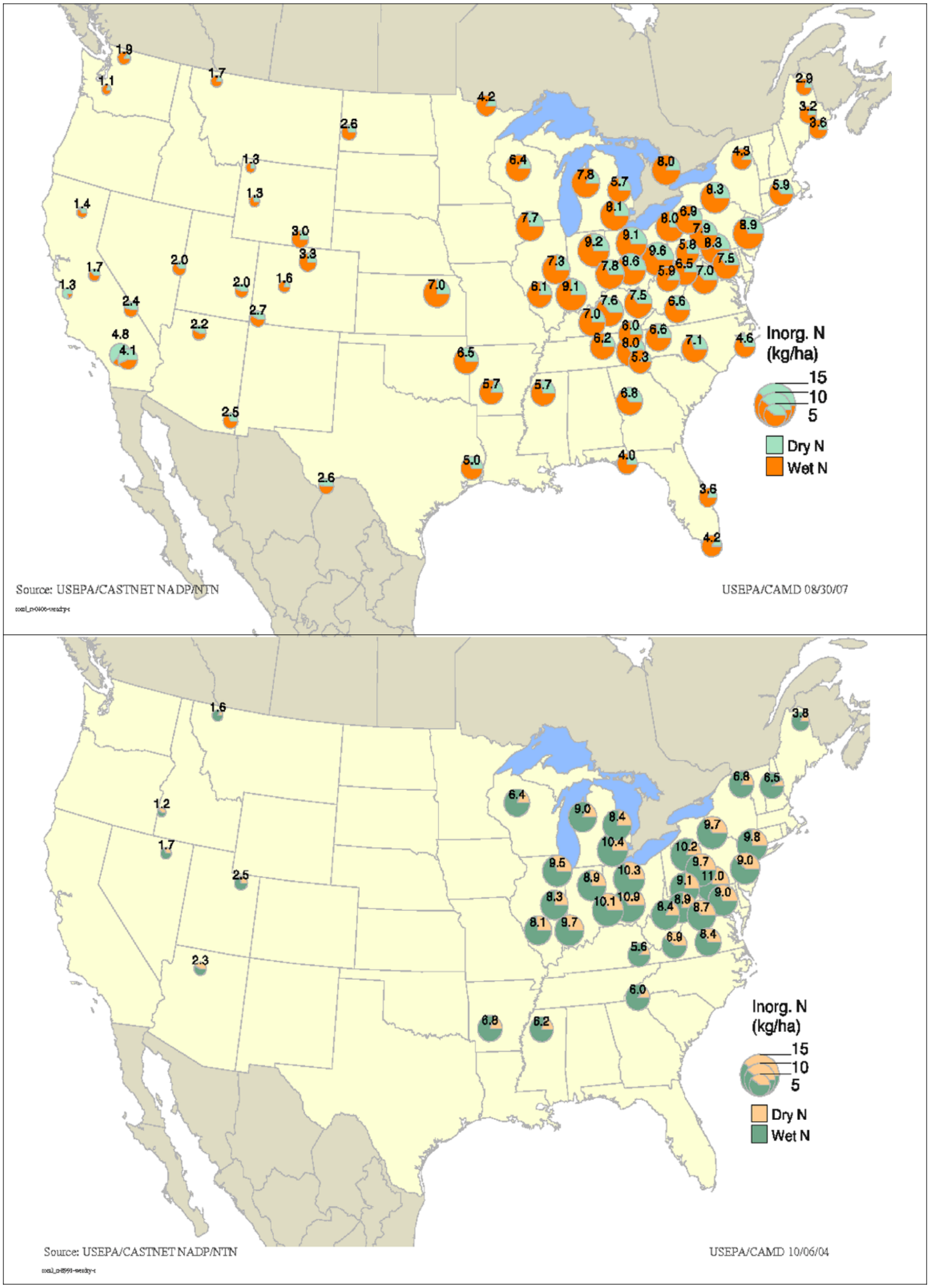
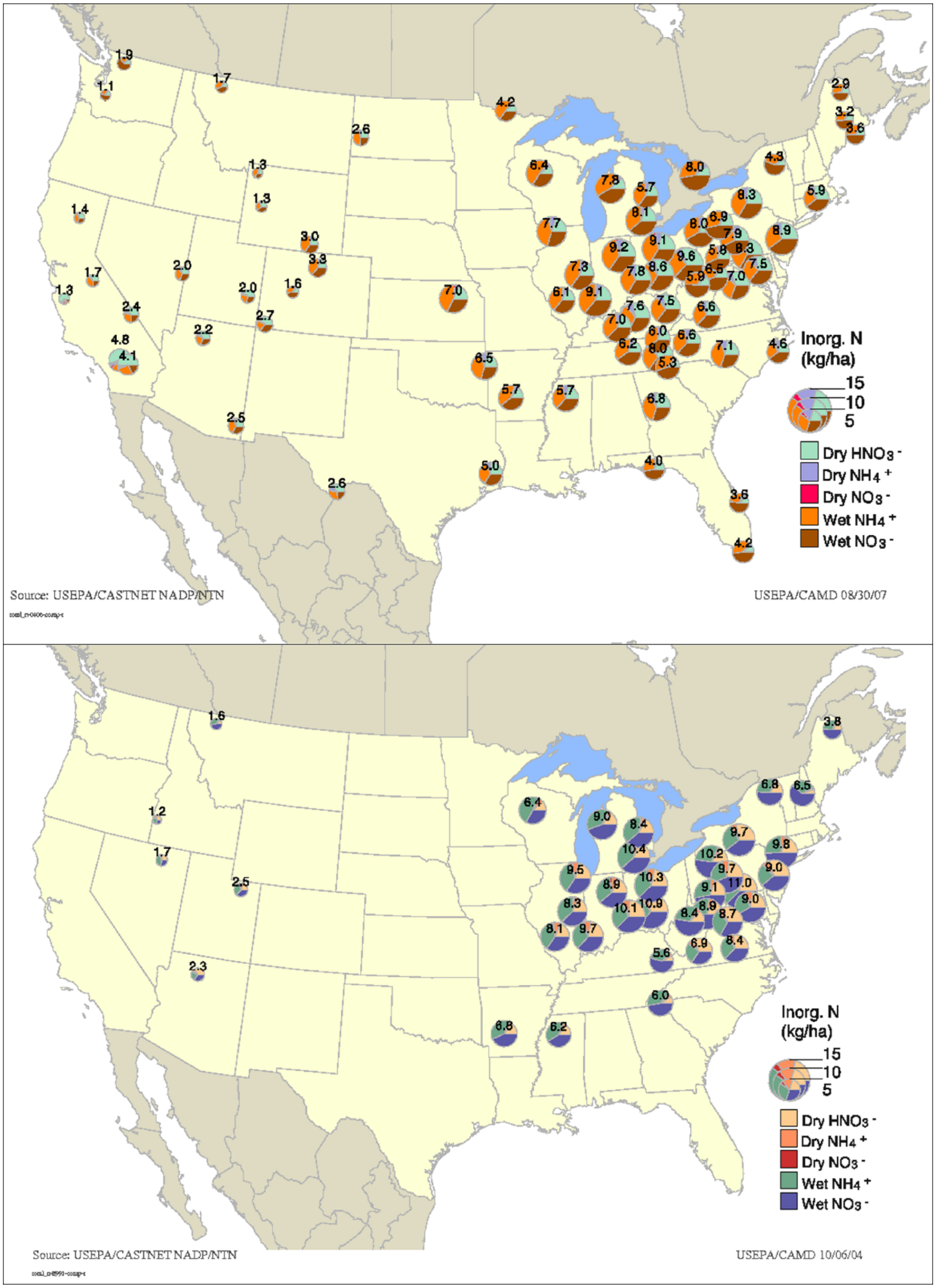


Figure 2-104. Total average yearly wet and dry inorganic N deposition, excepting NH_3, for 2004–2006 (top) and 1989–1991 (bottom).



Source: USEPA/CASTNET NADP/NTN

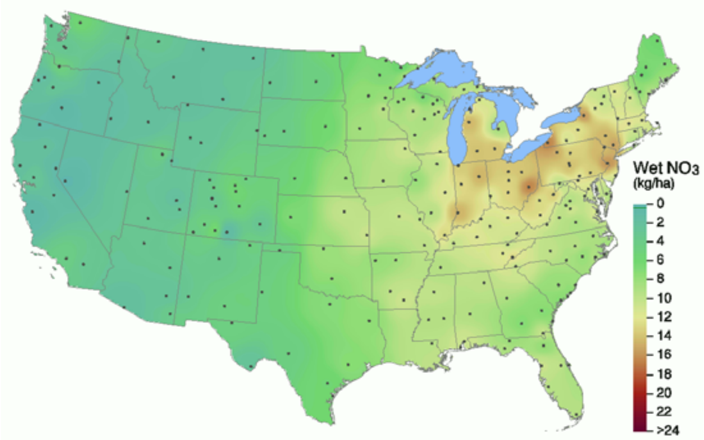
USEPA/CAMD 08/30/07

Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 10/06/04

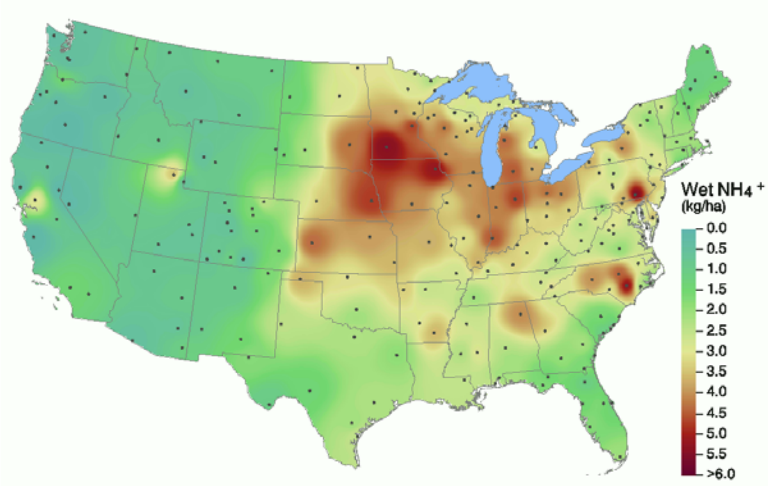
Figure 2-105. Total average yearly inorganic nitrogen deposition by species, excepting NH_3, for 2004–2006 (top) and 1989–1991 (bottom).

Figure 2-104 and Figure 2-105 show maps of wet deposition from NADP's data and IDW interpolation technique. NO_3 concentration and wet deposition amounts track dry deposition in locations where the two monitoring networks overlap. Thus NO_3 ambient concentration and deposition are highest in the upper Ohio River Valley, excepting the significant large pNO_3 deposition in excess of 6 kg/ha/yr where NADP has a substantial number of monitors, CASTNet does not; see the description of the middle-west NO_3 "bulge" in Section 2.9.5.2.



Source: NADP, USEPA, CAMD 7/19/07

Figure 2-106. NO_3^- concentration in NADP wet deposition samples, 2004–2006.



Source: NADP, USEPA, CAMD 7/19/07

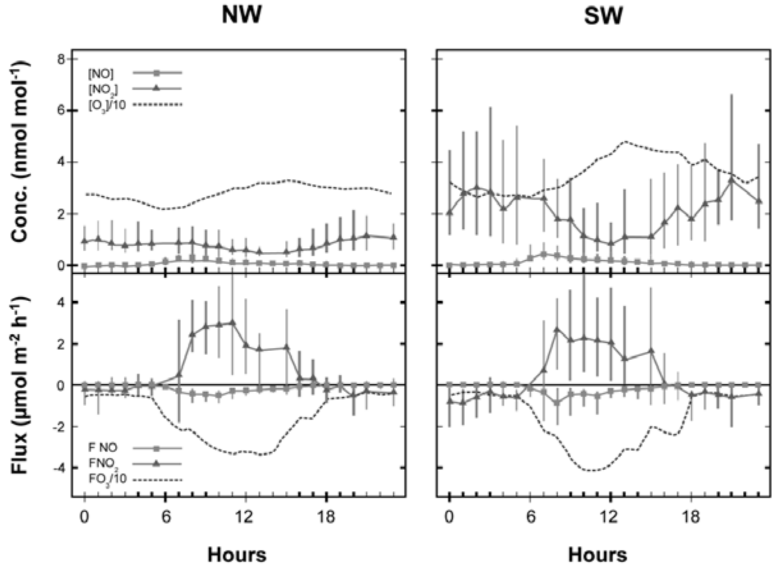
Figure 2-107. Average NO_3^- concentration in NADP wet deposition samples, 2004–2006.

2.10.1.1. Example of NO_2 and HNO_3 Deposition and Flux Data from Harvard Forest

Harvard Forest is a rural site in central Massachusetts, where ambient NO_X, NO_Y, and other pollutant concentrations and fluxes of total NO_Y have been measured since 1990 (Munger, 1996).

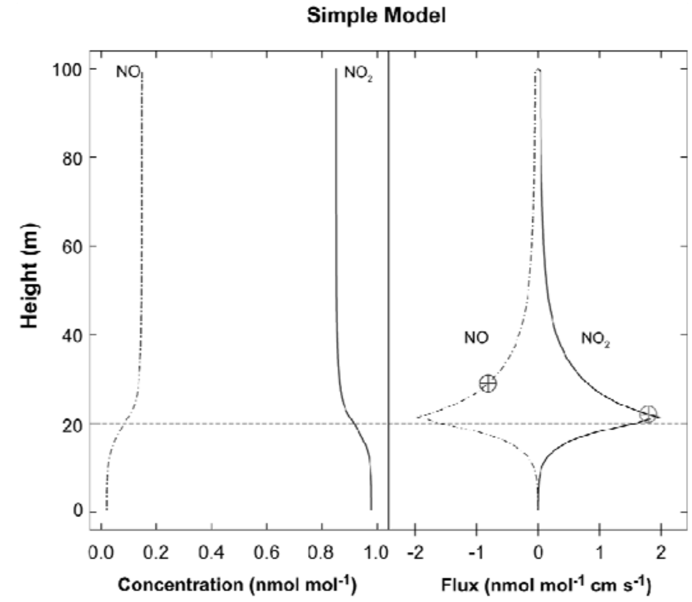
An intensive study in 2000 used a TDLAS to measure NO_2 and HNO_3 Absolute concentrations of HNO_3 were measured, and the flux inferred based on the dry deposition inferential method that uses momentum flux measurements to compute a V_d and derives an inferred flux (Wesely, 1977; Hicks, 1987). Direct eddy covariance calculations for HNO_3 were not possible because the atmospheric variations were attenuated by interaction with the inlet walls despite very short residence time and use of fluorinated silane coatings to make the inlet walls more hydrophobic. NO response was adequate to allow both concentration and eddy covariance flux determination. Simultaneously, NO and NO_Y eddy covariance fluxes were determined with two separate O_3 CL detectors, one equipped with a H_{2-}gold catalyst at the inlet to convert all oxidized N compounds to NO. Additionally, the measurements include concentration gradients for NO, NO_2, and O_3 over several annual cycles to examine their vertical profiles in the forest canopy.

Overall, the results show typical NO_2 concentrations of 1 ppb under clean-air conditions and mean concentrations up to 3 ppb at night and 1 ppb during daytime for polluted conditions. Net positive fluxes (emission) of NO_2 were evident in the daytime and negative fluxes (deposition) were observed at night (Figure 114). NO fluxes were negative during the daytime and near zero at night.



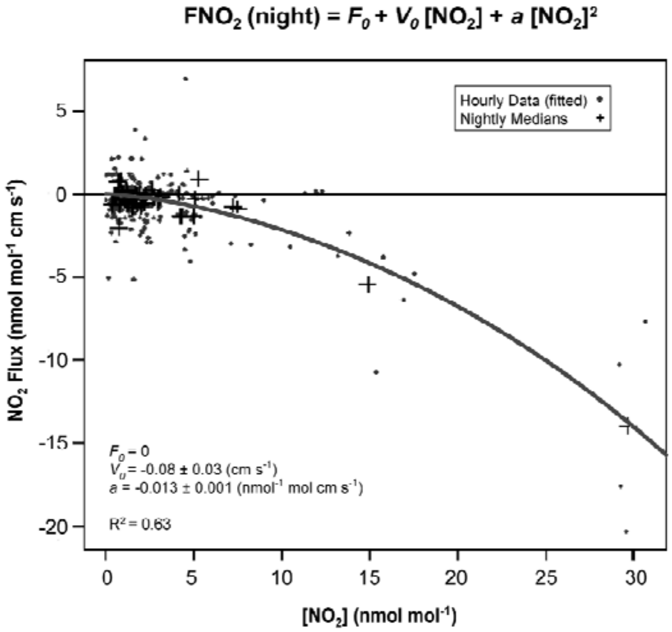
Source: Horii et al. (Horii, 2004).

Figure 2-108. Diel cycles of median concentrations (upper panels) and fluxes (lower panels) for the Northwest clean sector, left panels) and Southwest (polluted sector, right panels) wind sectors at Harvard Forest, April-November, 2000, for [NO], [NO_2], and [O_3/10]. NO and O_3 were sampled at a height of 29 m, and NO_2 at 22 m. Vertical bars indicate 25th and 27th quartiles for NO and NO_2 measurements. NO_2 concentration and nighttime deposition are enhanced under southwesterly conditions, as are O_3 and the morning NO maximum.



Source: Horii (Horii, 2002).

Figure 2-109. Simple NO_X photochemical canopy model outputs. Left panel, concentrations of NO (dashed) and NO_2 (solid); right, fluxes of NO (dashed) and NO_2 (solid). Symbols indicate measurement heights for NO (29m) and NO_2 (22m) at Harvard Forest. The model solves the continuity equation for NO concentration at 200 levels, d/dz(-Kc[dNO/dz]) = PNO⁻LNO, where PNO = [NO]/t1, LNO = [NO]/t2, and zero net deposition or emission of NO_X is allowed. NO_X (NO + NO_2) is normalized to 1ppb. t1 = 70s in this example. Due to the measurement height difference, observed upward NO_2 flux due to photochemical cycling alone should be substantially larger than observed downward NO flux attributable to the same process.

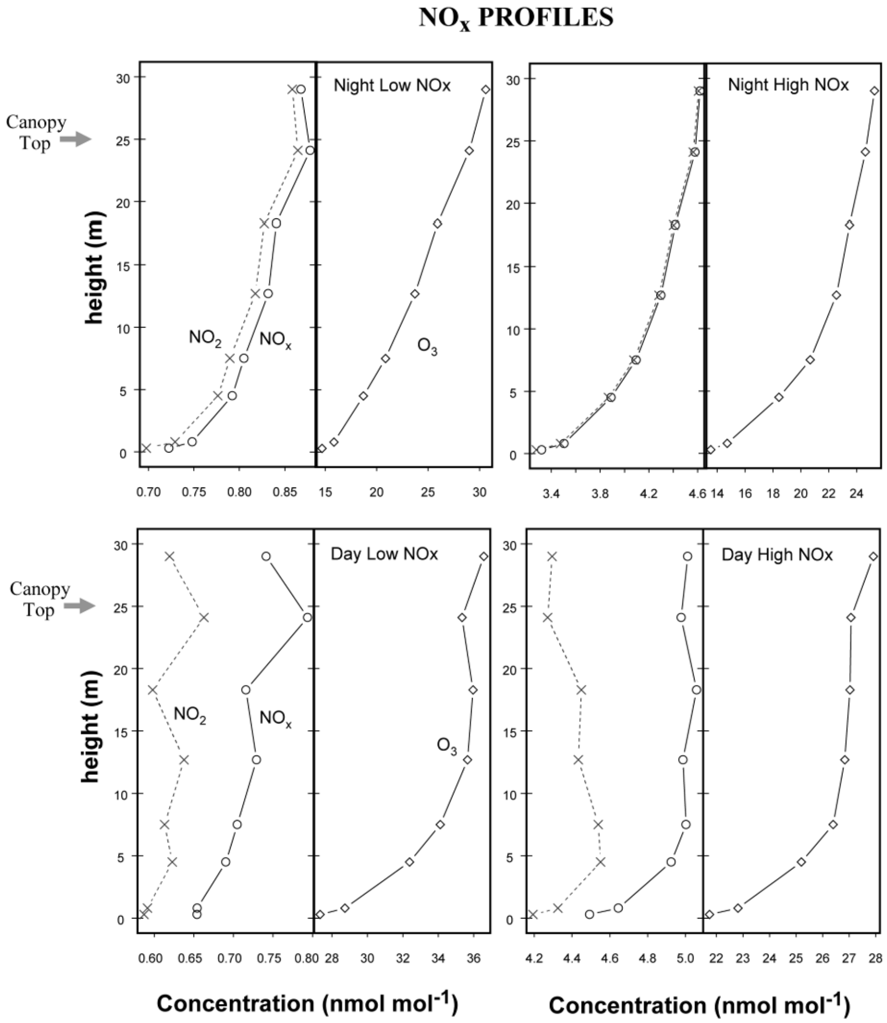


Source: Horii et al. (2004).

Figure 2-110. Hourly (dots) and median nightly (pluses) NO_2 flux vs. concentration, with results of least squares fit on the hourly data (curve). The flux is expressed in units of concentration times velocity (nmol/mol/cm/s) in order to simplify the interpretation of the coefficients in the least squares fit. Pressure and temperature corrections have been taken into account in the conversion from density to mixing ratio.

After accounting for the time of the NO-NO_2 null cycle during the measurement sampling period, the net NO_X flux can be derived. Overall, there was a net deposition of NO_X during the night and essentially zero flux in the day, with large variability in the magnitude and sign of individual flux observations. For the periods with $NO_2 > 2$ ppb, deposition was always observed. These canopy-scale field observations are consistent with a finite compensation point for NO_2 in the canopy that offsets foliar uptake or even reverses it when concentrations are especially low. At concentrations above the compensation point, NO_X is absorbed by the canopy. Examination of concentration profiles corroborates the flux measurements (Figure 117). During daytime for low-NO_X conditions, there is a local maximum in the concentration profile near the top of the canopy where O_3 has a local minimum, which is consistent with foliar emission or light-dependent production of NO_X in the upper canopy. Depletion is evident for both NO_X and O_3 near the forest floor. Air reaching the ground has passed through the canopy where uptake is efficient and the vertical exchange rates near the ground are slow. At night, the profiles generally decrease with decreasing height above the ground, showing only uptake. At higher concentrations, the daytime NO_X concentrations are nearly constant through the canopy; no emission is evident from the sunlit leaves.

Figure 118 compares observed fluxes of all the observed species. The measured NO_X and estimated PAN fluxes are small relative to the observed total NO_Y flux. In clean air, HNO_3 accounts for nearly all the NO_Y flux and the sum of all measured species is about equal to the NO_Y concentration. However, in polluted conditions, unmeasured species are up to 25% of the NO_Y, and HNO_3 fluxes cannot account for all the total NO_Y flux observed. These unmeasured NO_Y species likely are hydroxyalkyl nitrates and similar compounds rapidly deposited to surfaces but not routinely measured; see the descriptions of measurement techniques and challenges (Section 2.3). The deposition of HNO_3 and multifunctional $RONO_2$ are the largest elements of the measured N dry deposition budget. Two key areas of remaining uncertainty are the production of HNO_2 over vegetation and the role of very reactive biogenic VOCs. HNO_2 is important because its photolysis is a source of OH radicals, and its formation may represent an unrecognized mechanism to regenerate photochemically active NO_X from NO_3 that had been considered terminally removed from the atmosphere; see the discussion in Section 2.3 above on the atmospheric chemistry of NO_x and the role of oxidized N compounds in atmospheric N transport.

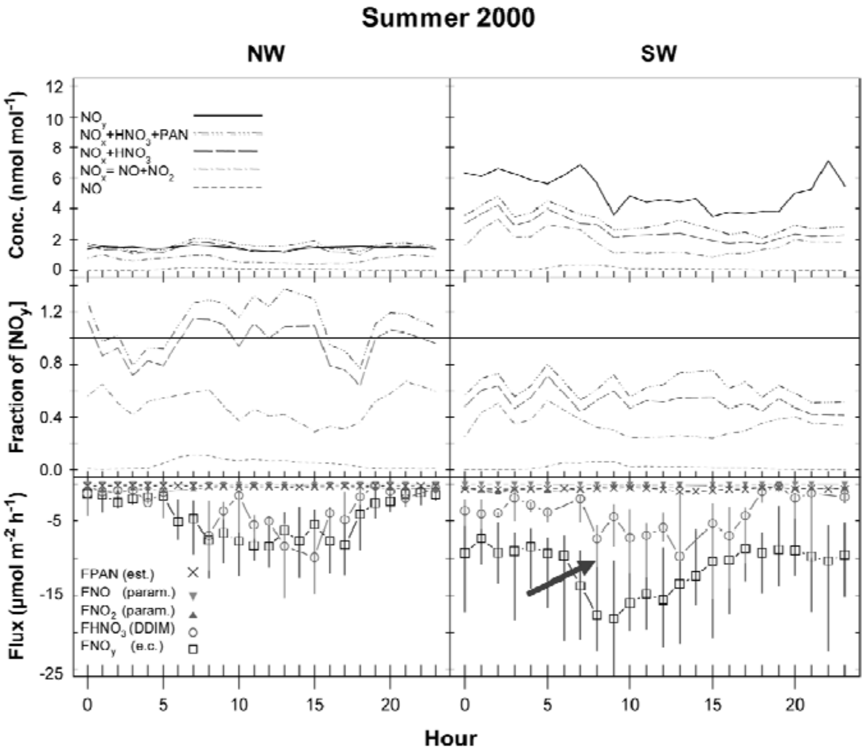


Source: Horii et al. (2004).

Figure 2-111. Averaged profiles at Harvard Forest give some evidence of some NO_2 input near the canopy top from light-mediated ambient reactions, or emission from open stomates.

2.10.2. Sulfur

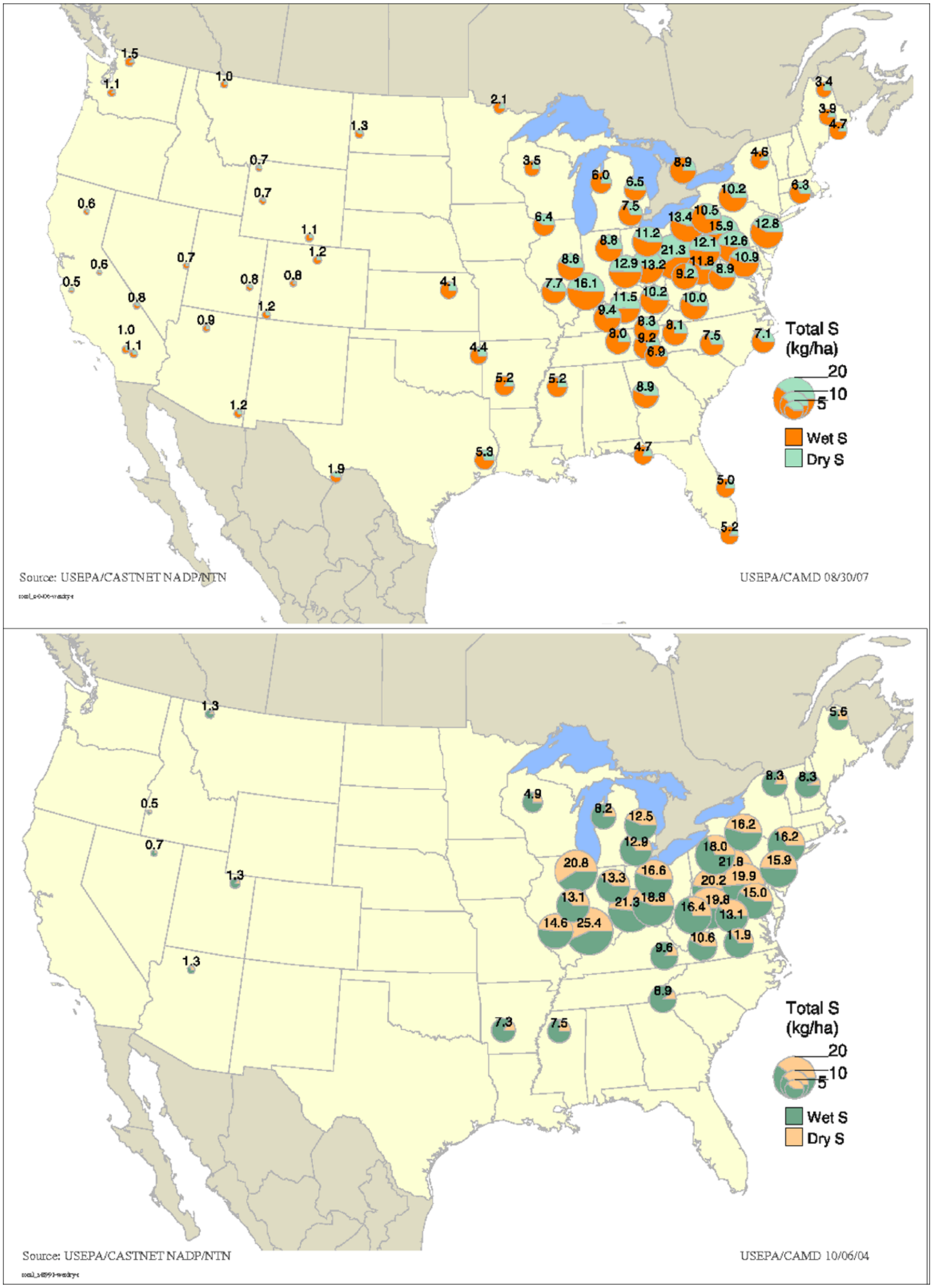
For the most recent 3−year reporting period available (2004 to 2006), mean S deposition was greatest in the eastern U.S. east of the Mississippi River, with the highest deposition of 21.3 kg/ha/yr in the Ohio River basin; see Figure 119. Most recording stations throughout the Ohio River basin report 3−year total S deposition averages >10 kg/ha/yr and many other stations in the East report deposition >5 kg/ha/yr. Data are sparse for the central and west U.S., but, where available, indicate lower values than in most of the East, ranging from 4.1 to 5.3 kg/ha/yr. Total S deposition in the U.S. west of the 100th meridian is lower, with all recording stations reporting <2 kg/ha/yr and many reporting <1.0 kg/ha/yr.



Source: Horii et al. (2006).

Figure 2-112. Summer (June-August) 2000 median concentrations (upper panels), fractions of NO_Y (middle panels), and fluxes (lower panels) of NO_Y and component species separated by wind direction (Northwest on the left and Southwest on the right). Vertical lines in the flux panels show 25th and 75th quartiles of F(NO_Y) and F(HNO_3); negative fluxes represent deposition; F(NO_X) is derived from eddy covariance F(NO) and F(NO_2) measurements (corrected for photochemical cycling), F(HNO_2) is inferred, and F(NO_Y) was measured by eddy covariance. The sum of NO_X, HNO_3, and PAN accounts for all of the NO_Y concentration and flux for Northwesterly (unpolluted background) flows, whereas up to 50% of NO_Y and F (NO_Y) under Southwesterly flows are in the form of reactive nitrogen species whose fluxes are not measured or estimated here.

These values can also be compared to S deposition totals from 1989–1991 in Figure 119. Station-by-station comparisons between averaging periods are difficult because some stations do not have sufficient data to report a mean for the sampling period. There are, however, clear regional decreases in S deposition across the country. S deposition for 1989–1991 (the earliest 3 year reporting period available) is almost uniformly greater than for the most recent three-year average (2004–2006). Deposition since 1989–1991 has declined throughout the Ohio River basin (from a previous high of 25.4 kg ha/yr), New England, and the Mid-Atlantic, consistent with the ~48% decrease in SO_2 emissions nationwide between 1990 and 2005. Very little coverage for the western and central U.S. was available for the 1989–2001 reporting period, but sites with data show a similar decrease. Figure 120 shows that for both the 1989–1991 and 2004–2006 reporting periods, S was primarily deposited as wet SO_4^{2-} followed by a smaller proportion as dry SO_2 and a much smaller proportion as dry SO_4^{2-}.



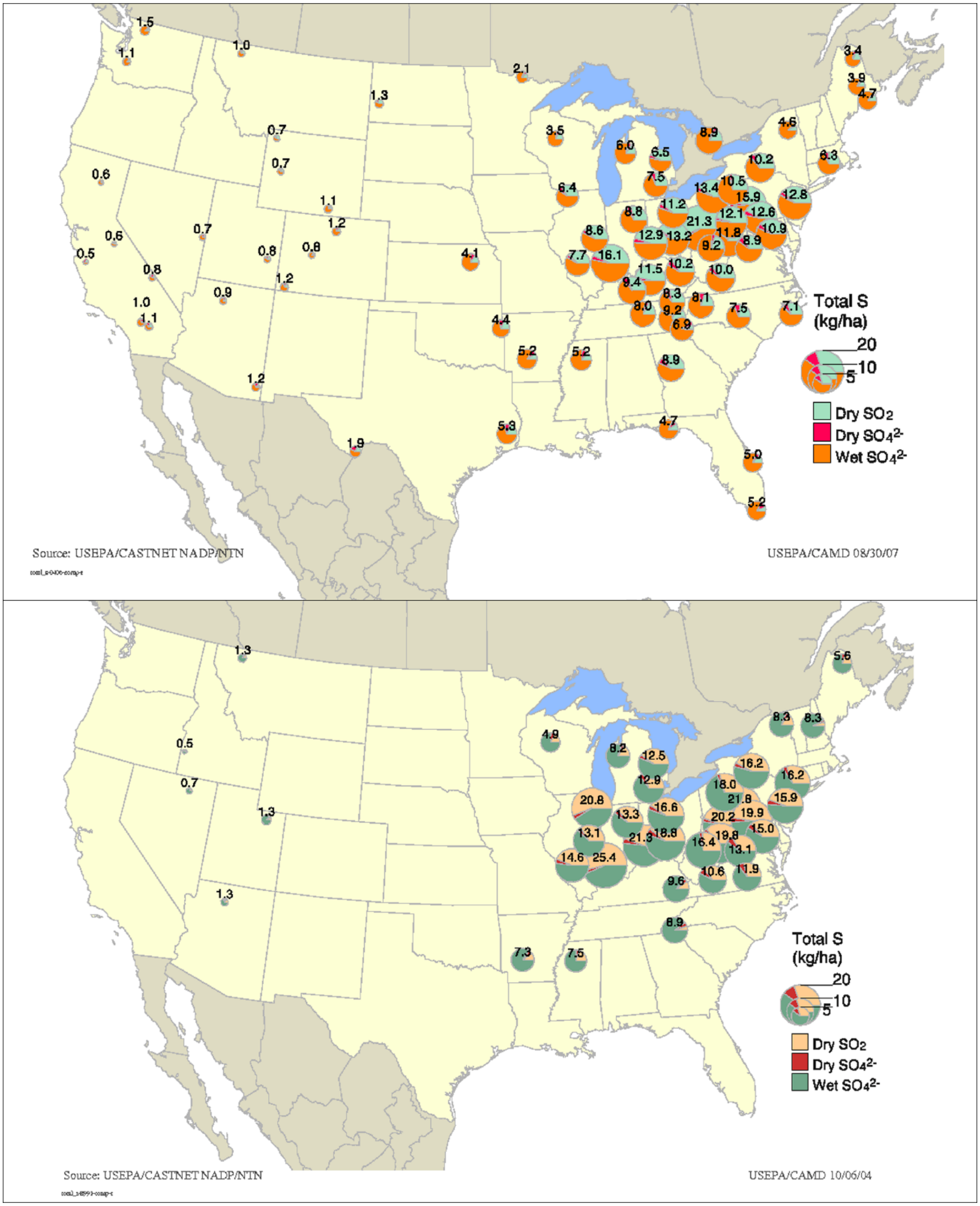
Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 08/30/07

Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 10/06/04

Figure 2-113. Total average yearly wet and dry sulfur deposition for 2004–2006 (top) and 1989–1991 (bottom).



Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 08/30/07

Source: USEPA/CASTNET NADP/NTN

USEPA/CAMD 10/06/04

Figure 2-114. Total average yearly sulfur deposition by species for 2004–2006 (top) and 1989–1991 (bottom).

2.11. Summary

2.11.1. Emissions and Atmospheric Concentrations

Total anthropogenic NO and NO_2 emissions in the U.S. in 2001 were ~23.19 Tg. Combustion chemistry at EGUs contributed ~22% of this total, and transportation-related sources contributed ~56%. Ambient annual NO_X concentrations have decreased ~35% in the period 1990–2005 to current annual average concentrations of ~15 ppb.

Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils. The NO and N_2O emitted from soils as intermediate products from denitrification can evolve either naturally or as stimulated by addition of N containing fertilizers to crops and other soil management practices. N_2O, another member of the oxides of N family of chemicals, is also a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2e basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this value.

Concentrations of NO_2 in the CONUS from biogenic sources in the U.S., Canada, and Mexico and from all sources elsewhere in the world are defined as policy-relevant background concentrations. On an annual average basis these concentrations are calculated to be <300 ppt over most of the CONUS and <100 ppt in the eastern U.S. where NO emissions are greatest. The 24-h ambient NO_2 levels in CMSAs where most of the regulatory monitors are located and where most anthropogenic emissions originate were, on average, <20 ppb with a 99% percentile value <50 ppb for the years 2003–2005. Annual-average NO_2 concentrations over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.

NO and N_2O can be emitted from soils as intermediate products from denitrification, either naturally; or as stimulated by addition of N containing fertilizers to crops and other soil management practices. N_2O is a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2e basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this value.

On a national scale, energy production at EGUs accounted for ~66% of total SO_2 emissions in the U.S. in 2001–2002; ~5% of total SO_2 is emitted by transportation-related sources, with on-road vehicles accounting for ~40% of the transportation fraction, and off-road diesel and marine traffic together accounting for the remainder. As with NO_X, emissions of SO_X have been significantly reduced in recent years: ambient annual SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~ 4 ppb for both aggregate annual and 24-h average concentrations nationwide.

Annual-average policy-relevant background SO_2 concentrations in the U.S. are <10 ppt over most of the CONUS, or <1% of observed SO_2 concentrations everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.

NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices. Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes high in N; 30 to 70% of these wastes may be emitted as NH_3. These increases in NH_3 emissions, and the consequent increases in ambient NH_3 concentrations and NH_4+ concentration and deposition, are highly correlated geospatially with the local and regional increases in agricultural intensity. However, estimates of total NH_3 emissions on national and sub-national scales range widely owing to three complex issues: (1) the high spatial and temporal variability in NH_3 emissions; 2) the high uncertainty in the magnitude of those emissions; and (3) the lack of real-time, reliable, ambient NH_3 monitoring techniques. Nonetheless, U.S. national NH_3 emissions totals have been calculated, taking into account these three drivers of uncertainty; for 2001-2002 the national NH_3 emissions total from the NEI and as corrected by means described in Section 2.5 and Section 0 was ~4.08 Tg/yr.

2.11.2. Field Sampling and Analysis

The coverage of the networks is very thin over large expanses of the interior U.S. and especially so west of the 100th meridian. This assessment concludes that this thorough-going lack of monitored sites increases the likelihood that significant exposure from deposition is now occurring at current atmospheric concentrations where no measurements are available, as predicted in numerical experiments with large-scale, first-principles models of atmospheric chemistry and physics and deposition, and as measured at some few special experimental sites.

The instrumentation deployed at present in the routine monitoring networks for determination of gas-phase NO_X and SO_2 concentrations is likely adequate for determining compliance with the current NAAQS standards. But in application for determining environmental effects, all these methods have important limitations which make them inadequate for fully characterizing the state of the atmosphere at present, for correctly representing the complex heterogeneity of N and S deposition across the landscape, and for realistically apportioning the contributions of reduced and oxidized forms of atmospheric N and S in driving observed biological effects at a national scale.

For example, routine NO_2 measurements by CL are contaminated by unknown and varying concentrations of higher-order oxidized N species, including gas-phase HNO_3, important as in itself for N deposition to the biosphere and also as a precursor to pNO_3. Moreover, dry deposition of NO, NO_2, and

PANs is not estimated in the dry deposition networks, but could account for as much as 30% of total dry oxidized N deposition in areas near strong NO_X sources. This would include estuaries and other wetlands near large urban areas.

As concerns SO_2, the present-day ambient annual avg SO_2 concentrations are very near or even below the operating limit of detection of most of the FRM monitors in the largest regulatory network. This produces irresolvable uncertainty in these data which may be important for environmental effects from S compounds since they result in some cases from exposure at these current low concentrations

Routine field sampling techniques for NH_3 are at present limited to integrated values from several days to one week because higher frequency semi-continuous methods are not yet sufficiently robust to deploy for routine operation in national networks. Estimates for the contribution of NH_3 to the total N deposition budget range as high as 30% of total N, and perhaps the dominant source of reduced N. Moreover, routine national-scale sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the long time-integrated measurement.

This assessment concludes that the aggregate effect of these uncertainties and errors very likely is to underestimate total N and S atmospheric deposition and subsequent biological exposures.

2.11.3. Deposition of N and Sulfur

Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises ~50 to 75% of the total N atmospheric deposition.

For the period 2004–2006, the routine monitoring networks report the mean N deposition in the U.S. was greatest in the Ohio River Valley, specifically in Indiana and Ohio, with values as high as 9.2 and 9.6 kg/ha/yr, respectively. N deposition was lower in other parts of the East, including the Southeast and northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition: 7.0 and 6.5 kg/ha/yr, respectively.

Estimated N deposition from measurements primarily occurred in the form of wet NO_3 and NH_4, followed with decreasing amounts of dry HNO_3, dry NH_4, and dry NO_3. Although deposition in most areas of the U.S. occurred in wet form, there were some exceptions, including parts of California where N deposition was primarily dry. Data are very sparse for the central U.S. between the 100th meridian and the Mississippi River; but, where available, N deposition values there were lower than in most of the eastern U.S., ranging from 4.1 to 5.3 kg N/ha/yr.

Table 2-25. Regional changes in wet and dry N and S atmospheric concentrations and deposition, 1989-1991 and 2003-2005.

Measurement	Unit	Region	Average 1989–1991	Average 2003–2005	Percent Change*
Wet SO_4^{2-} deposition	kg/ha	Mid-Atlantic	27	20	-24
		Midwest	23	16	-32
		Northeast	23	14	-36
		Southeast	18	15	-19
Wet SO_4^{2-} concentration	mg/L	Mid-Atlantic	2.4	1.6	-33
		Midwest	2.3	1.6	-30
		Northeast	1.9	1.1	-40
		Southeast	1.3	1.1	-21
Ambient sulfur dioxide concentration	µg/m^3	Mid-Atlantic	13	8.4	-34
		Midwest	10	5.8	-44
		Northeast	6.8	3.1	-54
		Southeast	5.2	3.4	-35
Ambient SO_4^{2-} concentration	µg/m^3	Mid-Atlantic	6.4	4.5	-30
		Midwest	5.6	3.8	-33
		Northeast	3.9	2.5	-36
		Southeast	5.4	4.1	-24
Wet inorganic N deposition	kg/ha	Mid-Atlantic	5.9	5.5	-8
		Midwest	6.0	5.5	-8
		Northeast	5.3	4.1	-23
		Southeast	4.3	4.4	+2
Wet NO^3 concentration	mg/L	Mid-Atlantic	1.5	1.0	-29
		Midwest	1.4	1.2	-14
		Northeast	1.3	0.9	-33
		Southeast	0.8	0.7	-9
Ambient ^{3} concentration	µg/m^3	Mid-Atlantic	0.9	1.0	+5
		Midwest	2.1	1.8	-14
		Northeast	0.4	0.5	+20
		Southeast	0.6	0.7	+17
Total ambient ^{3} concentration (^{3} + Nitric acid)	µg/m^3	Mid-Atlantic	3.5	3.0	-14
		Midwest	4.0	3.5	-12
		Northeast	2.0	1.7	-13
		Southeast	2.2	2.1	-5

* Percent change is estimated from raw measurement data, not rounded; some of the measurement data used to calculate percentages may be at or below detection limits.

Source: CASTNET and the National Atmospheric Deposition Program / National Trends Network (NADP/NTN)

For the period 2004–2006, mean S deposition in the U.S. was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg S/ha/yr, in the Ohio River Valley where most recording stations reported three-year averages >10 kg S/ha/yr. Numerous other stations in the East reported S deposition >5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is relatively low, with all recording stations reporting less than 2 kg S/ha/yr and many reporting less than 1.0 kg S/ha/yr.

S was primarily deposited in the form of wet SO_4^{2-} followed in decreasing order by a smaller proportion of dry SO_2 and a much smaller proportion of deposition as dry SO_4^{2-}. However, these S data in the western U.S., like those for N deposition, are derived from measurements in networks with many fewer nodes in the West than in the East.

Table 2-25 lists separate concentration and deposition totals for wet and dry N and S species in 4 sub-regions of the U.S. as annual averages for the years 1989–1991 and 2003–2005 as a summary of the foregoing data.

Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape, are computed using the measurements of wet and dry N deposition (as reported above) where these are available, and then can be interpolated with or without a set of air quality model predictions to determine the relative contribution from the atmosphere of various species of reduced and oxidized N. Measurement and modeling experiments like these have shown that atmospheric inputs of reactive N directly to the surface of some coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of external N loadings to these systems. For example, atmospheric N inputs to the northeast Atlantic coast of the U.S., the southeast Atlantic coast of the U.S., and the eastern Gulf of Mexico have been estimated to be 11, 5.6, and 5.6 kg N/ha/yr, respectively. More specifically and at finer spatial scales, atmospheric N loads to great waters and estuaries in the U.S. have been estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the Catherines-Sapelo estuary at the highest end. At Chesapeake Bay, atmospheric N is estimated to contribute up to 30% of total N and 14% of the NH_4 loadings to the Bay.

Chapter 3. Ecological and Other Welfare Effects

This chapter is organized into four sections. The introduction (Section 3.1) frames the organizing principle of this chapter and several basic concepts of ecology. A discussion of acidification is presented in Section 3.2. N enrichment is discussed in Section 3.3. Lastly, other welfare effects are presented in Section 3.4, including interactions between sulfur (S) deposition and mercury (Hg) methylation and direct gas-phase injury to vegetation.

3.1. Introduction to Ecological Concepts

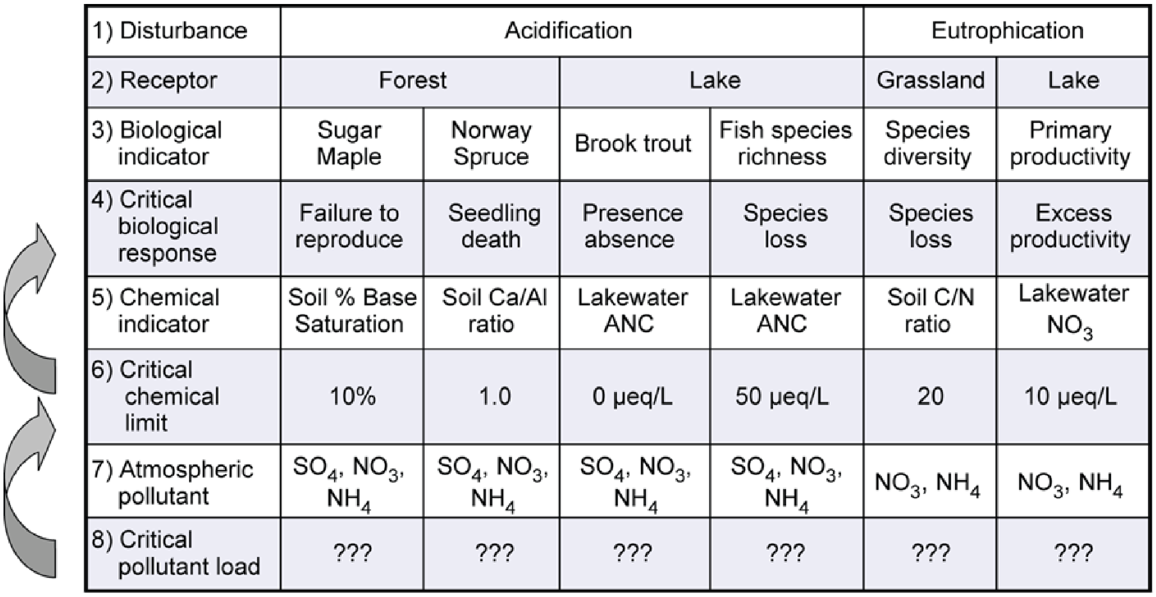
3.1.1. Critical Loads as an Organizing Principle for Ecological Effects of Atmospheric Deposition

This chapter uses the critical loads concept as an organizing principle. The components that are necessary to develop a critical load provide a conceptual framework for linking atmospheric pollutants to ecological endpoints that indicate impairment. The generally accepted definition of a critical load of atmospheric pollutant deposition emerged from a pair of international workshops held in the late 1980s (Nilsson, 1986; Nilsson, 1988). The workshop participants defined a critical load as:

> "A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge."

The development of a quantitative critical load estimate requires a number of steps. An illustrative example of the eight general steps is shown in Table 3-1. A more detailed description of these steps is given in Annex D.

Table 3-1. An example of the matrix of information that must be considered in the definition and calculation of critical loads (see discussion in text). Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits could be used.



1) Disturbance	Acidification				Eutrophication	
2) Receptor	Forest		Lake		Grassland	Lake
3) Biological indicator	Sugar Maple	Norway Spruce	Brook trout	Fish species richness	Species diversity	Primary productivity
4) Critical biological response	Failure to reproduce	Seedling death	Presence absence	Species loss	Species loss	Excess productivity
5) Chemical indicator	Soil % Base Saturation	Soil Ca/Al ratio	Lakewater ANC	Lakewater ANC	Soil C/N ratio	Lakewater NO_3
6) Critical chemical limit	10%	1.0	0 µeq/L	50 µeq/L	20	10 µeq/L
7) Atmospheric pollutant	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	SO_4, NO_3, NH_4	NO_3, NH_4	NO_3, NH_4
8) Critical pollutant load	???	???	???	???	???	???

This chapter presents information with a focus on the following questions:

- What is the disturbance?
- What receptors are affected?
- What indicator organisms are (or previously were) present and observable?
- What chemical indicators are changing and can be measured?
- What atmospheric pollutant is driving the changes in the chemical indicators?

It is important to recognize that there is no single “definitive” critical load for a natural resource. Critical loads estimates reflect the current state-of-knowledge and policy priorities. Changes in scientific understanding may include, for example, new dose-response relationships; better resource maps and inventories; larger survey datasets; continuing time-series monitoring; improved numerical models. Changes in the policy elements may include: new mandates for resource protection; focus on new pollutants; and inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

This procedure can result in calculation of multiple critical loads for a given pollutant at a single location. The multiple solutions derive from the nested sequence of disturbances, receptors, and biological indicators that must be considered for a given pollutant. Multiple critical load values may also arise from an inability to agree on a single definition of “significant harm.” Calculation of critical loads for multiple definitions of “harm” may be deemed useful in subsequent discussions of the analysis and in the decision-making steps that may follow critical load calculation.

Finally, there is the inescapable heterogeneity of all natural environments. Consider soils, for instance. The high spatial variability of soils almost guarantees that for any reasonably sized soil-based “receptor” that might be defined in a critical load analysis, there will be a continuum of critical load values for any indicator chosen. The range of this continuum of values may be narrow enough to be ignored; nevertheless, there is an *a priori* expectation in any critical load analysis that multiple values (or a range of values) will result from the analysis. Given the heterogeneity of ecosystems affected by N and S deposition, examples of published critical load values for a variety of endpoints and locations in the U.S. are presented here (see Section 3.3.7).

3.1.2. Ecosystem Scale, Function, and Structure

Information presented in this ISA was collected at multiple scales, ranging from the physiology of a given species to population, community, and ecosystem-level investigations. For the purpose of this assessment, “ecosystem” is defined as a functional entity consisting of interacting groups of living organisms and their abiotic (chemical and physical) environment. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, biomes at the continental scale, or small, well-circumscribed systems such as a small pond.

Ecosystems have both structure and function. Structure may refer to a variety of measurements including the species richness, abundance, community composition and biodiversity as well as landscape attributes. Competition among and within species and their tolerance to environmental stresses are key elements of survivorship. When environmental conditions shift, for example, by the presence of anthropogenic air pollution, these competitive relationships may change and tolerance to stress may be exceeded. Function refers to the suite of processes and interactions among the ecosystem components and their environment that involve nutrient and energy flow as well as other attributes including water dynamics and the flux of trace gases. Plant processes including photosynthesis, nutrient uptake, respiration, and carbon (C) allocation, are directly related to functions of energy flow and nutrient cycling. The energy accumulated and stored by vegetation (via photosynthetic C capture) is available to other organisms. Energy moves from one organism to another through food webs, until it is ultimately released as heat. Nutrients and water can be recycled. Air pollution alters the function of ecosystems when elemental cycles or the energy flow is altered. This alteration can also be manifested in changes in the biotic composition of ecosystems.

3.1.3. Ecosystem Services

Ecosystem structure and function may be translated into ecosystem services. Ecosystem services identify the varied and numerous ways that ecosystems are important to human welfare. Ecosystems provide many goods and services that are of vital importance for the functioning of the biosphere and provide the basis for the delivery of tangible benefits to human society. Hassan et al. (2005) define these to include supporting, provisioning, regulating, and cultural services:

- Supporting services are necessary for the production of all other ecosystem services. Some examples include biomass production, production of atmospheric O_2, soil formation and retention, nutrient cycling, water cycling, and provisioning of habitat. Biodiversity is a supporting service that is increasingly recognized to sustain many of the goods and services that humans enjoy from ecosystems. These provide a basis for three higher-level categories of services.

- Provisioning services, such as products (cf. Gitay, 2001), i.e., food (including game, roots, seeds, nuts and other fruit, spices, fodder), fiber (including wood, textiles), and medicinal and cosmetic products (including aromatic plants, pigments).

- Regulating services that are of paramount importance for human society such as (a) C sequestration, (b) climate and water regulation, (c) protection from natural hazards such as floods, avalanches, or rock-fall, (d) water and air purification, and (e) disease and pest regulation.

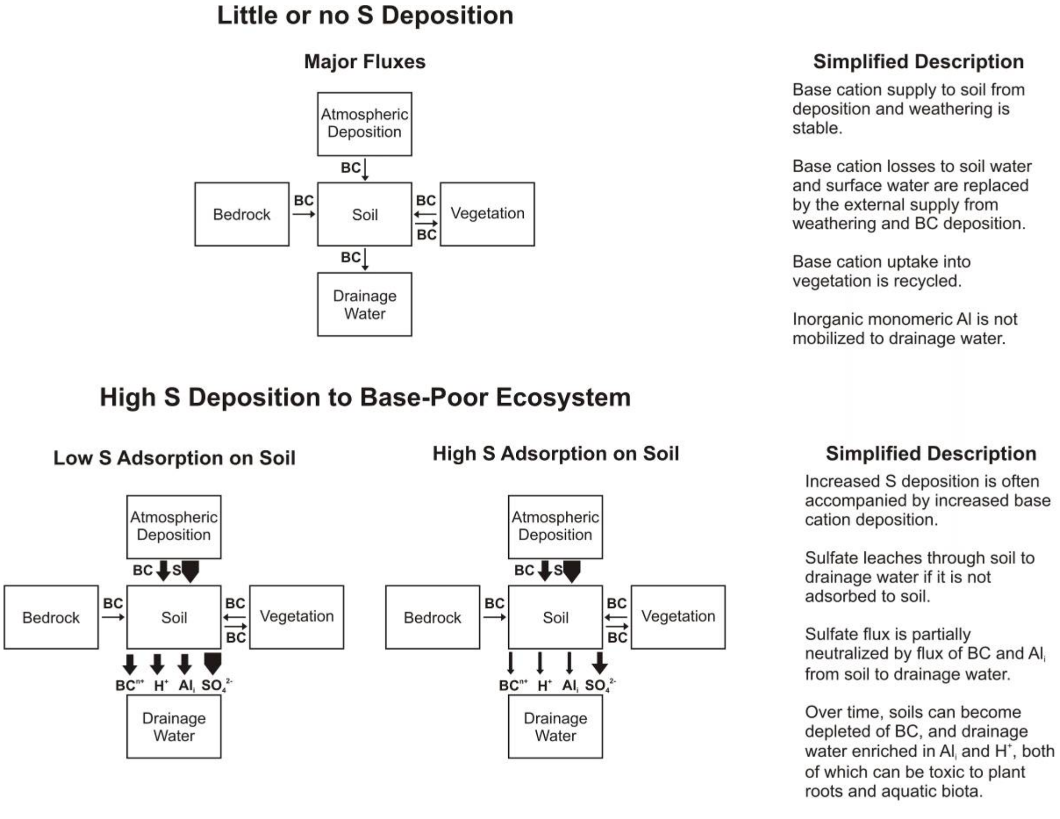
- Cultural services that satisfy human spiritual and aesthetic appreciation of ecosystems and their components.

Wetlands also offer key ecosystem services such as sequestering carbon, providing habitats, regulating flood, maintaining water quality, and stabilizing coastal slope (EPA, 1993).

3.2. Ecological Effects of Acidification

3.2.1. Effects on Major Biogeochemical Processes

Acidifying deposition has altered major biogeochemical processes in the U.S. by increasing the S (Figure 3-1) and N content of soils, accelerating SO_4^{2-} and NO_3^- leaching from soil to drainage water, depleting base cations (especially Ca and Mg) from soils, and increasing the mobility of Al. The extent of soil acidification is a critical factor that regulates virtually all acidification-related ecosystem effects from S and N deposition. Soil acidification occurs in response to both natural factors and acidifying deposition. To best integrate the effects of acidifying deposition, this assessment starts with a description of the effects on soils and major biogeochemical processes within ecosystems, then summarizes the chemical and biological effects on terrestrial, transitional, and aquatic ecosystems. More detailed information on acidification effects is provided in Annex B.



Simplified Description

Base cation supply to soil from deposition and weathering is stable.

Base cation losses to soil water and surface water are replaced by the external supply from weathering and BC deposition.

Base cation uptake into vegetation is recycled.

Inorganic monomeric Al is not mobilized to drainage water.

Simplified Description

Increased S deposition is often accompanied by increased base cation deposition.

Sulfate leaches through soil to drainage water if it is not adsorbed to soil.

Sulfate flux is partially neutralized by flux of BC and Al_i from soil to drainage water.

Over time, soils can become depleted of BC, and drainage water enriched in Al_i and H^+, both of which can be toxic to plant roots and aquatic biota.

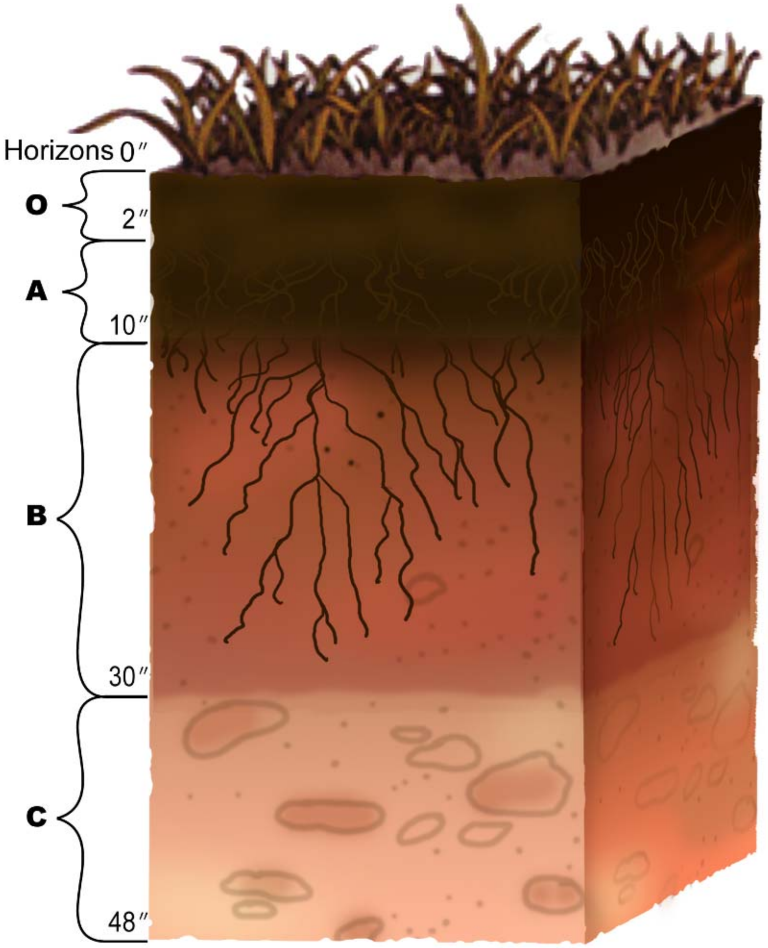
Figure 3-1. Illustration of major fluxes of ions associated with S-driven acidification of drainage water. The upper diagram represents ion fluxes in the absence of S deposition. The two lower diagrams illustrate changes to these fluxes in response to S deposition on two types of soils, with (right) and without (left) substantial S adsorption on soil. Effects are most pronounced under high deposition with little adsorption, and include increased leaching of base cations (contributes to soil acidification), H (reduced pH), and Al_i (toxic to many plant roots and aquatic species). Larger fluxes are represented by thicker arrows.

3.2.1.1. Soil Acidification

Soil acidification is the loss of base cations plus the accumulation of acidic cations such as hydrogen (H^+) and aluminum (Al^{n+}) in the soil; this happens when a proton donor is added to the soil. Soil acidification is a natural process. Such natural acidity is contributed by carbonic acid, organic acids, and plant cation uptake (Turner, 1990; Charles, 1991). However, the donor can also be a mineral acid, such as HNO_3 and H_2SO_4, the common components of acid rain that result from NO_X and SO_X air pollution. Decreases in soil pH attributable to acidifying deposition have been documented in the U.S. (Johnson, 1994; Johnson, 1994; Bailey, 2005; Sullivan, 2006). Effects in the Eastern U.S. appear to have been limited mainly to the Northeast and portions of the Appalachian Mountains in both hardwood and coniferous forests. Soil acidification has also likely occurred in localized areas of mixed conifer forest and chaparral vegetation in, and near, the Los Angeles Basin, in response to locally high levels of atmospheric dry N deposition (Fenn, 2003; Fenn, 2003).

To evaluate soil acidification, the soil must be considered in terms of the surface organic layer (the primary rooting zone), of which the Oa horizon (or in some studies the O horizon, which combines the Oe and Oa horizons) is an important component (See Figure 3-2). In addition, the mineral soil including the A and/or B horizon, which lie below the Oa horizon and are primarily comprised of mineral matter, must be considered.

Acidifying deposition can have a direct effect on soil pH. However, net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter. This process can decrease the pH of soil water in the Oa horizon well below the lowest pH values measured in acidifying deposition (Krug, 1985; Lawrence, 1995). Oa-horizon soils under coniferous vegetation are strongly acidified by organic acids and are unlikely to have experienced a lowering of pH as a result of acidifying deposition (Johnson, 1992; Lawrence, 1995). Soils influenced by the growth of hardwood species tend to have surface horizons that are less acidic naturally and are, therefore, more susceptible to decreased pH in the Oa horizon from acidifying deposition. By taking up larger amounts of Ca from the soil, hardwoods can acidify lower soil horizons more than conifers even though they enrich surface horizons with Ca via litterfall (Alban, 1982).



Source: http://soils.usda.gov/education/resources/

Figure 3-2. Diagram illustrates "ideal" soil horizons to which many soils conform. Each main horizon is denoted by a capital letter: O) Organic matter: Litter layer of plant residues in relatively undecomposed form. A) Surface soil: Layer of mineral soil with most organic matter accumulation and soil life. This layer is depleted of iron, clay, aluminum, organic compounds, and other soluble constituents. B) Subsoil: This layer accumulates iron, clay, aluminum and organic compounds. C) Substratum: Layer of unconsolidated soil parent material. This layer may accumulate the more soluble compounds that bypass the "B" horizon.

Several studies document declines in soil pH within the Oa/A horizons and the upper B horizon in sensitive regions of the U.S. over the past several decades (Johnson, 1994; Johnson, 1994; Drohan, 1997; Bailey, 2005). These declines have been attributed at least partly to acidifying deposition (Bailey, 2005).

In summary, soil acidification is a natural process, which is often exacerbated by acidifying deposition. Natural acidification is particularly pronounced in coniferous forests. Acidifying deposition can contribute to soil acidification, with consequent effects on the availability of nutrient cations in soil and the chemistry of drainage water that flows from soil into streams and lakes. More detailed descriptions of soil acidification are provided by van Breemen et al. (1983) and Binkley and Richter (1987).

3.2.1.2. Sulfur Accumulation and SO_4^{2-} Leaching

Most acidification-related consequences of atmospheric S and N deposition in the U.S. are caused by SO_4^{2-} (Sullivan, 2000; Driscoll, 2001). The mobility within the watershed of SO_4^{2-}, derived from atmospheric S deposition, is a key factor governing many aspects of soil and water acidification at locations in the U.S. that are affected by acidifying deposition.

Upon deposition to the Earth's surface, S may be assimilated by vegetation or microbes, accumulate in the soil or act as a mobile ion and leach out of the soil. When a given area is affected by acidifying deposition, S deposition levels are typically much higher than plant demand for S and consequently almost all deposited S is transported to the soil where it may accumulate and is available for leaching as SO_4^{2-}. SO_4^{2-} acts as a mobile anion at many locations in the U.S. that receive high levels of S deposition, notably the glaciated Northeast and Upper Midwest, where much of the deposited S leaches through soils into streams and lakes. SO_4^{2-} leaching leads to most of the ecological effects from atmospheric S deposition because it is accompanied by leaching of cations, and this contributes to acidification of soil, soil water, and surface water.

Over time, sustained SO_4^{2-} leaching and associated soil acidification contribute to pronounced changes in soils in some areas. When S is transported from soils to surface waters in the form of SO_4^{2-}, an equivalent amount of cations, or countercharge, is also transported. When the countercharge is provided by base cations, the base saturation of the soil is reduced as the acidity of the soil water is neutralized. However, this process acidifies the soil, thereby decreasing the soil's capacity to neutralize additional acidity deposited from the atmosphere and prevent acidification of soil water, and by connection, surface water. As the base cations become depleted, the countercharge provided by acidic cations (H and inorganic Al) increases, sometimes resulting in toxic conditions for plant roots and aquatic organisms (Turner, 1990; Charles, 1991).

In the U.S., there are some regional trends of soil accumulation, retention, and leaching of S that are discussed below.

Southeast

Accumulation of atmospherically deposited S in soil has resulted from anion adsorption and incorporation of S into organic matter through biological assimilation. Such retention of S can temporarily reduce SO_4^{2-} leaching and cause a delay in ecosystem recovery in response to decreases in S deposition, as some accumulated S is slowly released from the soil into drainage water. S adsorption on soil is especially pronounced in the Southeastern U.S. Under continued loading of S deposition, it is expected that many southeastern watersheds will exhibit a gradual decrease in the extent of S adsorption in the future. This will likely contribute to further acidification of some streams, even under substantially reduced levels of S deposition (Turner, 1990; Elwood, 1991; Sullivan, 2004).

Northeast

In the Northeast, the accumulation of a portion of the historic legacy of atmospheric S deposition in soil was demonstrated by a positive relationship between wet deposition of SO_4^{2-} and concentrations of total S in the forest floor of 12 red spruce stands (Driscoll, 2001). However, net loss of S from soils now appears to be occurring in a number of Northeastern watersheds in response to decreased levels of atmospheric S deposition. The potential for net mineralization of stored S might affect recovery of drainage waters (Novák, 2007; Likens, 2002; Gbondo-Tugbawa, 2002). Where leaching of previously stored S occurs, it delays soil and surface water chemical recovery from acidification (Driscoll, 2001).

Weathering contributes substantial S in some watersheds (Shanley, 2005). Uncertainties in estimates of ecosystem S fluxes, such as weathering and dry deposition, and the difficulty in discerning the effects of net SO_4^{2-} desorption and net S mineralization make it difficult to predict when S outputs in the northeastern U.S. will no longer exceed inputs. Recent research results, based on experimental reduction of S inputs, suggest that this process will occur on a decadal timescale (Martinson, 2005; Mörth, 2005). The long-term role of C-bonded S adds further uncertainty because enhancement of S mineralization by a warming climate could also affect S retention and release from soil (Knights, 2000; Driscoll, 2001).

In summary, atmospheric S deposition alters soil chemistry through the following mechanisms: (1) sustained SO_4^{2-} leaching and associated changes in soil chemistry, and (2) accumulation of S in the soil through physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S from soils at a number of sites in the Northeast is a likely response to recent decreases in atmospheric S inputs (Driscoll, 2001). The gradual loss of previously accumulated S is further contributing to continued SO_4^{2-} leaching and soil acidification.

3.2.1.3. N Accumulation and NO_3^- Leaching

The scope of this section is the role of N deposition in the process of acidification. This assessment divides the effects of N deposition into the two broad categories of acidification and N nutrient enrichment effects. The latter is discussed in Section 3.3. N deposition may cause acidification of ecosystems via three main mechanisms: (1) excess accumulation in soils followed by increased rates of nitrification by microbes, (2) change in base cation status of soils caused by NO_3^- leaching, and (3) increased growth of vegetation causing increased cation uptake.

Nitrification and Accumulation

Atmospherically deposited N accumulates in soil through incorporation of N into organic matter. Accumulation is either documented or suggested to occur across large areas of the U.S. (Aber, 2003).

Direct evidence for such accumulation has been found in the Northeastern U.S. and in Colorado. Increased accumulation of N in soil is suggested, for example, by a positive correlation between atmospheric deposition levels and total N concentration in the Oa soil horizon at red spruce sites in New York, Vermont, New Hampshire, and Maine (Driscoll, 2001). Mass balance studies also show soil N retention (e.g.,, Campbell, 2005). Further evidence that atmospheric deposition has increased the availability of N in soil is provided by the strong negative correlation between atmospheric N deposition and the C:N ratio of the Oa soil horizon across the northeastern U.S. (Aber, 2003).

The nitrification process is mediated by autotrophic bacteria that derive energy by reducing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils (Aber, 2003; Emmett, 1998). This process often results in elevated NO_3^- concentration in soil waters and surface waters (Aber, 2003; Ross, 2004). Thus, data collected from streams and lakes can yield important information about processes that occur in the soil. N saturation refers to the condition when N inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem. Excess N supply reduces competition between plants and heterotrophic microbes for NH_4^+ to the point that net nitrification occurs (Aber, 2003; Aber, 1998).

Leaching

In many upland forested areas in the U.S., a large fraction of the N received in atmospheric deposition is retained in soil or in plant biomass. Nevertheless, elevated NO_3^- concentration in surface waters during the growing season is common and widespread in the U.S. (Charles, 1991). High concentrations of NO_3^- in lakes and streams, indicative of ecosystem N saturation in most natural systems, have been found at a variety of locations throughout the U.S. (Stoddard, 1994) EPA, 2004). In general, atmospheric deposition of 8 to 10 kg N/ha/yr or more, results in NO_3^- leaching to surface waters in the Eastern U.S. Lower N deposition levels (less than 5 kg N/ha/yr) may lead to NO_3^- leaching in the mountainous West because of colder temperatures, shorter growing season, little soil development, extensive exposed bedrock, and rapid melting of large snowpacks (Baron, 1994; Williams, 1996).

NO_3^- leaching usually contributes to the leaching of base cations from soils to surface waters. Although concentrations of NO_3^- are typically less than SO_4^{2-} in drainage waters in most ecosystems in the U.S., concentrations of NO_3^- in some streams are high enough to suggest a substantial role for NO_3^- in base cation loss from soil, particularly during periods of high soil-water NO_3^- flux during the non-growing season (Van Miegroet, 1992; Cook, 1994).

The relationship between atmospheric N deposition and NO_3^- leaching from forest ecosystems is often modified by land-use history, current land-use, land disturbance, tropospheric ozone levels, and climate. The N retention capacity of soils is highly dependent on land-use history and its effects on N cycling and pool sizes. For example, the removal of trees reduces the amount of N in the watershed and enhances the demand of vegetative regrowth for added N. This effect results in little or no NO_3^- leaching and can last for decades to more than a century (Goodale, 2000). NO_3^- leaching is also affected by current land use (U.S. EPA 2006). In the northeastern U.S., concentrations of N in streams of upland forested watersheds tend to be considerably lower than in streams draining watersheds with other land uses (Aber, 1997; Aber, 2003). Perhaps the most noteworthy effect of urban land use on processes of nutrient enrichment from N deposition concerns the transport of NO_3^- to N-limited estuarine and near-coastal waters. This topic is discussed in Section 0. In agricultural, and especially in forested areas, it is generally expected that most atmospherically deposited N is taken up by terrestrial vegetation. This is usually not the case in urban landscapes, although it is sometimes possible. Due to the relatively large impervious surface area in the urban landscape (e.g., buildings, roads, parking lots), a higher percentage of precipitation is routed directly to surface waters, with less opportunity for vegetative uptake of deposited N.

Climatic factors also play an important role in determining the extent of NO_3^- leaching. In particular, temperature and moisture have large effects on N cycling and NO_3^- leaching. Murdoch et al. (1998) found that, for at least one site, annual mean NO_3^- concentrations in stream water were not related to annual wet N deposition, but rather, were positively correlated with mean annual air temperature. This pattern was likely due partly to the fact that microbial processes responsible for NO_3^- production are very sensitive to temperature. Fluctuations in microbial immobilization and mineralization in response to climatic variability affect NO_3^- losses to drainage waters.

Long-term data sets also suggest that climate may affect patterns of NO_3^- loss. Many of the original (sampled periodically since the early 1980s) long-term monitoring lakes in the Adirondack Mountains showed increased NO_3^- leaching from terrestrial ecosystems throughout the 1980s, which was followed by a decline during the 1990s (Driscoll, 2003; Driscoll, 2003). Decreasing stream NO_3^- concentrations during the 1990s were also observed in the Catskill Mountains and in New Hampshire (Driscoll, 2003; Driscoll, 2003). There was not a substantial change in N emissions or deposition in the Northeast region over that period. Climatic factors, increases in atmospheric CO_2, and interactions with increasing availability of dissolved OC have been proposed as possible contributing factors for regional decreases in NO_3^- in drainage water during the 1990s, but the driver of this decadal scale pattern remains under investigation. Snowmelt and rain-on-snow, along with soil freezing, can influence N cycling in cold climates (Eimers, 2007; Campbell, 2005; Park, 2003).

3.2.1.4. Base-Cation Leaching

Acidifying deposition has been shown to be an important factor causing decreases in concentrations of exchangeable base cations in soil. Loss of base cations from soil is a natural process. Under conditions of low atmospheric deposition of S and N the limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching. Inputs of S and N in acidifying deposition enhance inputs of strong acid anions that can accelerate natural rates of base-cation leaching (Cronan, 1978; Lawrence, 1999).

Leaching of base cations from watershed soils to surface waters is a mechanism that (1) depletes essential plant nutrients from soil; and (2) limits the extent of surface water acidification in response to acidifying deposition. When SO_4^{2-} and NO_3^- leaching occur in equal magnitude to base cation leaching, the drainage water is not acidified. However, in the process of neutralizing the acidity of drainage water, base cation release from soil causes depletion of the base saturation of the soil. Soil base saturation expresses the concentration of exchangeable bases (Ca, Mg, potassium [K], sodium [Na]) as a percent of the total cation exchange capacity (which includes exchangeable hydrogen ion and inorganic Al). Once base cations in the soil become depleted, Al is moved from soil into drainage water, with potentially harmful consequences for sensitive terrestrial plants and aquatic organisms throughout the food web.

In the 1990s, data were published supporting the occurrence of base cation depletion from soils in the U.S. (Lawrence, 1999; Lawrence, 1995; Lawrence, 1997), although decreases in exchangeable Ca concentrations had earlier been identified in European soils through repeated sampling. Recent data reveal that decreases in concentrations of exchangeable base cations and base saturation in the Oa and B soil horizons have occurred over the past several decades in the eastern U.S. and most studies attribute this change to the effects of acidifying deposition. For example, the most thorough soil re-sampling study in the U.S. was conducted in northwestern Pennsylvania by Bailey et al. (2005). This study showed that between 1967 and 1997 pronounced decreases, attributed largely to acidifying deposition, were measured in exchangeable Ca and Mg concentrations in Oa/A horizons and throughout the B horizon. Similarly, data compiled by Sullivan et al. (2006; , 2006) suggested decreases in base saturation of B-horizon soils in the Adirondack Mountains between the mid-1980s and 2003. Depletion of base cations contributes to soil acidification and influences the ability of watershed soils to support acid-sensitive vegetation and to neutralize acidity in future acidifying deposition. Both plant uptake of cations, for example via forest regrowth subsequent to logging or land use conversion, and acidifying deposition can acidify soils (Johnson, 1990; Trettin, 1999) Richter and Markewitz 2001,.

Upslope decreases in exchangeable soil base cation concentrations were found to be positively correlated with higher S deposition in the Catskill Mountains (Lawrence, 1999). Furthermore, declines in soil exchangeable pools of base cations have been documented in New Hampshire (Likens, 1996) and Norway (Kirchner, 1995). In summary, leaching of base cations associated with acidifying deposition is occurring in sensitive regions in the U.S. Base cation loss increases the sensitivity of the watershed to further acidifying deposition. Watersheds that were capable of fully neutralizing a particular level of acidifying deposition in the past may no longer be capable of fully neutralizing that level today or at some time in the future because of the cumulative effect of acidifying deposition on soil base saturation. Where the availability of exchangeable base cations is limited, the leaching of potentially toxic inorganic Al into soil and surface waters can result.

3.2.1.5. Aluminum Leaching

If soil base saturation is 20 to 25%, or lower, acidifying deposition can mobilize inorganic Al, which can lead to the leaching of this potentially toxic form of Al into soil waters and surface waters (Reuss, 1985; Cronan, 1990). This is an extremely important effect of acidifying deposition because some forms of inorganic monomeric Al, including Al^{3+} and various hydroxide species, are toxic to tree roots, fish, algae, and aquatic invertebrates (see Section 3.2.3). In fact, fish mortality in response to surface water acidification is usually attributable to Al toxicity. Increased concentrations of exchangeable inorganic Al in the mineral soil have been identified through repeated sampling in the U.S. and Europe over periods ranging from 17 years to 41 years in studies by Billet et al. (Billett, 1990), Falkengren-Grerup and Eriksson (Falkengren-Grerup, 1990), Bailey et al. (2005), and Lawrence et al. (1995). In areas of Europe with excessively high acidic deposition levels, evidence of Al depletion in the mineral soil has also been found (Mulder, 1989; Lapenis, 2004), but Al depletion has not been documented in the U.S.

Acidifying deposition is an important cause of increased mobilization of inorganic Al from soils to streams and lakes (Turner, 1990). Acidifying deposition introduces mineral acidity associated with anions that are more mobile than those from organic matter. If the release of base cations from the soil is insufficient to neutralize the inputs of sulfuric and nitric acid, then Al that had previously been deposited by normal soil development in the upper mineral soil is mobilized. Al may also be mobilized by organic acids. However, acidifying deposition mobilizes Al in inorganic forms, and in doing so increases the amount of exchangeable inorganic Al within the B horizon and results in transport of inorganic Al into soil waters and surface waters (Driscoll, 1984; Driscoll, 1985). Inorganic Al is minimally soluble at pH about 6.0, but solubility increases steeply at pH values below about 5.5. This distinction between organic and inorganic forms of Al is important because organic Al is not toxic, whereas inorganic Al is toxic to a variety of plants and aquatic organisms (Baker, 1982; Baldigo, 1997; Joslin, 1988; Joslin, 1989)(Section 3.2.3.1). Discussions in this document of inorganic Al in solution refer to dissolved, rather than particulate or colloidal, forms. These dissolved inorganic Al species are often collectively called inorganic monomeric Al (cf., (Driscoll, 1984).

Recovery of soil chemistry will require a decrease in exchangeable Al concentrations and Al leaching. It is unclear what length of time would be required to decrease soil exchangeable Al concentrations to levels characteristic of unpolluted systems. Furthermore, in most cases it is unclear whether exchangeable Al concentrations are continuing to increase, remaining stable, or decreasing. Predictions of trends in exchangeable Al concentrations remain uncertain because of our incomplete understanding of mechanisms through which mineral matter and organic matter interact to control dissolved Al concentrations. Possible changes in the dynamics of soil organic matter that could be expected from climate change add further uncertainty to predictions of future change in exchangeable Al concentrations in soils.

In summary, the natural downward movement and deposition of Al within the upper soil profile is altered by acidifying deposition if the release of base cations is insufficient to buffer atmospheric inputs of acidity. Rather than be deposited as an alumino-organic complex, Al mobilized by acidifying deposition tends to remain in solution in inorganic forms that can be transported out of the soil and into surface waters. Depletion of exchangeable base cations generally precedes the mobilization of inorganic Al; therefore, as base cation concentrations in drainage water decrease, inorganic Al concentrations may increase. Increases in concentrations of inorganic Al have been documented at several locations in base-cation depleted soils in the U.S. and Europe. In soils with base saturation values less than about 15 to 20%, the ratio of exchangeable Ca to Al is typically low in upper mineral soils (Lawrence, 1995).

3.2.1.6. Episodic Acidification

The status of surface water chemistry can be examined and reported as chronic condition or episodic condition. Chronic condition refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic condition refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralization of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry exhibits lower pH and acid neutralizing capacity (ANC) during episodes than during baseflow conditions.

One of the most significant effects of acidifying deposition on surface water chemistry is the short-term change in chemistry termed “episodic acidification.” While natural processes contribute to seasonal and short-term increases in the acidity of surface waters, research from several regions in the U.S. indicates that acidifying deposition likely has substantially increased the magnitude, frequency, and biological effects of episodic acidification events. Many streams that exhibit chemical conditions during base flow (relatively stable flows that occur between storms) that is suitable for aquatic biota, are subject to occasional episodic acidification with adverse consequences. During such episodes, both stream flow and water chemistry can change markedly (Figure 3-3). Episodic acidification can cause declines in pH and ANC, and most significantly, increases in inorganic Al concentrations in stream waters of the

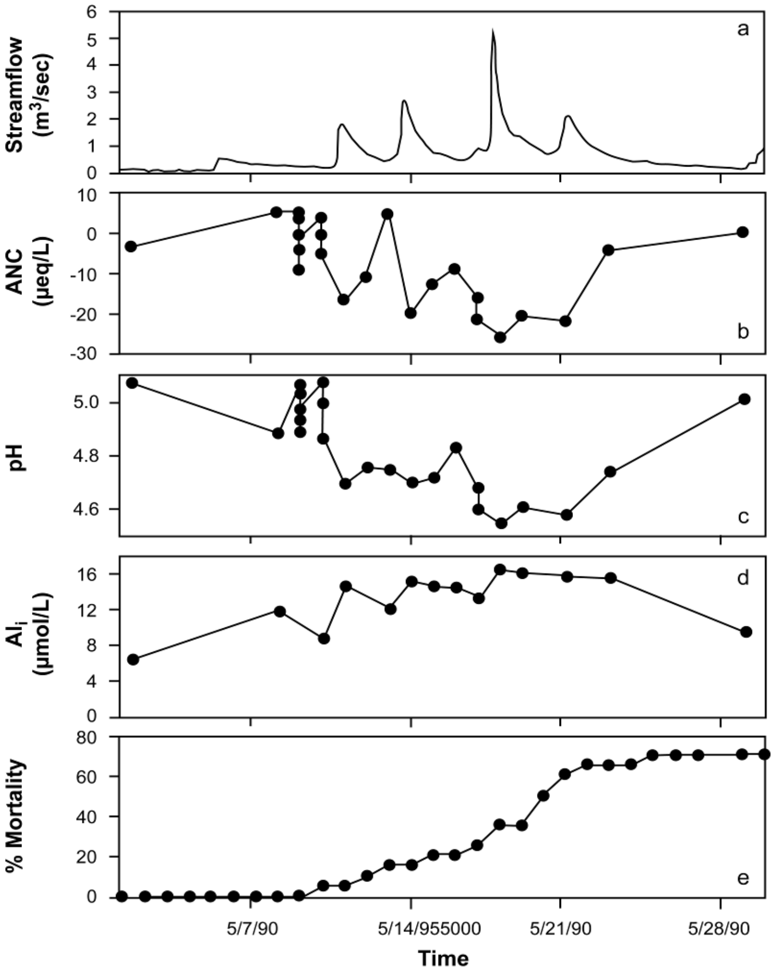
Northeast, Pennsylvania, and in the central Appalachian Mountain region (Charles, 1991). Episodic decreases in pH and ANC have been documented throughout the country (Wigington et al, 1990).

The EPA's Episodic Response Project (ERP) confirmed the chemical and biological effects of episodic pH and ANC depressions in lakes and streams in parts of the eastern U.S. The ERP illustrated the processes of episodic acidification and the role played by SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition in the episodic acidification of surface waters. The ERP also clearly showed that the episodic chemical response that has the greatest effect on aquatic biota is increased inorganic Al concentration (Wigington Jr., 1996). During drought periods, atmospherically deposited S that has been stored in wetland soils in reduced form can be reoxidized and mobilized by heavy rains. This remobilized S, as SO_4^{2-}, has been shown to contribute to episodic acidification of receiving waters in southeastern Canada and the northeastern U.S. (Eimers, 2007; Eimers, 2002; Mitchell, 2006).

Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in inorganic Al in waters having low Ca concentration. Baker et al. (1990a) concluded that episodes are most likely to affect biota if the episode occurs in waters with pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. The most thorough characterization of episodic variation in stream chemistry in the U.S. was conducted through the ERP, in which 13 low-order streams (watershed areas less than 24 km^2) in the Adirondack and Catskill regions of New York and the Appalachian Plateau in Pennsylvania were monitored from 1988 to 1990 (Wigington Jr., 1996). About 10% of the acid episodes involved decreases in ANC of up to 200 μeq/L, decreases in pH of up to one unit, and increases in concentrations of inorganic Al of up to 15 μM (Wigington Jr., 1996). Results showed that acid episodes reduced the size of fish populations and eliminated acid-sensitive species if median high-flow pH was less than 5.2 and inorganic Al concentration exceeded 3.7 μM, despite the relatively short duration of episodes (Baker, 1996).

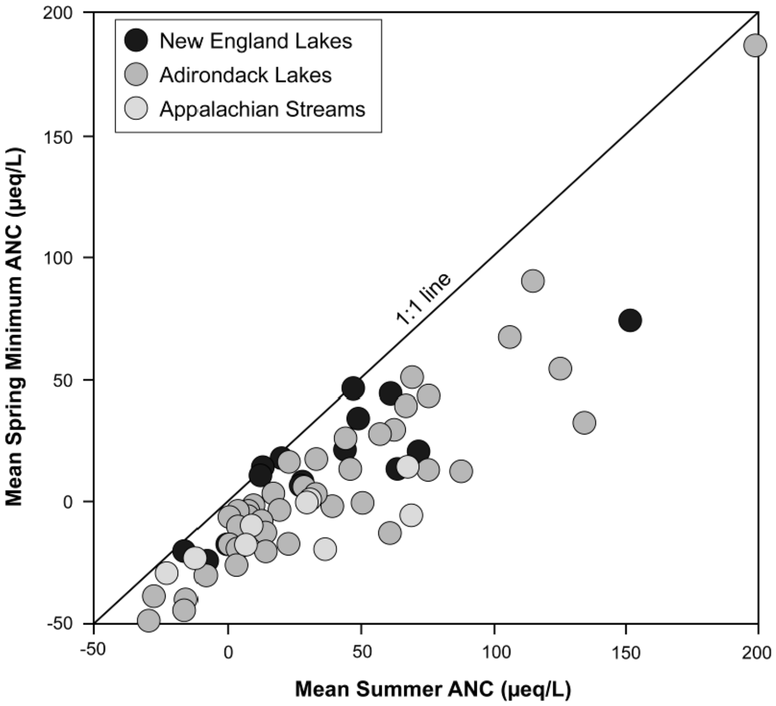
Results from the ERP demonstrated that episodic acidification can have long-term adverse effects on fish populations. Streams with suitable chemistry during low flow, but low pH and high inorganic Al levels during high flow, had substantially lower numbers and biomass of brook trout than were found in non-acidic streams (Wigington Jr., 1996).

In many regions, the most severe acidification of surface waters generally occurs during spring snowmelt (Charles, 1991). Stoddard et al. (2003) found that, on average, the difference between spring and summer ANC during baseflow in New England, the Adirondacks, and the Northern Appalachian Plateau was about 30 μeq/L during the period 1990 to 2000 (see Figure 3-4). This implies that lakes and streams in these regions would need to recover to chronic ANC values above 30 μeq/L before they could, on average, be expected to not experience acidic episodes (Stoddard, 2003). However, the estimate of 30 μeq/L is certain to be low because the comparison was made with non-episodic sampling in spring, expressed as average spring ANC. ANC measured during episodic spring events would be expected to be lower than average ANC during spring.



Source: Driscoll et al. (2001b)

Figure 3-3. Results of an in situ bioassay during a period of episodic acidification in Buck Creek, Adirondack Mountains, in spring 1990. (a) discharge, (b) acid neutralizing capacity, (c) pH, (d) concentration of inorganic monomeric aluminum, and (e) cumulative percentage of mortality of brook trout over time.



Source: Stoddard et al. (2003).

Figure 3-4. Relationship between mean summer acid neutralizing capacity (ANC) and the mean of minimum spring ANC values at long-term monitoring lake and stream sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

The most important factor governing watershed sensitivity to episodic acidification is the pathway followed by snowmelt water and storm-flow water through the watershed. The routing of water as it flows through a watershed determines the degree of contact with acidifying or neutralizing materials and therefore influences (along with soils and bedrock characteristics) the amount of episodic acidification that occurs. In any given watershed, surface water ANC may vary in time depending upon the proportion of the flow that has contact with ANC supplying substrate; in general, the more subsurface contact, the higher the surface water ANC (Turner, 1990). This pattern can be attributed in part to higher base saturation and (in some watersheds) greater SO_4^{2-} adsorption capacity in subsurface soils. It may also relate to the accumulation in the upper soil horizons of acidic material derived from atmospheric deposition and decay processes (Lynch, 1989; Lynch, 1989; Turner, 1990).

Streams having acidic episodes show significantly higher fish mortality and other aquatic community changes as compared with streams in which ANC remains above zero (Wigington, 1993). Results from in situ bioassay studies from across the Eastern U.S. show that acidic episodes (with associated low pH and elevated inorganic Al concentrations, and high streamwater discharge) caused rapid fish mortality under some conditions (Baker, 1996; Bulger, 1999)Driscoll et al., 2001b). For example, streams with suitable conditions during low flow, but moderate-to-severe episodic acidification during high flow, had higher fish mortality in bioassays, higher net downstream movement of brook trout during events, and lower brook trout abundance and biomass compared to streams that did not experience appreciable episodic acidification. These episodically affected streams lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into refugia (areas with higher pH and lower inorganic Al) during episodes only partially mitigated the adverse effects of episodes (Baker, 1996).

Consideration of episodic acidification greatly increases the extent and degree of estimated effects for acidifying deposition on surface waters. In the Northeast, inclusion of episodically acidified water bodies in regional assessments substantially increases estimates of the extent of surface water acidification. For example, baseflow samples collected from 1991 to 1994 through the EPA Temporally Integrated Monitoring of Ecosystems (TIME) Program indicated that 10% of the 1,812 lakes larger than 1 ha surface area in the Adirondack region could be considered chronically acidic (fall index ANC values less than 0 μeq/L), but that an additional 31% of these lakes had fall index ANC values less than 50 μeq/L and were, therefore, estimated to be susceptible to episodic acidification (Driscoll, 2001).

Lawrence (2002) estimated the extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km^2) using an index site at the base of the watershed that became episodically acidified at high flows. Upstream sites with a lower base flow ANC than the index site at the same date and time were found to have a high likelihood of becoming episodically acidified. Base flow sampling of 122 upstream sites indicated that approximately 16% of the total upstream reaches had chronic ANC less than 10 μeq/L, but that 66% of the stream reaches had episodic ANC less than 10 μeq/L.

In the Southeast, a recent study by Deviney et al. (2006) within Shenandoah National Park, Virginia used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the Shenandoah National Park catchments using catchment geology and topography to stratify watershed response patterns. On the basis of the models, they concluded that a large number of Shenandoah National Park streams had 6– to 168–h periods of low ANC values, which may stress resident fish populations (Deviney, 2006). Specifically, on the basis of a 4–year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions that are classified with respect to brook trout response categories (Bulger, 1999) as indeterminate (ANC 20 to 50), episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous hours. Many catchments were predicted to have successive years of ANC values sufficiently low as to potentially extirpate some aquatic species (Deviney, 2006). The authors of the study reported that smaller catchments are more vulnerable to episodic acidification than larger catchments underlain by the same bedrock. Results from a study of six intensively monitored sites in the Park demonstrated a clear pattern of larger episodic ANC depressions in streams having higher median ANC than in streams with lower ANC. However, streams with low median ANC typically experienced decreases that resulted in minimum ANC values associated with toxicity to biota. These low ANC conditions were more likely to occur in streams underlain by siliclastic bedrock than in those with granitic or basaltic bedrock.

In the West, episodic acidification is an especially important issue for surface waters throughout high-elevation areas. Where soils are sparse, as in alpine regions, most snowpack N is flushed to surface waters early in the snowmelt period. Even though there is evidence through use of isotopic tracers that much of the N was cycled microbially, snowpack N has been reported to cause temporary acidification of alpine streams (Williams, 2000; Campbell, 2002). Snowmelt-related temporary acidification of alpine lakes and streams and associated effects have been reported in the Rocky Mountains (Brooks, 1996; Williams, 1996) and Sierra Nevada (Johannessen, 1978; Stoddard, 1995).

There have been no studies in the U.S. to determine if either the severity or frequency of episodic acidification has lessened in response to recent decreases in acidifying deposition over the past three decades. In a study of two streams in Nova Scotia (Laudon, 2002) noticeable trends in ANC during different phases of storm hydrographs from 1983 to 1998 were generally not detected other than during the peak-flow phase of one stream (an increase of 0.87 μeq/L).

In summary, the vast majority of water chemistry data for acid-sensitive lakes and streams in the U.S. were collected at low stream flow. It is well known, however, that water chemistry changes with season and with weather. Water chemistry is most stressful to aquatic biota (lowest pH and ANC; highest inorganic Al concentration) during high flow following snowmelt and rainstorms. During such conditions, stream chemistry can be toxic to species that thrive under chemical conditions more typical of base flow. The EPA's ERP and other more localized studies have quantified the effects of episodes on fish. Episodes are driven by hydrological processes, but the acidification that occurs is largely a result of acidifying deposition, especially in cases where inorganic Al has been mobilized. Consideration of such variability in water chemistry is critical for accurate assessment of the extent, magnitude, and biological effects of surface water acidification. The biological effects of changes in surface water chemistry are discussed in greater detail in Section 3.2.3.2.

3.2.2. Terrestrial Ecosystems

The changes in major biogeochemical processes and soil conditions described above contribute to a series of effects on terrestrial ecosystems. These changes are manifest in both chemical and biological effects that can include reduced soil base saturation, altered key element ratios, changes in plant productivity, reduced stress tolerance of sensitive plant species, and in some cases, increased mortality of canopy trees. Specific chemical indicators of change can be used to assess sensitivity to, and effects from, acidifying deposition. In the U.S., terrestrial effects of acidification are best described for forested ecosystems, with supportive information on other plant communities, including shrubs and lichens.

3.2.2.1. Chemical Effects

There are several chemical indicators that provide useful information about the acid-base status of soils and its influence on terrestrial vegetation. These include (1) soil base saturation, (2) Ca:Al ratio, and (3) C:N ratio (see Table 3-2). Each chemical indicator provides insight into the level to which the ecosystem has acidified and may be susceptible to associated biological effects. These chemical indicators may also be used to monitor the extent of acidification or recovery that occurs in forest ecosystems as deposition rates of S and N change. As such, several chemical indicators and possible effect thresholds have been developed and applied in conjunction with efforts to estimate critical loads. The critical loads approach is discussed in more detail in Section 3.1.2.

Table 3-2. Examples of chemical indicators of effects from acidifying deposition to terrestrial ecosystems.

Examples of Chemical Indicators	Example Possible Effect Threshold	References
Soil base saturation	10–20%	Lawrence et al. (Lawrence, 2005) Driscoll et al. (Driscoll, 2001) Cronan et al. (Cronan, 1990)
Soil solution Ca:Al ratio	1.0	Cronan and Grigal (Cronan, 1995)
Soil C:N ratio	20–25	Aber et al. (2003)

Soil Base Saturation

In soils with a base saturation less than about 15 to 20%, exchange ion chemistry is dominated by Al (Reuss, 1983). Under this condition, responses to sulfuric and nitric acid inputs largely involve the release and mobilization of inorganic Al through cation exchange. This is the form of Al that interferes with uptake of Ca by plant roots and is also toxic to many forms of aquatic biota (Cronan, 1995; Baker, 1990).

The soil O horizon tends to have a much higher base saturation than the underlying mineral soil, despite having lower pH due to organic acidity. The base saturation of the B horizon is in a Spodosol can be sensitive to base cation depletion from leaching by SO_4^{2-} and NO_3^-, and is therefore useful for assessing base status with regard to acidifying deposition. Little direct work has been done to relate soil base saturation to forest health, but Cronan and Grigal (1995) determined that base saturation values below about 15% in the B horizon of forests in the northeastern U.S. could lead to effects from Al stress. Lawrence et al. (1995) also observed pronounced decreases in diameter growth of Norway spruce in northwestern Russia, where base saturation decreased from 30% to 20% in the upper 10 cm of the B horizon over a period of 37 years.

Base saturation values less than 10% predominate in the soil B horizon in the areas in the U.S. where soil and surface water acidification from acidifying deposition have been most pronounced, including conifer and hardwood forests in the Adirondack Mountains (Sullivan, 2006), red spruce forests throughout the Northeast (David, 1996, hardwood forests in the Allegheny Plateau (Bailey, 2004, and conifer and hardwood forests in the southern Appalachian Mountains (Sullivan, 2003). In a study of sugar maple decline throughout the Northeast, Bailey et al. (2004) found threshold relationships between base cation availability in the upper B soil horizon and sugar maple mortality at Ca saturation less than 2%, and Mg saturation less than 0.5% (Bailey et al., 2004). The authors concluded that base saturation varied as a function of topography, geologic parent material, and acidifying deposition.

Aluminum Concentration in Soil Solution: Calcium to Aluminum Ratio

Al may be toxic to tree roots. Plants affected by high Al concentration in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially Ca (Parker, 1989). Ca is well known as an ameliorant for Al toxicity to roots in soil solution, as well as to fish in a stream. However, because inorganic Al tends to be increasingly mobilized as soil Ca is depleted, elevated concentrations of inorganic Al tend to occur with low levels of Ca in surface waters. Mg, and to a lesser extent Na and K, have also been associated with reduced Al toxicity.

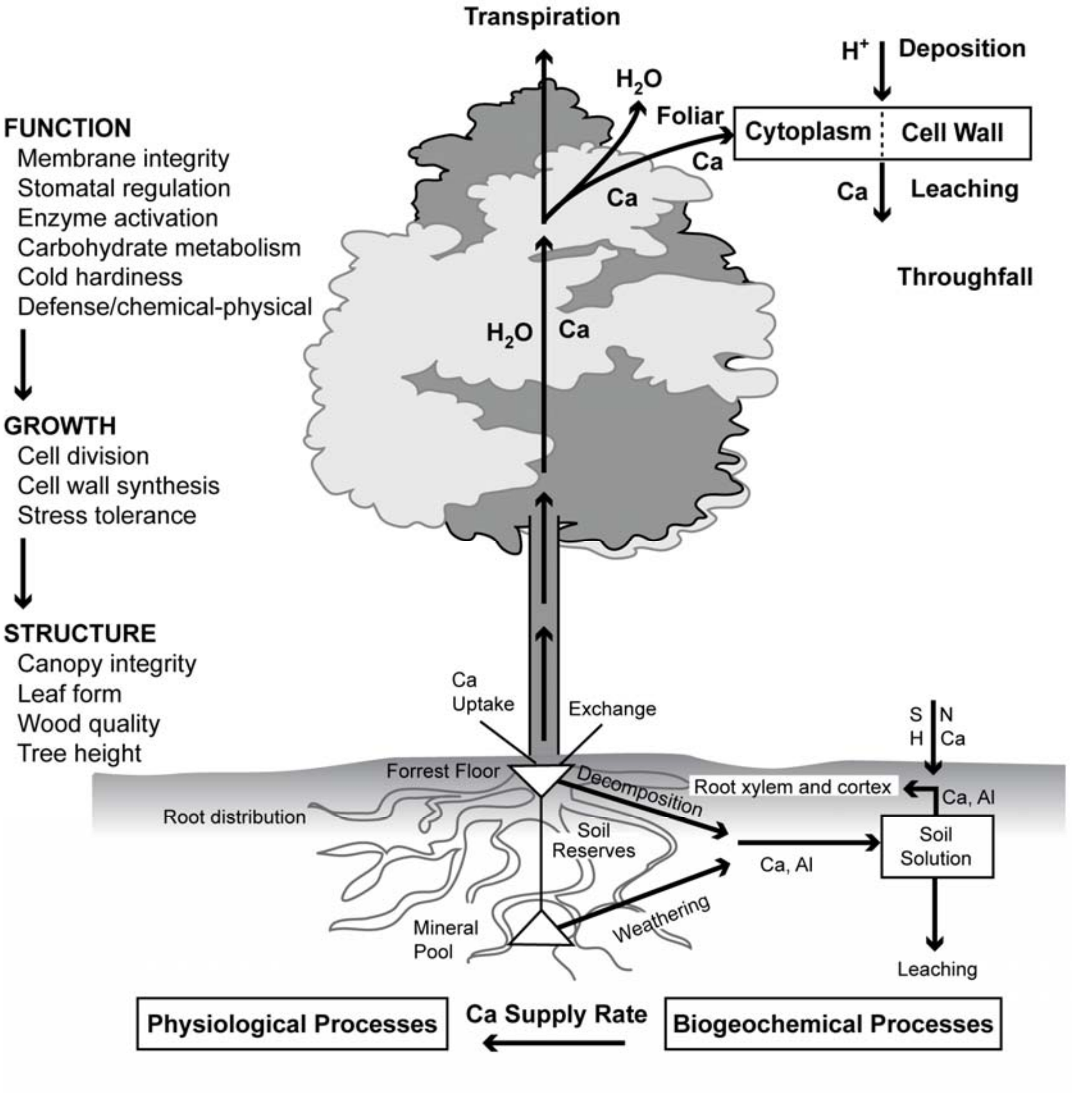
Dissolved Al concentrations in soil solution at spruce-fir study sites in the southern Appalachian Mountains frequently exceed 50 µM and sometimes exceed 100 µM (Johnson, 1991; Joslin, 1992^1996). All studies reviewed by Eagar et al. (1996) showed a strong correlation between Al concentrations and NO_3^- concentrations in soil solution. They surmised that the occurrence of periodic large pulses of NO_3^- in solution were important in determining Al chemistry in the soils of southern Appalachian Mountain spruce-fir forests.

The negative effect of Al mobilization on Ca uptake by tree roots was proposed by Shortle and Smith (1988), and substantial evidence of this relationship has accumulated over the past two decades through field studies (McLaughlin, 1992; Schlegel, 1992; Minocha, 1997; Shortle, 1997; Kobe, 2002) and laboratory studies (Sverdrup and Warfvinge, 1993; see also review of (Cronan, 1995). Based on these studies, it is clear that high inorganic Al concentration in soil water can be toxic to plant roots. The toxic response is often related to the concentration of inorganic Al relative to the concentration of Ca, expressed as the molar ratio of Ca to inorganic Al in soil solution. As a result, considerable effort has been focused on determining a threshold value for the ratio of Ca to Al that could be used to identify soil conditions that put trees under physiological stress.

From an exhaustive literature review, Cronan and Grigal (1995) estimated that there was a 50% risk of adverse effects on tree growth if the molar ratio of Ca to Al in soil solution was as low as 1.0. They estimated that there was a 100% risk for adverse effects on growth at a molar ratio value below 0.2 in soil solution.

The information available to define levels of risk for the Ca:Al ratio is complicated by differences in natural soil conditions. As a result of these complications, the risk levels for the ratio defined in laboratory experiments have not necessarily been successfully applied to field conditions. For example, Johnson et al. (Johnson, 1994; , 1994) reported Ca:Al ratios above 1.0 through most of 4 years in the Oa and B horizons of a high-elevation red spruce stand experiencing high mortality. In the 3−year study of DeWitt et al. (2001), Al additions lowered molar Ca to inorganic Al ratios in soil solutions of a Norway spruce stand below 0.5, but the authors found no response other than reduced Mg concentrations in needles in the third year, which was a possible precursor to damage.

In summary, a molar ratio of Ca to Al in soil solution can be used as a general index that suggests an increasing probability of stress to forest ecosystems as the ratio decreases. The ratio value of 1.0 is proposed as a general damage threshold, but cannot be interpreted as a universally applicable threshold in all natural systems. Tree species vary widely in their sensitivity to Al stress (See Figure 3-5). In addition, Al concentrations in soil solution often exhibit pronounced spatial and temporal variability that is difficult to relate to root activity. Finally, the form of Al present in solution plays an important role in determining toxicity. For example, organically complexed Al, which predominates in upper, organic-rich soil horizons, is essentially nontoxic (Baker, 1982; Cronan, 1995).



Source: Fenn et al. (2006)

Figure 3-5. Diagram based on Fenn et al. (Fenn, 2006) shows indicators of forest physiological function, growth and structure that are linked to biogeochemical cycles through processes that control rates of Ca supply. Calcium affects plant physiological processes that influence growth rates and the capacity of plants to resist environmental stresses such as extremes of temperature, drought, insects, and diseases. Therefore, acidifying deposition, which can deplete soil Ca or interfere with Ca uptake through mobilization of soil Al, is a concern for maintenance of forest health.

Soil N: Carbon to N Ratio

Mechanisms of retention and release of N in forest ecosystems are not fully understood, but the adverse effects of nitrification and associated acidification and cation leaching have been consistently shown to occur only in soils with a C:N ratio below about 20 to 25 (Aber, 2003; Ross, 2004) .This observation makes the C:N ratio especially useful because N mineralization and nitrification rates are difficult to measure directly under natural conditions. All available measurement approaches disturb the soil and often cause artificially high rates. Therefore, field measurement provides a relative index rather than a realistic quantitative rate (Ross, 2004). Approaches for measuring N mineralization and nitrification also are subject to high degrees of variability, both temporally (hourly to seasonal) and spatially (down to the sub meter level). Measurements of total OC and N however, are less variable in space and time and are therefore more straightforward to document than N mineralization and nitrification rates. Also, ratios of C to N in the forest floor are inversely related to acidifying deposition levels, although the relationship is stronger for hardwood stands than conifer stands (Aber, 2003). In summary, these factors make the C:N ratio a reliable and relatively straightforward measure for identifying forest ecosystems that may be experiencing soil acidification and base leaching as a result of N input and increased nitrification.

Summary of Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to terrestrial ecosystems. The strongest evidence for a causal relationship comes from studies of forested ecosystems, with supportive information on other plant communities, including shrubs and lichens; grasslands are likely less sensitive to acidification than woodlands. Soil acidification occurs in response to inputs of sulfuric acid (H_2SO_4) and nitric acid (HNO_3); the effect can be neutralized by weathering or base cation exchange. Soil acidification is a natural process, but is often accelerated by acidifying deposition. Acidifying deposition is important in decreasing concentrations of exchangeable base cations in soils. The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidifying deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

Nitrification is mediated by autotrophic bacteria that derive energy by reducing NH_4^+ to NO_3^-. Nitrification produces acidity in the form of HNO_3 as a byproduct. The HNO_3 produced contributes to the acidification of soils and surface waters.

There are three useful indicators of chemical changes and acidification effects on terrestrial ecosystems, showing consistency and coherence among multiple studies: soil base saturation, Al concentration in soil water, and soil C:N ratio.

- Soil base saturation is the concentration of exchangeable bases as a percent of the total soil cation exchange capacity. Once base saturation decreases to a critical level (approximately 15–20%), inputs of H_2SO_4 and HNO_3 are increasingly buffered by release of inorganic Al through cation exchange.

- Aluminum is toxic to some tree roots. Plants affected by high inorganic Al concentrations in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially calcium (Ca) (Parker, 1989).

- The C:N ratio of soil is used to indicate alterations to the N biogeochemical cycle. If the C:N ratio of soils falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils.

3.2.2.2. Biological Effects

Acidifying deposition can affect terrestrial ecosystems via direct effects on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to Al toxicity and decreased ability of plant roots to take up base cations (especially Ca) and water from the soil (Cronan, 1995). Acidifying deposition to acid-sensitive soils can cause soil acidification, increased mobilization of inorganic Al from soil to drainage water, and depletion of the pool of stored base cations in the soil. Effects on the soil and direct effects of acidifying deposition on foliage can influence the response of plants to climatic stresses such as drought and cold temperature. They can also influence the sensitivity of plants to other stresses, including insect pests and disease (Joslin, 1992).

The combined effects of acidifying deposition and other stressors on terrestrial vegetation are typically measured using indices such as percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback (see Table 3-3). Each of these variables has a rating system used to quantify forest condition and relate the variables to foliar and soil nutrient concentrations.

Table 3-3. Example biological effects indicators in terrestrial ecosystems.

Indicator Species	Example of Health Indices	References
Red spruce	Percent dieback of canopy trees	Shortle et al. (Shortle, 1997) DeHayes et al. (1999)
Sugar maple	Basal area dead sugar maple (as %) Crown vigor index Fine twig dieback	Bailey et al. (1999) Drohan and DeWalle (2002)

The effects of acidifying deposition on the health, vigor, and productivity of terrestrial ecosystems in the U.S. are best documented in spruce-fir and northern hardwood forests of the eastern U.S. Some information is also available for individual species such as red spruce, sugar maple, and some species of lichen. In the western U.S., the health of ponderosa pine and Jeffrey pine has been affected by air pollution, but such effects have largely been attributed to ozone exposure, not acidifying deposition.

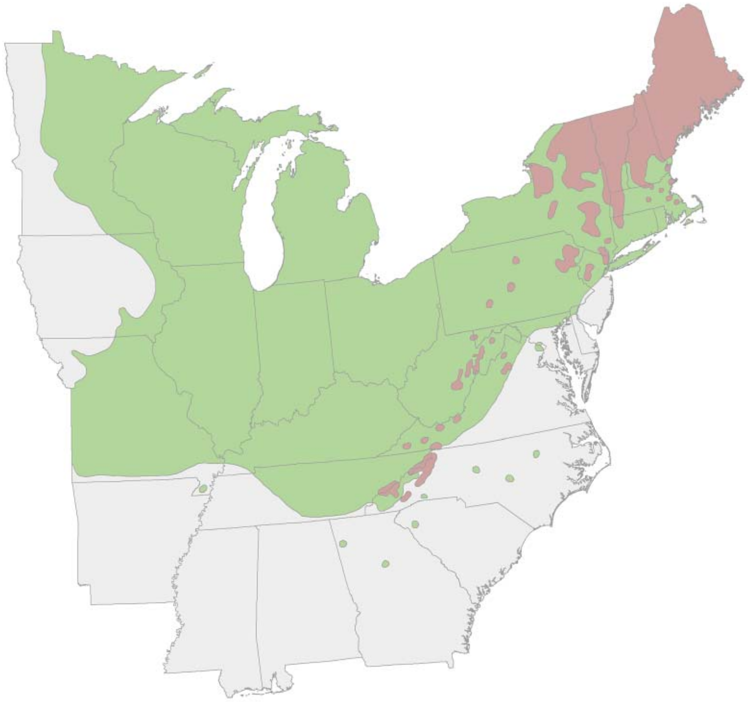
Health, Vigor, and Reproduction of Tree Species in Forests

Both coniferous and deciduous forests throughout the eastern U.S. are experiencing gradual losses of base cation nutrients from the soil due to accelerated leaching from acidifying deposition. This change in base cation nutrient availability may reduce the quality of forest nutrition over the long term. Evidence suggests that red spruce and sugar maple in some areas in the eastern U.S. have experienced declining health as a consequence of acidifying deposition. Existing information regarding the effects of acidifying deposition on these two forest tree species is summarized below and reference is made to specific health indicators where such information is available.

Red Spruce

Red spruce (*Picea rubens*) is a conifer that occurs mainly in the Northeastern U.S. and at scattered high-elevation sites in the Appalachian Mountains (see Figure 3-6). Red spruce dieback or decline has been observed across high elevation landscapes of the northeastern, and to a lesser extent, southeastern U.S. At high elevations in the Adirondack and Green Mountains, more than 50% of the canopy red spruce trees died during the 1970s and 1980s. In the White Mountains, about 25% of the canopy spruce died during that same period. Dieback of red spruce has also been observed in mixed hardwood-conifer stands at relatively low elevations in the western Adirondack Mountains, an area that receives high inputs of acidifying deposition (Shortle, 1997); acidifying deposition has been implicated as a causal factor (DeHayes, 1999). The frequency of freezing injury to red spruce needles has increased over the past 40 years, a period that coincided with increased emissions of S and N oxides and increased acidifying deposition (DeHayes, 1999).

From the 1940s to 1970s, red spruce growth also declined at high elevation in the Southeastern U.S. (McLaughlin et al., 1987; and Zelaker, 1992; Eager et al., 1996), as emissions of both NO_X and SO_2 increased to maxima of about 25 and 30 million tons/yr, respectively. The growth decline in Great Smoky Mountains National Park in North Carolina and Tennessee started earlier at higher elevations (around the 1940s and 1950s) and was steeper, while the growth decline developed at lower elevation sites 20 years later. After the 1980s, red spruce growth increased substantially at both the higher- and lower-elevation sites, corresponding to a decrease in SO_2 emissions in the U.S. (to about 20 million tons/yr by 2000), while nitrogen oxide emissions held fairly steady (at about 25 million tons/yr). Annual emissions of S plus nitrogen oxides explained about 43% of the variability in red spruce tree ring growth between 1940 and 1998. Climatic variability accounted for about 8% of the growth variation for that period. At low elevation, changes in radial growth could be explained by climatic variables only, and there was no correlation with national S plus nitrogen oxide emissions trends. Recent reductions in S oxide emissions may have changed growth trajectories (Webster, 2004).

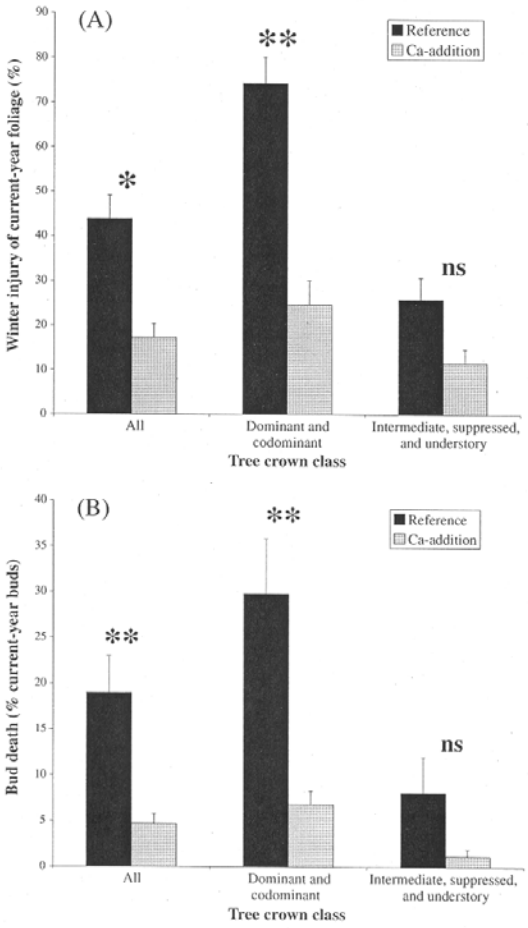


Source: Little (1971) http://esp.cr.usgs.gov/data/atlas/little/

Figure 3-6. Distribution of red spruce (rose) and sugar maple (green) in the eastern U.S. These two tree species have experienced adverse effects in portions of their ranges that have been attributed to acidification from acidifying deposition. Tree distribution data were obtained from Little's Ranges.

The observed dieback in red spruce has been linked, in part, to reduced cold tolerance of red spruce needles, caused by acidifying deposition. Results of controlled exposure studies showed that acidic mist or cloud water reduced the cold tolerance of current-year red spruce needles by 3 to 10 ºC (DeHayes, 1999). There is a significant positive association between cold tolerance and foliar Ca in trees that exhibit foliar Ca deficiency. The membrane-associated pool of Ca, although a relatively small fraction of the total foliar Ca pool, strongly influences the response of cells to changing environmental conditions. The plant plasma membrane plays an important role in mediating cold acclimation and low-temperature injury (EPA, 2004). The studies of DeHayes et al. (DeHayes, 1999) suggested that direct acidifying deposition on red spruce needles preferentially removes membrane-associated Ca. More recently, a link has been established between availability of soil Ca and winter injury (Hawley, 2006)based on an experimental addition of Ca at the Hubbard Brook Experimental Forest, New Hampshire. This study demonstrated that Ca depletion from soil was associated with winter injury of red spruce foliage during 2003 when winter injury was unusually high throughout the region (see Figure 3-6).

In summary, the weight of evidence suggests that changes in soil chemistry have contributed to high mortality rates and decreasing growth trends of red spruce trees in some areas over the past three decades (Sullivan et al., 2002a). In forests where this has occurred, which are mainly located at high elevation, changes in red spruce growth rates are attributable, at least in part, to base cation deficiencies related to decreased availability of Ca and increased availability of Al as a result of acidifying deposition effects on soils. Important factors appear to include depletion of base cations in upper soil horizons by acidifying deposition, Al toxicity to tree roots, and accelerated leaching of base cations from foliage as a consequence of acidifying deposition. Recent studies also show improvements in red spruce growth with decreasing emissions of SO_2 in the U.S. (Webster, 2004).



Source: Hawley et al. (2006)

Figure 3-7. Mean (± standard error) of current-year red spruce needle winter injury in reference and calcium-addition watersheds and among crown classes, expressed as foliar injury (A) and bud mortality (B). Watershed means were either not significantly different (ns) or statistically different at $p < 0.05$ (*) or $p < 0.01$ (**) based on nested analyses of variance.

Sugar Maple

Sugar maple (*Acer saccharum*) is the deciduous tree species of the Northeastern U.S. that is most commonly associated with adverse acidification-related effects of S and N deposition, though other base cation accumulating hardwoods may also be at risk (Driscoll et al., 2001b). Sugar maple is distributed throughout the northeastern U.S. and central Appalachian Mountain region as a component of the northern hardwood forest Figure 3-6.

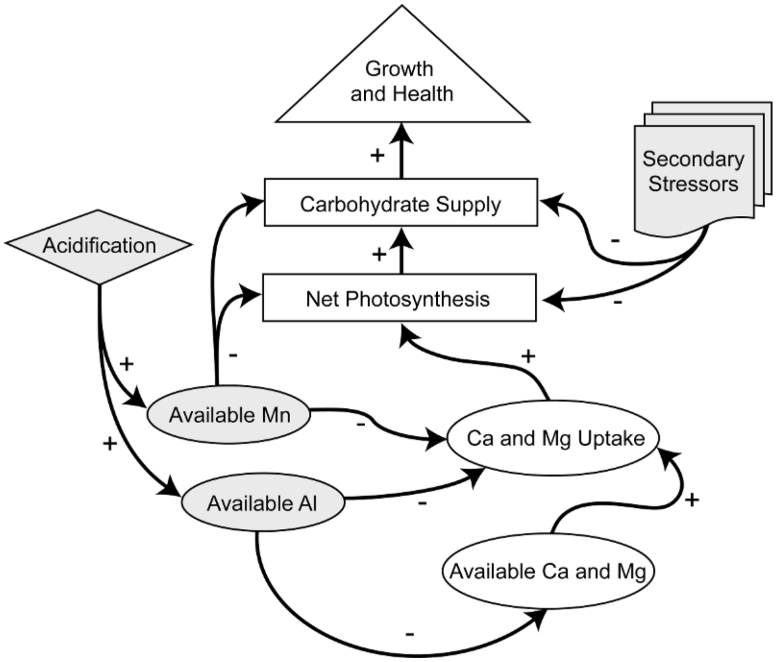
A conceptual view of the interactions of acidifying deposition and other stressors in sugar maple decline is provided in Figure 3-8. Several studies, mainly in Pennsylvania, have hypothesized that sugar maple decline is linked to the occurrence of relatively high levels of acidifying deposition and base-poor soils (Horsley et al., 2000; Bailey et al., 2004; Hallett et al., 2006; Moore and Ouimet, 2006).

Acidifying deposition may be contributing to episodic dieback of sugar maple in the Northeast through depletion of nutrient cations from marginal soils (Figure 3-8). Horsley et al. (2000) found that dieback at 19 sites in northwestern and northcentral Pennsylvania and southwestern New York was correlated with combined stress from defoliation and soil deficiencies of Mg and Ca. Dieback occurred predominately on ridgetops and on upper slopes, where soil base cation availability was much lower than occurred in the deeper soils found on middle and lower slopes (Bailey et al., 2004). A long-term decrease in soil pH since 1960 (0.78 pH unit decrease in the O horizon, and 0.23 pH unit decrease in the A horizon) in Pennsylvania hardwood forests has been documented, along with decreases in soil Ca and Mg concentrations. Declining sugar maples were shown to be deficient in foliar Ca and Mg (Drohan, 1997). More recent research has strengthened understanding of the role of cation nutrition in sugar maple health at a regional scale across a broad range of conditions (Hallett et al., 2006).

Drohan et al. (2002) investigated differences in soil conditions in declining versus non-declining sugar maple plots in northern Pennsylvania from the U.S. Department of Agriculture (USDA) Forest Service's Forest Inventory and Analysis (FIA) program. Soils in plots with declining sugar maple tended to have lower base cation concentrations and pH, and Ca:Al ratio less than 1. Regressions between foliar and soil chemistry showed that foliar nutrition was highly correlated with the chemistry of the upper 50 cm of soil (Drohan et al., 2002).

Juice et al. (Juice, 2006) added Ca to watershed 1 (W1) at HBEF in October 1999 sufficient to raise the pH of the O_{ie} soil horizon from 3.8 to 5.0 and the O_a horizon from 3.9 to 4.2. Subsequently, they measured the response of sugar maples to the Ca fertilization. Foliar Ca of canopy sugar maples increased markedly and foliar Mn declined. By 2005, crown condition was much healthier then in the untreated reference watershed (W6). The density of sugar maple seedlings increased significantly following high seed production in 2000 and 2002. In addition, sugar maple germinants were 50% larger on W1 and mycorrhizal colonization of seedlings was much higher in the treated watershed (22.47% of root length) as compared with the reference watershed (4.4%) (Juice, 2006).

In general, evidence indicates that acidifying deposition in combination with other stressors is a likely contributor to the decline of sugar maple trees that occur at higher elevation, on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils having high percentages of rock fragments (Drohan, 2002). Such site conditions are representative of the kinds of conditions expected to be most susceptible to adverse effects of acidifying deposition because of probable low initial base cation pools and high base cation leaching losses.



Source: Hallett et al. (2006).

Figure 3-8. Conceptual diagram outlining the current understanding of sugar maple decline. Positive and negative signs indicate the nature of the correlative relationship between variables.

Other Forest Ecosystems

Loss of base cations, specifically Ca^{2+}, has also been implicated in increased susceptibility of flowering dogwood (*Cornus florida*) to its most destructive disease, dogwood anthracnose (Figure 3-9). Flowering dogwood is a dominant understory species of hardwood forests in the Eastern U.S. (Holzmueller et al. 2006), with important ecosystem functions as a food source for numerous species of animals, and as a large contributor to available Ca in forest litter. It is also recognized as a significant cultural and aesthetic resource throughout its range. Since dogwood anthracnose, a mostly fatal disease, was first reported in 1976 in New York State, it has spread over a large portion of the species' range, generally resulting in mortality greater than 90% in affected stands. Pacific dogwood (*Cornus nutallii*) is similarly affected, but because its abundance within its range was much lower before the disease first appeared, the effect has received less notice. Susceptibility to the disease, and disease severity in stands, appear dependent on several factors, including acid deposition and various edaphic characteristics and meteorological conditions.

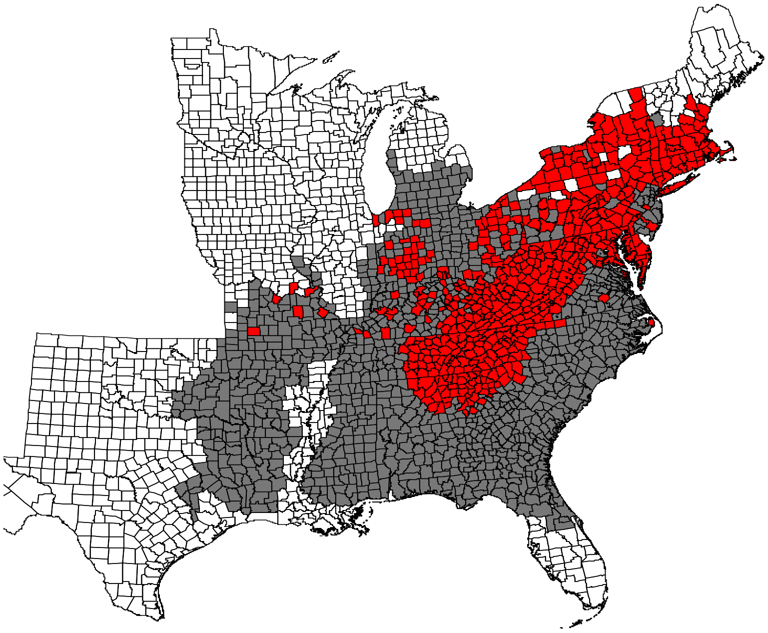


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Figure 3-9. Native range of flowering dogwood (*Cornus florida*) (dk. gray) and the documented range of dogwood anthracnose in the eastern U.S. (red). 2002 data from the U.S. Forest Service.

In 1990 and 1991, Britton and Berang (Britton, 1996) exposed 200 potted dogwood plants to simulated acid rain (SAR) at 4 levels of pH between 2.5 and 5.5. The plants were then placed among natural stands showing symptoms of the disease. In both years, there was a fourfold increase in percentage of leaf area affected from the plants treated with SAR at a pH of 5.5 to those treated with SAR at a pH of 2.5. In 1992 and 1993, four combinations of SAR with a pH of 2.5 or 5.5 were applied separately to the foliage and the soil before inoculation. The percent of leaf area affected was approximately two to four times greater for plants grown in soil treated with acidic SAR, regardless of foliar treatment, suggesting that the worsening of anthracnose damage by acid deposition occurs mostly through soil effects.

In a study of the effects of Ca, K, and Mg on dogwood density in forest stands, and on resistance to anthracnose in containerized dogwood plants, Holzmueler et al. (2007) found a strong relation between soil available cations, particularly Ca^{2+}, and dogwood density in Great Smoky Mountains National Park, where dogwood anthracnose has resulted in significant damage. The mortality of potted dogwood plants fertilized with solutions varying in Ca^{2+}, K^{+}, or Mg^{2+} concentration, and exposed to anthracnose, was both greatest and most rapid when Ca^{2+} was deficient, but not when K^{+} and Mg^{2+} were deficient.

Data on the possible effects of S and N deposition on the acid-base characteristics of forests in the U.S., other than the spruce-fir and northern hardwood forest ecosystems, are limited. Ponderosa pine (*Pinus ponderosa*) seedlings exposed to acidic precipitation (pH 5.3, 4.4, 3.5 of 1:1 NHO_3:H_2SO_4)

showed no significant changes in growth (Temple et al., 1992). Fenn et al. (2003a) reported that deposition of 20 to 35 kg N/ha/yr contributed to increased NO_3^- leaching and soil acidity and decreased base saturation in southern California forest ecosystems, but they did not report quantitative measures of growth. Baron et al. (2000) showed that small differences in the N deposition between the east (3 to 5 kg N/ha/yr) and the west (1 to 2 kg N/ha/yr) side of the Rocky Mountains were associated with significant declines in foliar Mg levels and increased foliar N:Mg and N:Ca ratios in old-growth stands of Engelmann spruce (*Picea engelmanii*). It is not known if such changes in nutrient ratios affect the health or growth of these forests.

Despite the evidence for effects of acidifying deposition on the health and vigor of some terrestrial plant communities, we found a lack of scientific literature directly documenting species loss, reduced biodiversity, or adverse effects on threatened and endangered species. A notable exception is the effect of acidifying deposition on lichen abundance and diversity within forest communities (Lichens are discussed in Section 3.2.2.2.3). In Eastern North America and central Europe, areas that receive relatively high levels of acidifying deposition and high atmospheric concentrations of SO_2, N oxides, and reduced N have experienced noticeable reductions in cyanolichen abundance on both coniferous and deciduous trees (Richardson and Cameron, 2004). Effects on lichen species biodiversity are also likely (McCune, 1988; Van Haluwyn and Van Herk, 2002). In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas where NO exceeded 40 $\mu g/m^3$ and total N oxides exceeded 70 $\mu g/m^3$.

Health and Biodiversity of Other Plant Communities

Shrubs

Forest trees are not the only vascular plants that are potentially sensitive to acidifying deposition. Available data suggest that it is possible, or perhaps likely, that a variety of shrub and herbaceous species are sensitive to base cation depletion and/or Al toxicity. However, conclusive evidence is generally lacking.

Research in Europe has illustrated a shift from shrub to grass dominance in heathlands in response to acidifying deposition. However, such effects are probably more related to the nutrient enrichment effects of N deposition than to the acidification effects of S and N deposition. (See further discussion in Section 3.3.3.1). In summary, whereas some evidence suggests that effects on shrubs and perhaps herbaceous plants are possible, data in the U.S. are insufficient to support the use of shrub or herbaceous plant species as indicators of the acidification-related effects of acidifying deposition at this time.

Lichens

Typically, lichens and bryophytes are among the first components of the terrestrial ecosystem to be affected by acidifying deposition. Vulnerability of lichens to increased N input is generally greater than that of vascular plants (Fremstad et al., 2005). Even in the Pacific Northwest, which receives uniformly low levels of N deposition, changes from acid-sensitive and N-sensitive to pollution-tolerant and nitrophillic lichen taxa are occurring in some areas (Fenn et al., 2003a). Lichens remaining in areas affected by acidifying deposition were found by Davies et al. (2007) to contain almost exclusively the families Candelariaceae, Physciaceae, and Teloschistaceae.

Effects of SO_2 exposure on lichens includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K absorption, and structural changes (Fields, 1988; Farmer et al., 1992). In response to reductions after the 1970s in SO_2 exposure and acidifying deposition in London, lichen diversity increased dramatically (Hawksworth, 2002). However, the recovery of lichens in response to reduced S and N inputs is inconsistent. Improvement for bryophytes has been reported to occur in 1 year by Power et al., (2006) and Mitchell et al., (2004), 5 years by Gordon et al., (2001), and 49 years by Strengbom et al., (2001).

Scott (1989a,b) concluded that the S:N exposure ratio was as important as pH in causing toxic effects on lichens, based on experiments on *Cladina rangiferina* and *C. stellaris*. Thus, it is not clear to what extent acidity may be the principal stressor under high levels of air pollution exposure. The toxicity of SO_2 to several lichen species is greater under acidic conditions than under neutral conditions. The effects of excess N deposition to lichen communities are discussed in Section 3.3.3.1.5.

Grasslands

Due to structural differences and their lower canopy, grasslands are thought to be less sensitive to acidification than woodlands (Blake et al., 1999; Kochy and Wilson, 2001). Among grasslands, those with calcareous soils will be less sensitive than those with acidic soils (Bobbink et al., 1998). Most literature on the effects of atmospheric S and N deposition on grasslands documents effects of fertilization from N deposition, not acidification. Such fertilization effects are discussed in Section 3.3.3.1.2.

Arctic and Alpine Tundra

The possible effects of acidifying deposition on arctic and alpine plant communities are also of concern. Especially important in this regard is the role of N deposition in regulating ecosystem N supply and plant species composition (See further discussion of such effects in Section 3.2.2). Soil acidification and base cation depletion in response to acidifying deposition have not been documented in arctic or alpine terrestrial ecosystems in the U.S. Such ecosystems are rare and spatially limited in the eastern U.S., where acidifying deposition levels have been high. These ecosystems are more widely distributed in the western U.S. and throughout much of Alaska, but acidifying deposition levels are generally low in these areas. Key concerns are for listed threatened or endangered species and species diversity. However, for most rare, threatened, or endangered herbaceous plant species, little is known about their relative sensitivities to acidification from atmospheric deposition inputs. Although plant species diversity of arctic and alpine ecosystems is highly valued, it is difficult to document changes in this parameter in response to acidifying deposition.

Summary of Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in terrestrial biota. The strongest evidence for a causal relationship comes from studies of terrestrial systems exposed to elevated levels of acidifying deposition that show reduced plant health, reduced plant vigor, and loss of terrestrial biodiversity. Consistent and coherent evidence from multiple species and studies shows that acidifying deposition can affect terrestrial ecosystems by causing direct effects on plant foliage and indirect effects associated with changes in soil chemistry. Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum toxicity and decreased ability of plant roots to take up base cations. There are several indicators of stress to terrestrial vegetation (see Table 3-3) including percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback.

Species Level

- Changes in soil chemistry (depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water) have contributed to high mortality rates and decreasing growth trends of red spruce trees (*Picea rubens*) in some areas of the Eastern U.S. over the past three decades.

- Acidifying deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple (*Acer saccharum*) trees that occur at higher elevation, in some portions of the eastern U.S., on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils.

- Lichens and bryophytes are among the first species affected by acidifying deposition in the terrestrial ecosystem. Effects of SO_2 on lichens include reduced photosynthesis and respiration, damage to the algal component of lichen, leakage of electrolytes, inhibition of N fixation, reduced potassium (K) absorption and structural changes.

- Data are insufficient to draw general conclusions for other species.

Community Level

Species loss and reduced biodiversity of forests, shrubs, and meadow plant communities may occur, but have not been clearly demonstrated in the U.S.

3.2.3. Aquatic Ecosystems

3.2.3.1. Chemical Effects

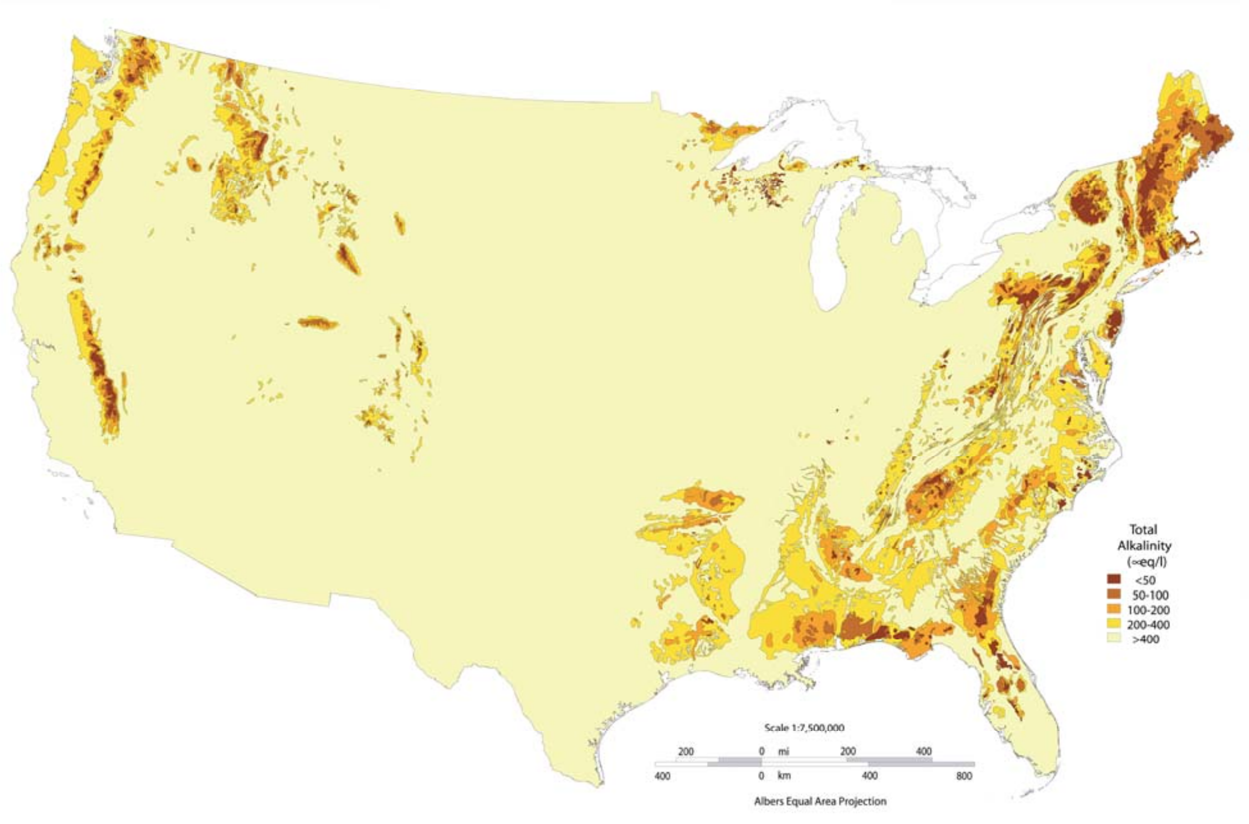
The changes in major biogeochemical processes and soil conditions caused by acidifying deposition have significant ramifications for the water chemistry and biological functioning of associated surface waters. Surface water chemistry indicates the adverse effects of acidification on the biotic integrity of fresh water ecosystems. Because surface water chemistry integrates the sum of soil and water processes that occur upstream within a watershed, it also reflects the results of watershed-scale terrestrial effects, including N saturation, forest decline, and soil acidification (Stoddard, 2003). Thus, water chemistry integrates and reflects changes in soil and vegetative properties and biogeochemical processes.

The effects on aquatic ecosystems can be described by changes in several chemical effects indicators such as: SO_4^{2-} concentration, NO_3^- concentration, base cation concentration, pH, ANC, and inorganic Al. All of these are of interest, and each can provide useful information regarding both sensitivity to surface water acidification and the level of acidification that has occurred. Importantly, these chemical changes can occur over both long- and short-term timescales. Short-term (hours or days) episodic changes in water chemistry have perhaps the most significant biological effects. The acidification effects on aquatic biota are most commonly evaluated using either Al or pH as the primary chemical indicator (Table 3-4). ANC is also used because it integrates overall acid status and because surface water acidification models do a better job projecting ANC than pH and inorganic Al concentrations. However, ANC does not relate directly to the health of biota. The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al. The base cation surplus (Lawrence, 2007) is an alternate index that integrates acid-base status. It is based on a measurement of ANC (calculated from the charge balance of ionic concentrations in water) and also accounts for the influence of natural organic acidity.

A synoptic illustration of the national patterns of surface water alkalinity in the conterminous U.S. is provided in Figure 3-10. Alkalinity is the most readily available measure of the sensitivity of lakes and streams to acidifying deposition. Although the actual sensitivity of a water body depends on many watershed characteristics and processes, the low-alkalinity areas on the map indicate where sensitive surface waters are most likely to be found. The map is based on data from approximately 39,000 lake and stream sites and the associations of the data values with factors such as land use, physiography, geology, and soils.

Table 3-4. Examples of chemical indicators of effects from acidifying deposition to aquatic ecosystems.

Chemical Indicator	Examples of Potential Thresholds	Reference
Surface water pH	5.0–6.0	Baker et al. (1990)
Surface water ANC	0–50 μeq/L	Bulger et al. (1999)
Inorganic Al	2–4 μmol/L	Wigington Jr. et al. (1996) Driscoll et al. (2001) Baldigo et al. (2007)



Source: Omernik, J.M et al. 1988.

Figure 3-10. Surface water alkalinity in the conterminous U.S. Shading indicates the range of alkalinity within which the mean annual values of most of the surface waters of the area fall.

Surface Water SO_4^{2-}

Measurements of SO_4^{2-} concentration in surface water provide important information on the extent of cation leaching in soils and how SO_4^{2-} concentrations relate to ambient levels of atmospheric S deposition. Assessments of acidifying deposition effects dating from the 1980s to the present have shown SO_4^{2-} to be the primary anion in most, but not all, acid-sensitive waters in the U.S. (Driscoll, 1985; Driscoll, 1988; Driscoll, 2001) Webb et al., 2004). In an analysis representative of over 10,000 acid-sensitive lakes in the Northeast, inorganic anions represented the majority of negative (anionic) charge in 83% of the lakes, and in this group of lakes, 82% of the total negative charge was due to SO_4^{2-} (Driscoll, 1988; Driscoll, 2001). In contrast, naturally derived organic anions represented an average of 71% of total negative charge in the 17% of lakes in which organic anions predominated (Driscoll, 1988; Driscoll, 2001).

Atmospheric deposition of S is widely acknowledged as causing changes in concentrations of SO_4^{2-} in surface water. No long-term data sets exist to document changes in SO_4^{2-} in surface waters since the onset of the Industrial Revolution. One of the longest-running monitoring programs exists at the Hubbard Brook Experimental Forest in New Hampshire. Surface water data from this Long-Term Ecological Research site have been used to develop historic estimates of SO_4^{2-} concentrations using the Photosynthesis and EvapoTranspiration-BioGeoChemical (PnET-BGC) model (Gbondo-Tugbawa, 2002). Results from Hubbard Brook suggest that acidifying deposition has contributed to a nearly four-fold increase in stream SO_4^{2-} concentration between 1850 and 1970 (Driscoll, 1988; Driscoll, 2001).

Long-term data in other regions suggest similar trends in some cases. For example, a study of seven streams in the Catskill region of New York, Stoddard (1991) identified increasing trends in SO_4^{2-} concentrations from 1952–54 to 1970 in three streams and no trend in the four other streams.

As emissions and deposition of S have declined over approximately the last 30 years, surface water concentrations of SO_4^{2-} have decreased in most regions in the eastern U.S. For example, Stoddard et al. (2003) found that surface waters monitored in EPA's Long-Term Monitoring program showed consistent decreases in SO_4^{2-} concentrations from 1990 to 2000 in New England lakes (1.77 μeq/L/yr), Adirondack lakes (2.26 μeq/L/yr), Appalachian streams (2.27 μeq/L/yr) and Upper Midwest lakes (3.36 μeq/L/yr). The only exception to the pattern of decreasing SO_4^{2-} concentration in surface waters during this period was for streams in the Blue Ridge Mountain region of Virginia, which showed a significant increase in SO_4^{2-} concentrations (0.29 μeq/L/yr) during this period. The increasing trend in Virginia streams is presumably the result of decreased S adsorption on soils and net desorption from the soil in response to decreased S deposition.

In summary, available data indicate a pattern of increasing concentrations of SO_4^{2-} in surface waters before the year of peak S emissions in the early 1970s, followed by widespread decreasing trends in SO_4^{2-} concentrations after the peak (with the only exception being the Blue Ridge Mountain region in

Virginia). On this basis, continued decreases in S emissions would be expected to result in further decreases in SO_4^{2-} concentrations in surface waters, although the rate of response is variable and some model results suggest that recovery may be delayed as accumulated S leaches from watersheds, even as emissions and deposition decline.

Surface Water NO_3^-

As described in the previous section, the acidification potential of atmospherically deposited S is primarily a function of the extent of SO_4^{2-} anion mobility in watershed soils and drainage waters. Similarly, acidification of soil water and surface water from atmospheric N deposition is largely governed by the mobility of the NO_3^- anion. Both oxidized and reduced N deposition can contribute to the NO_3^- flux in drainage water. Once N is deposited, processes within the N cycle, including microbial assimilation, plant uptake, and loss to denitrification act to limit the extent of NO_3^- leaching. In contrast, processes such as mineralization, nitrification, fixation, and atmospheric deposition contribute to the NO_3^- flux and increase the likelihood that substantial leaching of NO_3^- in drainage water will occur. Such leaching of NO_3^- is required in order for N deposition to cause N saturation, surface water acidification, or base cation leaching and depletion. Ultimately, the balance of these processes in the N cycle will determine the extent to which such effects will be manifested.

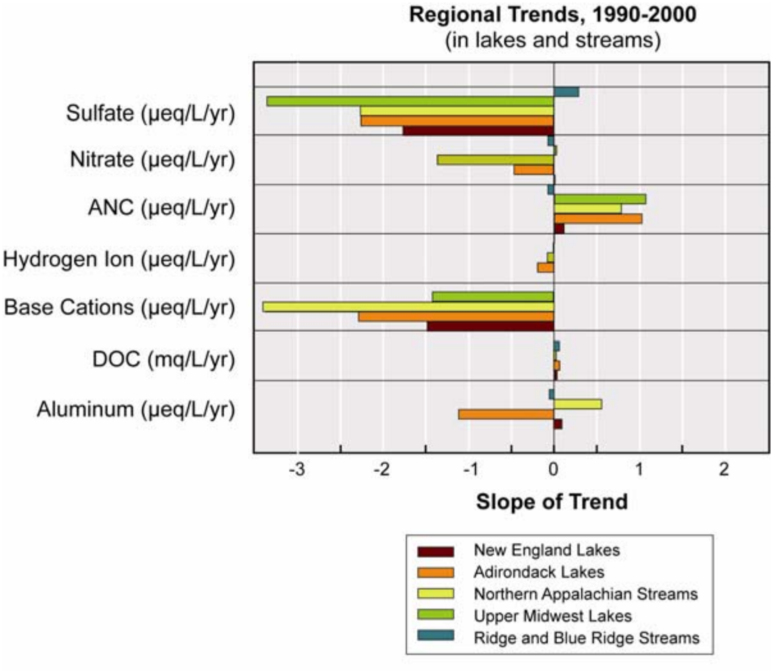
Whereas SO_4^{2-} is generally considered the dominant agent of surface water acidification in affected regions of the U.S., NO_3^- plays a large role in acidification of surface waters in some regions, particularly during snowmelt and rainstorms. Prior to the mid-1980s, atmospheric deposition effects research in the U.S. focused almost exclusively on S. Within the 1980 to 1990 National Acid Precipitation Assessment Program (NAPAP) research program, relatively little attention was paid to N research.

Release of NO_3^- from soil to surface waters may affect nutrient relationships and biological neutralization processes in aquatic ecosystems to a greater extent than SO_4^{2-} (Kelly, 1987) Bukaveckas and Shaw, 1998; Momen et al., 2006). The importance of NO_3^- as an agent of acidification varies by region. Driscoll and Newton, (Driscoll, 1985) found that NO_3^- concentrations in 20 lakes in the early 1980s in the Adirondack region of New York averaged 12% of SO_4^{2-} concentrations, whereas Lovett et al. (2000) found that baseflow NO_3^- concentrations in 1994–97 were an average of 37% of SO_4^{2-} concentrations in 39 streams in the Catskill region of New York. Murdoch and Stoddard (1993) demonstrated the importance of NO_3^- during high-flow conditions in Catskill streams in which concentrations periodically equaled or exceeded SO_4^{2-} concentrations. Average concentrations of NO_3^- in most southeastern streams tend to be considerably less than SO_4^{2-} concentrations (Webb et al., 2004). However, Cook et al. (1994) documented very high NO_3^- concentrations in stream water at high elevation in the Great Smoky Mountains in North Carolina.

Surface water NO_3^- concentration trends vary by region and over time. Several regions in the Northeastern U.S. showed increased NO_3^- concentrations during the 1980s. For example, in the Catskill Mountains of New York all 16 streams for which data were available showed increasing trends in NO_3^- concentration during that period. A similar increase in NO_3^- concentration was reported for Adirondack lakes in the 1980s (Stoddard, 1999). These increasing trends in NO_3^- concentration were initially attributed to N saturation in response to atmospheric deposition (Aber, 1998).

More recent information on NO_3^- trends during the 1990s, when atmospheric N deposition was relatively stable, suggest that the relationship between atmospheric N deposition and surface water NO_3^- concentrations is complex. During the 1990s, the only significant change occurred in the two regions with the highest ambient surface water NO_3^- concentrations: lakes in the Adirondack Mountains and streams in the Northern Appalachian Plateau (Figure 3-11). Both exhibited small but significant downward trends in NO_3^- concentration during the 1990s. The long-term record of dissolved inorganic N (which is largely NO_3^-) concentrations at the Hubbard Brook Experimental Forest showed a similar pattern: high concentrations in the late 1960s and 1970s, followed by decreases to minimum values in the mid-1990s (Aber, 2002). Across New England and the Upper Midwest, where ambient surface water concentrations are much lower than in the Adirondack Mountains and Northern Appalachian Plateau (Figure 3-11), NO_3^- concentrations in surface waters were unchanged during the 1990s. The Ridge/Blue Ridge province registered a small, but significant, decrease in NO_3^- concentration during the 1990s, but interpretation of trends for NO_3^- in this region was complicated by an outbreak of gypsy moths, which consumed foliage and caused large increases in the concentration of NO_3^- in soil water and stream water in affected watersheds (Eshleman, 1998).

Efforts to explain the complex patterns in NO_3^- concentrations under conditions of reasonably stable atmospheric N deposition have focused on both terrestrial and aquatic N cycling. Goodale et al. (Goodale, 2003) reported that lower NO_3^- concentrations measured in the 1990s at streams in New Hampshire could not be accounted for by differences in stream flow or forest succession, but inter-annual climate variation was proposed as a possible cause. In the Adirondacks, Driscoll et al., (Driscoll, 2007) proposed that increased concentrations of atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation. Studies by Mitchell et al. (1996) and Murdoch et al. (1998) provide some evidence of climate effects on trends in NO_3^- concentrations in surface waters in the Northeast. In particular, a region-wide spike in NO_3^- concentrations followed an unusually cold December that may have disrupted soil N cycling processes (Mitchell, 1996). Murdoch et al. (1998) also found that mean annual air temperature was strongly related to average annual NO_3^- concentration during most years in a Catskill watershed with elevated NO_3^- concentrations in stream water.



Source: Stoddard et al. (2003)

Figure 3-11. Summary of regional trends in surface water chemistry from 1990 to 2000 in regions covered by the Stoddard et al. (2003) report.

Processes within lakes may have also played a role in the measured trends in Adirondack lakes (Ito et al., 2005, 2007). In a study of 30 of the 48 long-term monitoring lakes investigated by Driscoll et al. (Driscoll, 2003; Driscoll, 2007) and Momen et al. (2006) found that concentrations of dissolved NO_3^- were inversely correlated with concentrations of chlorophyll *a* in 11 lakes, and that chlorophyll *a* was increasing in concentration in 9 lakes. The increase in pH observed in most of these lakes may have stimulated productivity so that N assimilation by plankton increased (Momen et al., 2006).

In summary, NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S. that have been affected by acidifying deposition, especially during spring months and under high-flow conditions. Nevertheless, there is little or no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in surface waters in the eastern U.S. This observation is in sharp contrast to observed responses for S deposition and SO_4^{2-} concentrations. These results likely reflect the complexities of N use within terrestrial and aquatic ecosystems. Uptake of atmospherically deposited N by plants and microorganisms in the terrestrial environment precludes drainage water acidification and base cation leaching that would be caused if excess N leached as NO_3^- from the terrestrial to aquatic ecosystems. While great uncertainty exists, and the timescales of N saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely

(Aber, 2003) and spatial patterns across the Northeastern U.S. are consistent with atmospheric N deposition contributing to elevated NO_3^- leaching.

Surface Water Base Cations

The results from several studies in the Eastern U.S. suggest that base cation concentrations in surface waters increased during the initial phases of acidification into the 1970s. This trend reversed and base cations decreased in response to decreasing SO_4^{2-} and NO_3^- concentrations. For example, the study of Likens et al. (Likens, 1996) evaluated trends in base cation concentrations in stream water in relation to long-term trends in SO_4^{2-} plus NO_3^- for the Hubbard Brook Experimental Forest. This record showed an approximately linear increasing relationship between concentrations of base cations and SO_4^{2-} plus NO_3^- from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994. The slope of the phase with increasing cation concentrations was steeper than the slope for the phase with decreasing cation concentrations. Regional declines in base cation concentrations were measured in the Long-Term Monitoring project from 1990 to 2000 for lakes in New England, the Adirondack Mountains, and the Upper Midwest (Figure 3-11). The study of Lawrence et al. (1999) showed decreased concentrations of base cations at a rate that exceeded decreases in (SO_4^{2-} plus NO_3^-) in Catskill Mountain streams from 1984 to 1997. In streams within western Virginia and in Shenandoah National Park, concentrations of base cations did not exhibit significant trends from 1988 to 2001, perhaps due to the influence of S adsorption to soil on stream water SO_4^{2-} concentrations.

In some surface waters, interpretation of the effects of, and changes in, the concentration of base cations and ANC is complicated by the influence of naturally occurring organic acidity. The base cation surplus provides an approach for distinguishing between the effects of organic acidity and acidifying deposition (Lawrence, 2007). Base cation surplus is defined as the difference between the summed concentrations of base cations (Ca, Mg, Na, K) and strongly acidic inorganic anions (SO_4^{2-}, NO_3^-, chloride), plus an estimate of the strongly acidic organic anions estimated from dissolved organic C and an assumed charge density. These strongly acidic organic anions are dissociated at low pH, and function essentially as mineral acid anions in terms of their effect on ANC. The calculated base cation surplus is similar to the calculated ANC, but explicitly accounts for strongly acidic organic acids. When the base cation surplus is plotted against inorganic Al concentration, a distinct threshold for Al mobilization occurs at a base cation surplus value that closely approximates 0, regardless of the dissolved OC concentration (Lawrence, 2007). This threshold provides an unambiguous reference point for evaluating the effects of acidifying deposition on mobilization of inorganic Al. To date, this calculated variable has only been used in one large-scale assessment of acidifying deposition effects on surface waters (Lawrence, 2007).

In summary, decreases in base cation concentrations in surface water in the Eastern U.S. over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. In most regions, rates of decrease for base cations have been similar to those for SO_4^{2-} plus NO_3^-, with the exception of streams in Shenandoah National Park, Virginia, which are affected by decreases in SO_4^{2-}adsorption in soils. Decreasing trends of base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

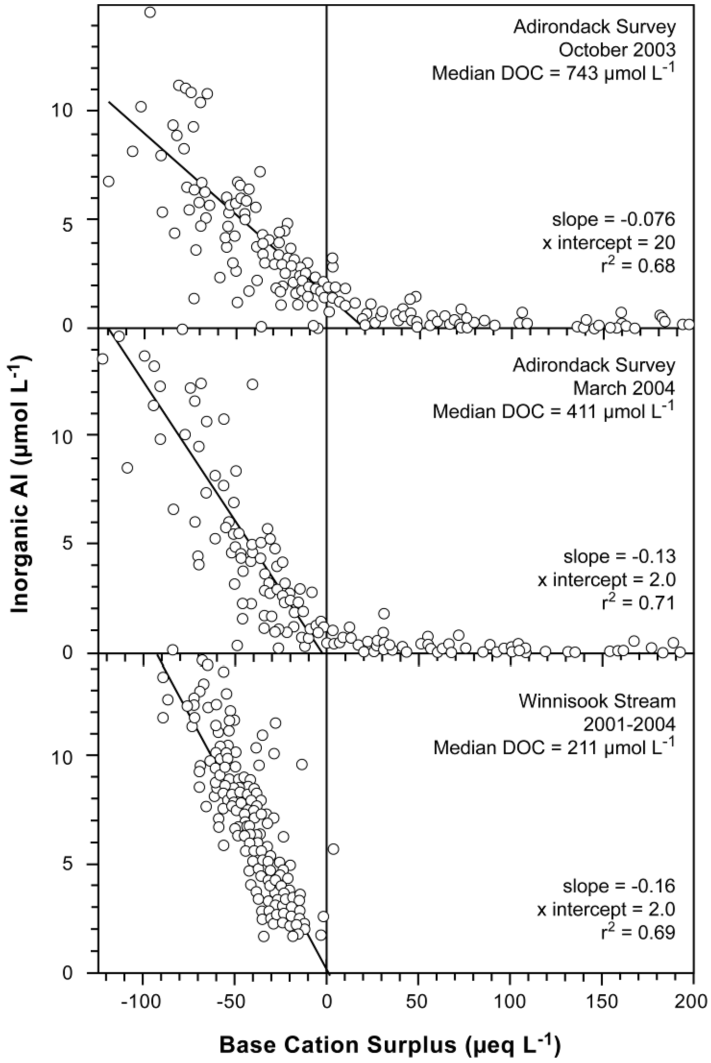
Surface Water pH

Surface water pH is a commonly used as an indicator of acidification. The pH of water quantifies the hydrogen ion concentration, which is toxic to many forms of aquatic life. In addition, pH correlates with other biologically important components of surface water acid-base chemistry, including ANC, inorganic Al, Ca concentration, and organic acidity. Low pH can have direct toxic effects on aquatic species (Driscoll, 2001). Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Haines and Baker, 1986; Baker et al., 1990a). Common reference values for pH, below which adverse biological effects are anticipated, are 6.0, 5.5, and 5.0. The effects of low pH are specific to the study organism and depend also upon the concentrations of other chemicals in the water, notably inorganic Al and Ca. Species-specific effects are discussed in more detail in Section 3.2.3.2.

Long-term past changes in surface water pH have been inferred for lakes in the Adirondacks through paleolimnological studies (Charles et al., 1989; Sullivan et al., 1990; Cumming et al., 1992, 1994). These studies of algal remains in lake sediments for regionally representative Adirondack lakes suggested that about 25 to 35% of the Adirondack lakes that are larger than 4 ha have acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had ambient pH less than 5.2 in the mid-1980s were inferred to have experienced declines in pH and ANC since the previous century. About 30 to 45% of the lakes with ambient pH between 5.2 and 6.0 have also acidified. The results suggest that the low-ANC lakes of the southwestern Adirondacks acidified the most since preindustrial time.

Additional information regarding long-term changes in surface water pH has been gained through site-specific dynamic modeling. For example, by applying the PnET-BGC model to the long-term stream chemistry record at the Hubbard Brook Experimental Forest, Gbondo-Tugbawa et al. (2002) estimated that past stream pH (circa 1850) was probably about 6.3, compared with values just above 5.0 in 2000 (Driscoll, 2007).

In recent decades, measurements of pH have been routinely collected in surface waters in the U.S. where effects of acidifying deposition have been monitored, but there has been a long-standing reliance on titrated ANC as the primary chemical measurement for evaluation of surface water acidification. Overall, between 1980 and 2000 most studies reported slight increases in surface water pH, including lakes in the Adirondack Mountains (rate variable) (Driscoll, 2007) and southern New England (0.002 pH units per year) (Warby, 2005), and streams in the Catskill/Poconos region of New York and Pennsylvania (0.008 pH units per year) (Warby, 2005).



Source: Lawrence et al. (Lawrence, 2007)

Figure 3-12. Concentration of inorganic Al in Adirondack streams as a function of the calculated base cation surplus.

Through frequent monitoring from 1990 to 2000, Stoddard et al. (2003) found a decrease in hydrogen ion (0.19 µeq/L/yr) that was similar to the rate of change observed in the same Adirondack lakes by Driscoll et al. (Driscoll, 2007) from 1992 to 2004 (0.18 µeq/L). Stoddard et al. (2003) also reported an increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq/L/yr) and Upper

Midwest lakes (0.01 μeq/L/yr). No trends were found in New England lakes in this study (see Figure 3-11).

In summary, increasing trends in pH (decreasing hydrogen ion concentration) in surface waters in the Northeastern U.S. were common through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have been small. Driscoll et al. (Driscoll, 2001; Driscoll, 2001; Driscoll, 2007) attributed the limited pH recovery of lakes in acid-sensitive regions to three factors: (1) The levels of acid-neutralizing base cations in surface waters have decreased markedly because of the depletion of available base cations from the soil, and to a lesser extent, a reduction in atmospheric inputs of base cations; 2) As forests mature, their requirements for N decrease, and they are expected to increasingly lose NO_3^- as forests develop; and (3) Sulfur has accumulated in the soil under previous conditions of high atmospheric S deposition and is now being gradually released to surface water as SO_4^{2-}, even though S deposition has decreased.

Surface Water ANC

The most widely used measure of surface-water acidification is ANC, which is often determined by Gran titration (titrated ANC). This measurement is the primary chemical indicator for assessing past effects of acidifying deposition, and the recovery expected from decreasing atmospheric deposition (Bulger, 2000; Stoddard, 2003). Titrated ANC is useful because it reflects the ANC of the complete chemical system, which is typically reduced by acidifying deposition in acid-sensitive landscapes.

In contrast to surface water pH, ANC is more stable and it reflects sensitivity and effects of acidification in a linear fashion across the full range of ANC values. Therefore, ANC is the preferred indicator variable for surface water acidification. Both titrated and calculated ANC values are commonly determined in studies aimed at resource characterization or long-term monitoring.

Bulger et al. (1999) defined ANC response categories for brook trout in Virginia as less than zero (chronic damage likely), 0 to 20 μeq/L (episodic damage likely), 20 to 50 μeq/L (likelihood of damage not determined), and greater than 50 μeq/L (brook trout not sensitive). ANC less than 0 μeq/L is of significance because waters at or below this level have limited capacity to neutralize acid inputs. Surface waters with ANC < 50 μeq/L have been termed “extremely acid sensitive” (Schindler, 1988), are prone to episodic acidification in some regions (DeWalle, 1987) Eshleman, 1988), and may be susceptible to future chronic acidification at current or increased rates of acidifying deposition. Baker et al. (1990c) used ANC cutoffs of 0, 50, and 200 μeq/L for reporting on national lake and stream population estimates.

In assessing changes in surface water ANC, it is important to distinguish between acidic waters and acidified waters. “Acidic” describes a condition that can be measured (i.e., Gran ANC less than or equal to 0). It may be due either to the effects of acidifying deposition, or to other causes such as the presence of organic acidity or the weathering of S-containing minerals in the watershed. “Acidified” refers to the consequences of the process of acidification (a decrease in ANC observed through time). It does not require that the water body be acidic, and does not imply a particular cause for the change in chemistry. The term "anthropogenically acidified" implies that human activity was responsible for the increase in acidity that occurred.

Some of the most detailed studies of ANC have been conducted in the Adirondack Mountains. Model simulations suggested that none of the lakes in the Adirondack target lake population identified by EPA's Environmental Monitoring and Assessment Program (EMAP) were chronically acidic or had ANC less than 20 μeq/L under preindustrial conditions, but that by 1980 there were hundreds of such lakes (Table 3-5). Many lakes were estimated to have had preindustrial ANC below 50 μeq/L, but this estimate more than doubled by 1990. Based on Model of Acidification of Groundwater in Catchments (MAGIC) model outputs extrapolated to the regional population of Adirondack lakes larger than 1 ha that currently have ANC below 200 μeq/L, maximum past acidification occurred by about 1980 or 1990, with median ANC of the lake population of about 61 μeq/L (reduced from a median of 92 μeq/L estimated for the preindustrial period). Changes in ANC produced an increase in not only the percentage of lakes that were chronically acidic, but also in those that were deemed likely to experience episodic acidification and its associated short-term changes in water chemistry (Sullivan et al., in press).

Table 3-5. Estimates of change in number and proportion of acidic surface waters in acid-sensitive regions of the North and East, based on applying current rates of change in Gran ANC to past estimates of population characteristics from probability surveys.

Results of Regional Survey					Results of Monitoring during 1990s			
Region	Population Size	Number Acidic[1]	% Acidic[2]	Time Period of Estimate	Rate of ANC change[3]	Estimated Number Acidic in 2000	% Acidic in 2000	% Change in Number of Acidic Systems
New England	6,834 lakes	386 lakes	5.6%	1991–94	+0.3	374 lakes	5.5%	-2%
Adirondacks	1830 lakes	238 lakes	13.0%	1991–94	+0.8	149 lakes	8.1%	-38%
N. Appalachians	42,426 km	5,014 km	11.8%	1993–94	+0.7	3,600 km	8.5%	-28%
Ridge/Blue Ridge	32,687 km	1,634 km	5.0%	1987	-0.0	1,634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	-68%

[1] Number of lakes/streams with Gran ANC < 0 in past probability survey by EPA (data collected at "Time Period of Estimate," in column 5).

[2] Percent of population (from Column 2) with Gran ANC < 0 in past probability survey (data collected at "Time Period of Estimate," in column 5).

[3] Based on regional trends presented in the Stoddard et al. (2003) report, in μeq/L/yr, for the 1990s.

In other regions, responses to reduced levels of acidifying deposition required by the Clean Air Act (CAA) and other emissions control legislation were reported by Stoddard et al. (2003). They found tendencies during the 1990s toward increasing surface water Gran ANC in all of the glaciated regions of the eastern U.S. (i.e., New England, Adirondacks, and Northern Appalachian Plateau) and Upper Midwest, and decreasing Gran ANC in the Ridge/Blue Ridge province. Changes in ANC were relatively modest compared with observed reductions in SO_4^{2-} concentrations in surface waters. The regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant (Table 3-6). Median increases of about +1 μeq/L/yr in the Northern Appalachian Plateau, Adirondacks, and Upper Midwest represent significant trends towards ecological recovery from acidification (Stoddard, 2003). Estimated change in the number of acidic surface waters decreased during the 1990s in all regions investigated by Stoddard et al. (2003), except the Ridge and Blue Ridge Provinces in the mid-Appalachian Mountains (Table 3-5). For other regions, the change in number of acidic systems ranged from −2% in New England to −68% in the Upper Midwest.

Table 3-6. Regional trend results for long-term monitoring lakes and streams for the period 1990 through 2000 (values are median slopes for the group of sites in each region).

Region	SO_4^{2-} (μeq/L/yr)	NO_3^- (μeq/L/yr)	Base Cations [Ca + Mg] (μeq/L/yr)	Gran ANC (μeq/L/yr)	Hydrogen (μeq/L/yr)	DOC (mg/L/yr)	Aluminum (μg/L/yr)
New England Lakes	−1.77**	+0.01ns	−1.48**	+0.11ns	−0.01ns	+0.03*	+0.09ns
Adirondack Lakes	−2.26**	−0.47**	−2.29**	+1.03**	−0.19**	+0.06**	−1.12**
Appalachian Streams	−2.27*	−1.37**	−3.40**	+0.79*	−0.08*	+0.03ns	+0.56ns
Upper Midwest Lakes	−3.36**	+0.02ns	−1.42**	+1.07**	−0.01*	+0.06**	−0.06ns
Ridge/Blue Ridge Streams	+0.29**	−0.07**	−0.01ns	−0.07ns	+0.01ns	NA	NA

ns Regional trend not significant ($p > 0.05$)
* $p < 0.05$
** $p < 0.01$
NA = insufficient data.

In summary, ANC is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. ANC can be measured in the laboratory by Gran titration or calculated on the basis of the difference between the base cation sum and the mineral acid anion sum. Acidic waters are defined as those having ANC less than or equal to zero μeq/L. Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the Eastern U.S. This effect has been well documented in monitoring programs, paleolimnological studies, and model simulations. Since about 1990 the ANC of many affected lakes and streams have shown some increase, but such increases have been relatively modest.

Surface Water Aluminum

The concentration of inorganic Al in surface waters is an especially useful indicator of acidifying deposition effects because (1) it is widely toxic, and (2) it generally does not leach from the terrestrial soils to surface waters in the absence of acidifying deposition (Driscoll, 1998; Lawrence, 2007), with exceptions such as acid mine drainage and relatively rare geologic deposits. Lawrence et al. (1995) showed that strong organic acid anions can contribute to the mobilization of inorganic Al in combination with SO_4^{2-} and NO_3^-, but in the absence of geologic S, the presence of inorganic Al in surface waters is an ambiguous indication of acidifying deposition effects.

Considerable work was done to define pH sensitivity ranges for a wide variety of aquatic organisms, but when pH values fall below approximately 5.5, inorganic Al generally becomes the greater health risk to biota. Although organically complexed Al (organic Al) can occur in surface waters as a result of natural soil and hydrologic processes, this form of Al is not harmful to aquatic life (Gensemer and Playle, 1999). Inorganic Al, however, has been found to be toxic to plant and animal species throughout the food web (Gensemer and Playle, 1999).

Earlier studies demonstrated reduced growth and survival of various species of fish (Baker, 1982; Baker, 1996) at inorganic Al concentrations between approximately 2 and 7.5 µmol/L. Most recently, 20% mortality of young-of-the year brook trout was documented in situ during a 30–day period with a median inorganic Al concentration of 2 µmol/L (Baldigo, 2007). This study estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

The development of methods to fractionate Al into organic and inorganic forms (Driscoll, 1984) Sullivan et al., 1986) resulted in collection of a considerable amount of data on Al concentrations in surface waters in the 1980s, but most of this sampling was done either once or for a limited period of time (Driscoll, 1985; Driscoll, 1987; Lawrence, 1987; Cronan et al., 1990). Available long-term trend information for inorganic Al is limited. In Adirondack lakes, inorganic Al concentrations decreased slightly (e.g., by 0.02 µM/yr to 0.18 µM/yr; Driscoll et al., 2007a) or remained unchanged between 1982 and 2004 (Stoddard, 2003) Driscoll et al., 2007a). There was no trend in inorganic Al for this period in New England lakes, Appalachian streams, or Midwest lakes. Monthly stream chemistry monitoring at the Hubbard Brook Experimental Forest showed decreases in inorganic Al concentrations at four locations along the reference stream for the experimental forest from 1982 to 2000, but no trends at two other locations along this stream (Palmer, 2004).

Most recently, Lawrence et al. (in press) found that 49 of 195 streams (25%) in the western Adirondack region had inorganic Al concentrations above 2.0 µM during August base flow. Although there is not a clear benchmark value above which inorganic Al is toxic to aquatic biota, 2 µM is generally recognized as a reasonable threshold for biological effects at a variety of trophic levels (Driscoll et al., 2001b; Baldigo, 2007).

In summary, inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water. It has well-documented effects on aquatic biota at specific thresholds. Limited data suggest that acid-sensitive regions of the Northeastern U.S. have elevated inorganic Al concentrations which have been induced by years of acidifying deposition and which pose a threat to aquatic life.

Concentrations have decreased slightly in some surface waters in the Northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

Quantification of Acidification

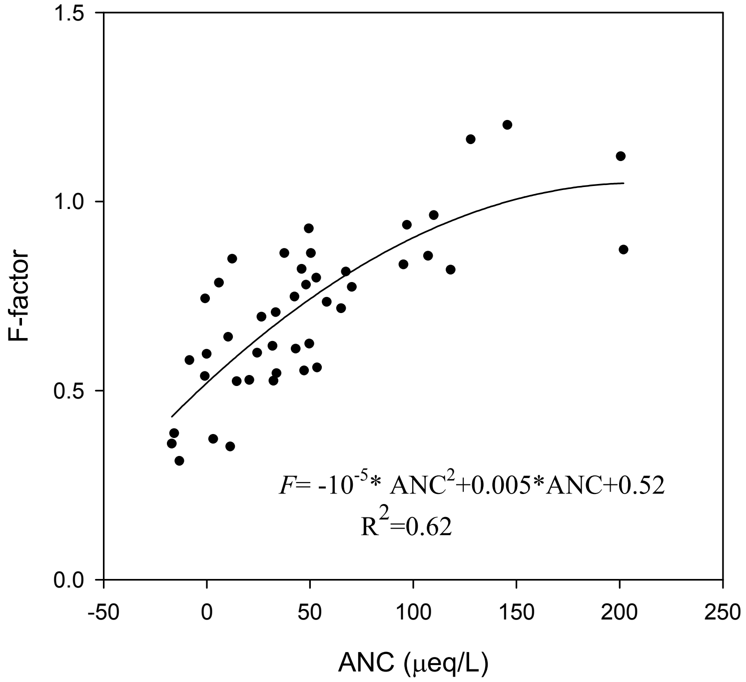
Changes in the acid-base status of soils and drainage waters operate on different time scales. Most temperate forest soils have high exchangeable acidity, and relatively small changes in the acidity of precipitation input would not be expected to have a large effect on soil acidity (Krug, 1983; Turner, 1990). Therefore, recent soil acidification in affected areas appears to have been modest (c.f.,, Sullivan, 2006), and projected recovery of soil acid-base chemistry in response to future decreases in acidifying deposition is expected to be limited (c.f.,, Gbondo-Tugbawa, 2002; Sullivan, 2006). In contrast, changes in the chemistry of drainage water in response to changes in acidifying deposition can occur more rapidly. This is because drainage water can become acidified by the leaching of a mobile acid anion such as SO_4^{2-} or NO_3^- even if the acidity of the soil is not measurably affected (Seip, 1980; Reuss, 1986; Turner, 1990). In areas (including the Northeastern U.S.) where S adsorption on soils is minimal, and therefore where SO_4^{2-} is highly mobile, changes in S deposition input have been shown to cause changes in the ANC and base cation concentrations in lakes and streams over a time period of years to decades (Driscoll, 2003).

One way to quantify acidification dose-response relationships is to calculate the changes in various ionic constituents in solution that occur in response to changes in mineral acid anion (SO_4^{2-} and NO_3^-) concentrations due to changes in acidifying deposition input. As $[SO_4^{2-} + NO_3^-]$ increases or decreases in solution, equivalent changes must also occur in the concentration of other anions (i.e., bicarbonate $[HCO_3^-]$, organic acid anion $[RCOO^-]$) or cations (i.e., hydrogen $[H^+]$ inorganic Al $[Al^{n+}]$, sum of base cations [SBC]) to maintain the charge balance. Typically, the largest counteracting change is in SBC. It is generally assumed that most of the base cation change is due to Ca^{2+} and Mg^{2+}. In acid-sensitive waters, additional changes can occur in ANC (which can be expressed as $[HCO_3^- \text{-}H^+]$), Al^{n+}, and/or $RCOO^-$) (Husar, 1991). Henriksen (1984) presented evidence for Norwegian lakes, suggesting that base cation release accounted for up to a maximum of 40% of the added mineral acid anions. This proportional change in base cations relative to SO_4^{2-} or $[SO_4^{2-} + NO_3^-]$ is called the F-factor:

$$F = \frac{\Delta SBC}{\Delta[SO_4^{2-} + NO_3^-]}$$

Subsequently, diatom reconstructions for Adirondack lakes suggested higher F-factors, generally ranging from 0.4 to greater than 1.0 (Sullivan, 1990).

Sullivan and Eilers (1994) compiled available data on proportional changes in SBC, ANC, and Al^{n+}, relative to the observed or estimated change in $[SO_4^{2-} + NO_3^-]$. Their analysis included: 1) measured short-term (< 20 yr) changes in drainage water chemistry in response to ambient or experimental increases or decreases in S deposition loading, 2) results of space-for-time substitution analyses, 3) results of diatom inferences of past lake chemistry, and 4) MAGIC model hindcast and forecast simulations. Results indicated a wide range in the estimated proportional changes in SBC as a percent of change in $[SO_4^{2-} + NO_3^{-}]$. Estimated F-factors generally ranged from about 0.5 to 1.0, although some watersheds in Norway and in the western U.S. showed F-factors as low as about 0.25. The estimated proportional change in ANC was typically less than 0.3, and change in Al^{n+} was smaller. Quantitative data were not available for the organic acid anion response, but this response is also expected to generally be relatively small. More recent PnET-BGC simulations for Adirondack lakes were in close agreement with the diatom results Figure 3-13; Zhai, 2008), ranging from about 0.4 to 1.0.



Source: Zhai et al. (Zhai, 2008)

Figure 3-13. F-factors calculated from PnET-BGC model results for the period 1850 to 1980 as a function of simulated ANC in 1980 for 44 EMAP lakes in the Adirondack region of New York.

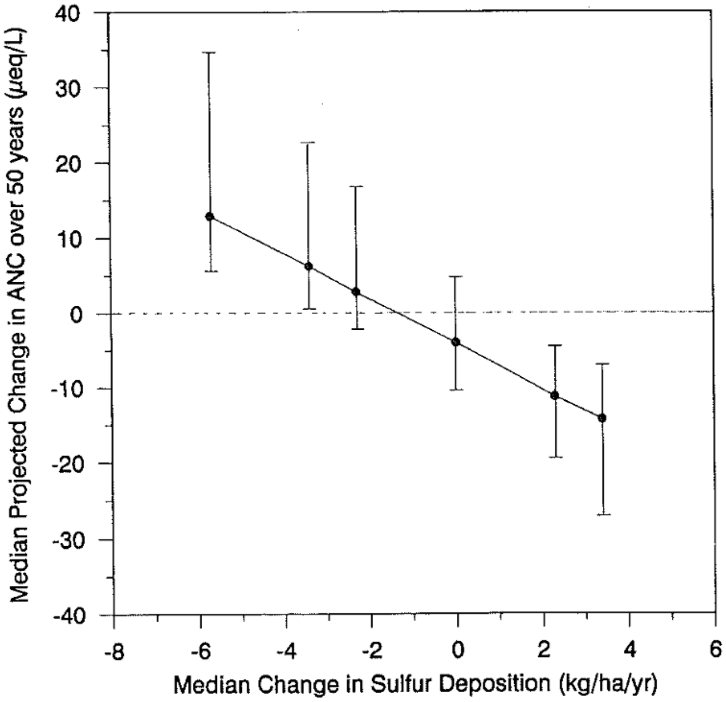
Measured, modeled, and inferred changes in surface water chemistry in areas that have experienced relatively short-term (less than three decades) changes in acid deposition loading are available from many sources. Process model hindcasts and paleolimnological reconstructions of pre-industrial surface water chemistry provide insight into the extent to which individual lakes and streams have acidified over the longer term. Evaluation of acidification effects from assessment of current conditions is generally not helpful. This is because lakes and streams vary with respect to their expected chemistry (i.e., ANC or pH) in the absence of acidifying deposition. In many regions, pre-disturbance lake and stream ANC values below 50 μeq/L and pH below 6.0 appear to have been common; in some cases, ANC below 0 and pH below 5.0 also occurred. The common occurrence of lakes and streams that were naturally low in ANC and pH prior to the advent of acidifying deposition is further complicated by the fact that disturbances other than air pollution have contributed to further changes in acid-base status, including both ANC and pH increases and decreases. Such disturbances have included logging, fire, forest regrowth, erosion, road-building, forest insect infestation and disease, and other land-disturbing activities and events. Current surface water chemistry is a complex function of inherent sensitivity (which to some degree was reflected in pre-disturbance chemistry), levels of acidifying deposition (historic and current), and the effects of other disturbances.

Dose-response functions may in some cases be similar from water body to water body within a defined region. For example, model simulations conducted for the NAPAP Integrated Assessment (NAPAP, 1991) reported by Sullivan et al. (1992) found that, although substantial variability was found in projected future change in ANC among the modeled Adirondack watersheds, there was a highly consistent relationship between median change in acidifying deposition and projected median change in ANC over 50 years. Each 1 kg/ha/yr change in future S deposition caused approximately a 3.5 μeq/L change in simulated lakewater ANC (see Figure 3-14). Results of MAGIC model hindcast simulations suggested that all of the Adirondack lakes modeled for NAPAP (NAPAP, 1991) had acidified (decreased in pH or ANC) since pre-industrial times. The median and range of estimated changes in ANC were -46 μeq/L and -31 to -84 respectively. None of the lakes were inferred to have been acidic (ANC ≤ 0) in pre-industrial times. The minimum simulated pre-industrial values were pH 5.4 and ANC = 30 μeq/L (Sullivan, 1994).

Historical changes in Adirondack lakewater chemistry inferred from measurements in diatoms suggested somewhat more conservative estimates of historical acidification. From these data, Sullivan (1990) and Sullivan et al. (1990) concluded :

- the “median” Adirondack lake had not acidified;
- acidification was generally limited to lakes that had ambient ANC during the 1980s less than about 50 μeq/L (or pH less than about 6.0);
- approximately 15% of the Adirondack lakes were inferred to have acidified by more than 0.28 pH units;
- the median historical acidification (expressed as Δ ANC – Δ Al_i) of lakes that were acidic (ANC < 0) at the time of sampling was -37 μeq/L;

- approximately 3% of the Adirondack lakes were acidic in pre-industrial times, compared to 14% in the 1980s.



Source: Sullivan et al. 1992

Figure 3-14. Median and range of projected change in ANC (μeq/L) of Adirondack lakes for 50–year MAGIC simulations versus median future change in sulfur deposition (kg/ha/yr) for each deposition scenario (points on each line correspond to -50%, -30%, -20%, 0%, +20%, +30% change from current deposition).

These paleolimnological estimates suggested that Adirondack lakes that were acidic in the 1980s had decreased a median of about 4 μeq/L in [$\mathrm{ANC_G - Al_i}$] for each kg/ha/yr change in S deposition. This was slightly more than one-half of the median historical rate of acidification projected by MAGIC (7 μeq/L of calculated ANC for each kg/ha/yr) for acidic Adirondack lakes (Sullivan, 1992).

In comparing estimates, derived from different approaches, of past and future changes in Adirondack lakewater chemistry in response to acidifying deposition, it is important to consider several factors (Sullivan, 1992):

- Chemical changes estimated from paleolimnology or monitoring data incorporate all influences on the acid-base chemistry of lakewater, including land use, disturbances, and climatic differences. Model estimates commonly include only postulated or estimated changes in acidifying deposition as having influenced the lakewater chemistry. Because watershed disturbances generally cause an increase in surface water ANC, they may partially explain the more conservative estimates of diatom-inferred acidification compared with MAGIC model estimates of acidification.

- The use of a process-based model for hindcasting requires assumptions regarding historical deposition of all major ions. In addition to uncertainties regarding historical sulfur deposition levels, base cation deposition has also likely changed by an unknown amount, and the degree to which sulfur and base cation deposition have been coupled is unclear (Driscoll, 1989; Chen, 1989).

- Organic acids may have exerted a greater influence on lakewater pH during pre-industrial times than they do currently because DOC and organic acid anion concentrations may have decreased in response to increased organic acid protonation and increased concentrations of Al (Almer, 1974; Krug, 1983; Davis, 1985; Kingston, 1990).

- Data sets from different points in time are often not directly comparable because of differences in ANC definition or pH measurement. For example, the calculated ANC used by MAGIC differs from titrated ANC (ANC_G) used to calibrate paleolimnological transfer functions and reported in surveys. The differences are due to the partially counteracting influences of Al and organic acids on ANC_G and their omission from calculated ANC. These differences can be appreciable for acidic and low-ANC waters (Sullivan, 1989).

There is not a clear definable relationship between atmospheric S deposition and ecological effects. A given amount of S deposition can cause a wide range of ecological responses, from no ecological effect to varying levels of adverse ecological effect. These can include changes in community composition, loss of sensitive species, reduced biological diversity, and altered ecosystem functions. Such effects can occur in both aquatic and terrestrial ecosystems. The observed wide range of responses within and among regions is attributable to varying ecosystem sensitivity. Some soils (notably in many watersheds in the southeastern U.S.) have the capacity to adsorb substantial quantities of S, with essentially no acidification of drainage water. Nevertheless, there is a finite limit to this S adsorption capacity, and under continual high S deposition loading, the adsorptive capacity of soil will eventually become depleted.

In addition to differences in S adsorption capacity of soils, watersheds also differ in their sensitivity to acidification effects as a consequence of differing sensitivity of the species that make up the local biological community. Some species of fish, aquatic insects, and mollusks, for example, are highly sensitive to adverse effects from low pH and high inorganic Al concentrations; others are less sensitive. Finally, watersheds differ in the size of the soil base cation pool available to neutralize deposited mineral acidity. Some watersheds have sufficient quantities of base cations in their soils such that drainage waters will remain well buffered, even under relatively high S deposition loads, for many decades or longer. Other watersheds had relatively low base cation supply during preindustrial times due to low weathering rates of the underlying geology, and the base cation supply may have been further depleted by past acidifying deposition.

As a consequence of these, and other, differences in sensitivity to S inputs, watersheds differ in the extent to which they acidify in response to a given amount of S deposition and they also differ in the extent to which that acidification translates to biological effects. Thus, one cannot specify a level of S deposition that would be likely to cause adverse effects across the landscape. Sensitivity differs from watershed to watershed.

Despite these differences in watershed sensitivity to acidification, it is possible to place bounds on the amount of acidification that has occurred in response to a given change in S deposition. Such quantitative estimates of acidification have been derived using watershed models of acidification response. Modeling results summarized in Table 3-7 illustrate a wide range in the model estimates of past acidification of acid-sensitive lakes and streams in the eastern U.S.

Table 3-7. Model estimates of long-terms S deposition load required to achieve certain surface water quality criteria (ANC above 0, 20, or 50 eq/L) in different endpoint years (approximately 2040 or 2100) and estimates of historic acidification in response to S deposition.

Region	Resource Description	Approach	Deposition Load (kg S/ha/yr) to Maintain Surface Water ANC Above[1]			Estimate of Acidification (ΔANC) Since Pre-Industrial Period (µeq/L)	Reference
			0 µeq/L	20 µeq/L	50 µeq/L		
			In the Year				
			2040/2100	2040/2100	2040/2100		
Adirondacks, NY	Median of population of lakes within region having current ANC ≤ 200 µeq/L	MAGIC				25	(Sullivan et al. 2006, 2007)
Adirondacks, NY	Median of population of lakes within region having current ANC ≤ 200 µeq/L	PnET-BGC				27	(Sullivan et al. 2006)
Adirondacks, NY	10th percentile of lakes within region having current ANC ≤ 200 µeq/L	MAGIC				39	(Sullivan et al. 2006, 2007)
Adirondacks, NY	10th percentile of lakes within region having current ANC ≤ 200 µeq/L	PnET-BGC				62	(Sullivan et al. 2006)
Adirondacks, NY	25th percentile of lakes within region having current ANC ≤ 200 µeq/L	MAGIC				36	(Sullivan et al. 2006, 2007)
Adirondacks, NY	25th percentile of lakes within region having current ANC ≤ 200 µeq/L	PnET-BGC				39	(Sullivan et al. 2006)
Shenandoah NP, VA	Median of streams on siliciclastic lithology	MAGIC	15/12	8/9	<0/3	71	Sullivan et al. (2008)
Shenandoah NP, VA	Most sensitive stream	MAGIC	9/9	8/6	<0/1	69	Sullivan et al. (2008)
Loch Vale, Rocky Mt. N.P., CO	The Loch	MAGIC	11.1/ND	7.8/ND	2.8/ND		(Sullivan et al. 2005)
Loch Vale, Rocky Mt. N.P., CO	Andrews Creek	MAGIC	8.1/ND	4.6/ND	<0/ND	28	(Sullivan et al. 2005)

Summary of Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems. The strongest evidence for a causal relationship comes from studies of changes in surface water chemistry including concentrations of SO_4^{2-}, NO_3^-, inorganic Al, and Ca, surface water pH, sum of base cations, ANC, and base cation surplus. Surface water chemistry integrates the sum of upstream soil and water processes and reflects the results of watershed-scale terrestrial effects of S and N deposition including, N saturation, forest decline, and soil acidification (Stoddard, 2003). In many cases, surface water chemistry indicates the effects of acidification on biotic species and communities found in fresh water ecosystems.

Surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralizing of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry has lower pH and ANC during storm runoff or snowmelt than during baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed “episodic acidification.” Some streams may have chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the Eastern U.S. caused partly by acidifying deposition and partly by natural processes.

Acidification effects on aquatic biota are often evaluated using measures of either Al or pH. ANC is also used because it is an indicator of buffering capacity (although ANC does not relate directly to the health of biota). The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

SO_4^{2-}, NO_3^-, and Base Cations

Changes in water chemistry resulting from acidifying deposition typically include changes in SO_4^{2-}, NO_3^-, and base cation concentrations. Each plays an important role in the acid-base chemistry of water, but none are directly toxic at concentrations commonly encountered in natural waters.

- SO_4^{2-} is the primary inorganic anion found in most acid sensitive waters. Continued decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in surface waters. However the rate of decrease in surface water SO_4^{2-} concentrations may be delayed as accumulated S leaches from watershed soils in some regions of the country, especially the Blue Ridge Mountains.

- The importance of NO_3^- as an agent of acidification varies by region, but it is particularly important during periods of high hydrologic flow from soils to streams such as those that occur during snowmelt and rain runoff. The relationship between N deposition and surface water NO_3^- concentration is complex and involves the terrestrial and aquatic cycling of N and other elements. NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S., but there is no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in these surface waters (in contrast to observed responses for S deposition and SO_4^{2-} concentrations). This suggests that the time scales of N saturation may be longer than previously considered (e.g., centuries rather than decades). Nevertheless, long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue indefinitely (Aber, 2003).

- Decreases in base cation concentrations in Eastern U.S. surface waters over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. Rates of base cation depletion have been similar to those for SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is a notable exception). Decreasing trends in base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

pH, Acid Neutralizing Capacity, and Aluminum

Acidification of surface water causes changes in pH, ANC, and inorganic aluminum concentration. Low pH and high inorganic aluminum concentration can be directly toxic to aquatic biota.

- The pH of freshwater streams and lakes is a common measure used to link acidification to adverse effects on aquatic biota. Decreases in pH below values of 6.0 typically result in species loss of benthic invertebrates, plankton species, and fish. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a greater likelihood that more aquatic species could be lost without replacement, resulting in decreased richness and diversity. (See the following discussion on biota).

- ANC reflects the difference between base cations and anions of strong acids in solution and is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. Acidic waters are defined as those having ANC equal to or below zero. Waters with ANC of < 50 μeq/L are considered “extremely acid sensitive” (Schindler, 1988) and are vulnerable to episodic acidification (DeWalle et al., 1987; Eshleman, 1988. Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the Eastern U.S. Since about 1990, the ANC of many affected lakes and streams has increased slightly. The number of acidic surface waters has decreased in some areas of the Northeast, but not in the mid-Appalachian Mountains.

- Dissolved inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water because it is toxic to aquatic life and generally does not leach from soils in the absence of acidification. When pH falls below approximately 5.5, inorganic Al generally becomes a greater health risk to biota. Limited data suggest that acid-sensitive regions of the Northeastern U.S. have elevated inorganic Al concentrations in surface waters induced by years of acidifying deposition, posing a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

3.2.3.2. Biological Effects

Aquatic effects of acidification have been well studied in the U.S. and elsewhere at various trophic levels. These studies indicate that aquatic biota have been affected by acidification at virtually all levels of the food web in acid sensitive aquatic ecosystems. Effects have been most clearly documented for fish, aquatic insects, other invertebrates, and algae.

Biological effects are primarily attributable to a combination of low pH and high inorganic Al concentration. Such conditions occur more frequently during rainfall and snowmelt that cause high flows of water and less commonly during low-flow conditions, except where chronic acidity conditions are severe. Biological effects of episodes include reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions. These conditions may also result in direct mortality as was shown from results of in situ bioassays (Van Sickle et al. 1996). High concentrations of Ca, and to a lesser extent other base cations, can lessen the toxicity of low pH and high inorganic Al concentration where they occur (Baker et al., 1990).

Biological effects in aquatic ecosystems can be divided into two major categories: (1) effects on health, vigor, and reproductive success; and (2) effects on biodiversity. The first category includes changes in biological indicators such as individual condition factor and recruitment success. The latter can be described by changes in species composition and taxonomic richness.

The following sections define concepts used to measure and evaluate acidification-related effects on aquatic biota. We present measures of changes in (1) health, vigor, and reproductive success, and (2) biodiversity for fish. Finally, the general effects literature is summarized for phytoplankton, zooplankton, benthic invertebrates, amphibians, and fish-eating birds. Specific reference is made to the biological indicators outlined above where such information exists.

Measures of Health, Vigor, and Reproductive Success

There are few measures of the effects of acidification on the health, vigor, and reproductive success of aquatic species. Condition factor is one measure of sublethal acidification stress that has been used to quantify effects of acidification on an individual fish. Condition factor is an index that describes the relationship between fish weight and length. Expressed as fish weight/length^3, multiplied by a scaling constant, this index reflects potential depletion of stored energy (Everhart and Youngs, 1981; Goede and Barton, 1990; Dennis, 1995). Condition factor is interpreted as depletion of energy resources such as stored liver glycogen and body fat in response to increased stress at sublethal levels (Goede and Barton, 1990). Fish with higher condition factor are more robust than fish having low condition factor. Field studies have shown lower condition factor in fish found in more acidic streams (Dennis, 1995).

Measures of Biodiversity

Species composition refers to the mix of species that are present in a particular ecosystem. Acidification alters species composition in aquatic ecosystems. There are a number of species common to many oligotrophic waters that are sensitive to acidifying deposition and that cannot survive, compete, or reproduce in acidic waters. In response to small to moderate changes in acidity, acid-sensitive species are often replaced by other more acid-tolerant species, resulting in changes in community composition, but little or no change in total community abundance or biomass. The extent of alteration of surface water biological community composition increases as surface waters become more acidic. There is also a common pattern of lower community diversity with increased acidification.

One important tool that aids in the determination of effects on species composition is the Acid Stress Index (ASI) developed by Baker et al. (1990a). This index uses fish bioassay survival data to predict the probability of fish survival expressed as a percent mortality. Separate ASI models were developed for tolerant, intermediate, and sensitive fish species.

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress on biota. It can be applied at various taxonomic levels. For example, the number of fish species present in a lake or stream can be used as an index of acidification (cf. Bulger, 1999). Similarly, acidification effects on aquatic insects can be evaluated on the basis of the number of families or genera of mayflies (order Ephemeroptera) (Sullivan, 2003). In the latter cases, the mayfly order was selected for study because it includes a number of genera and species having varying degrees of sensitivity to acidification.

Decreases in ANC and pH and increases in inorganic Al concentration have been shown to contribute to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish (Schindler, 1985; Keller, 1995). Species richness is positively correlated with pH and ANC (Rago and Wiener, 1986; Baker et al., 1990b) primarily because of the elimination of acid-sensitive species at lower pH and ANC (Schindler, 1985). Interpretation of species richness can be difficult because more species tend to occur in larger lakes and streams as compared with smaller ones, irrespective of acidity (Sullivan, 2003). Nevertheless, decreases in species richness have been observed for all major trophic levels of aquatic organisms (Baker et al., 1990a), even after adjusting for lake size (Harvey and Lee, 1982; Frenette et al., 1986; Rago and Wiener, 1986; Schofield, 1987) Matuszek and Beggs, 1988).

Health, Vigor, and Reproductive Success of Fish

Fish populations in acidified streams and lakes of Europe and North America have declined, and some have been eliminated as a result of atmospheric deposition of acids and the resulting changes in water quality (Baker et al., 1990a). A variety of water chemistry variables, including inorganic Al, dissolved OC, and Ca, along with the timing and magnitude of episodic fluctuations in toxic acid and inorganic Al concentrations, are related to the degree to which surface water acidification influences fish survival in natural systems (Baker et al., 1990c; Gagen et al., 1993; Siminon et al., 1993; Van Sickle et al., 1996; Baldigo, 1997).

The effects of acidification on the health, vigor, and reproductive success are manifested through a range of physiological effects on individual life stages and fish species. The primary mechanism for the toxic effects of low pH and elevated inorganic Al on fish involves disruption of normal ion regulation at the gill surface, resulting in increased rates of ion loss and inhibition of ion uptake (McWilliams and Potts, 1978; Leivestad, 1982; Wood and McDonald, 1987; Bergman et al., 1988). Additional effects might include (1) disruption of Ca metabolism (Peterson and Martin-Robichaud, 1986; Gunn and Noakes, 1987; Reader et al., 1988), and (2) decreased hatching success (Runn et al., 1977; Peterson et al., 1980; Haya and Waiwood, 1981; Waiwood and Haya, 1983).

There is marked variability among species, and among life stages within species, in the specific levels of pH and inorganic Al that produce measurable responses. In general, early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults (Baker, 1985; Johnson, 1987; Baker et al., 1990a). Also, small fish, especially swim-up fry, are probably less mobile and less able to avoid exposure to adverse chemical conditions than the relatively larger adults (Baker, 1996).

Here, effects are described by life stage. Several studies have shown that the earliest reproductive stages are highly sensitive to low pH. The processes of oogenesis and fertilization in fish are especially sensitive (Muniz, 1991; Havas et al., 1995), most likely due to adverse effects on the female spawner. For instance, Beamish (1976) reported that reduced serum and plasma Ca in female fish in acidified Canadian lakes caused a higher probability of failure in producing viable eggs. Depletion of Ca from bone and increased numbers of females with unshed eggs have also been linked to acidification at this life stage (cf. Rosseland, 1986; Muniz, 1991).

After fertilization, the embryo seems to be susceptible to acidic waters throughout the whole period of development, although periods shortly after fertilization and prior to hatching seem to be most critical (Rosseland, 1986). The susceptibility of the embryo can be the result of direct exposure to elevated hydrogen ion concentrations and also to the toxic effects of inorganic Al at intermediate pH-values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to either prolongation of hatching or to reduced hatching success (Rosseland, 1986). Eggs lying in gravel on stream and lake beds are, to some extent, protected from exposure to rapid changes in pH (Gunn and Keller, 1984b; Lacroix, 1985). Nevertheless, they can experience high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a). Yellowstone cutthroat trout (*O. c. bouveri*) were exposed to 7–day pH depressions by Farag et al. (1993). Of the four life stages studied, eggs were most sensitive to low pH. Eggs exposed for seven days to pH 5.0 test water showed a statistically significant reduction in survival compared with eggs exposed for seven days to pH 6.5 water. Survival of alevin and swim-up larvae were significantly reduced from near 100% at pH 6.5 to near 0% at pH 4.5. Intermediate pH values (6.0, 5.5) in all cases showed reduced survival compared with the control (6.5), but not by statistically significant amounts ($p > 0.05$).

Emergent alevins show susceptibility to the adverse effects of inorganic Al and hydrogen ion that increases with age (Baker, 1982). Rosseland (1986) indicated that this increasing sensitivity results from changes that take place in the respiratory system. Shortly after hatching, alevins still respire through their skin but gradually gills become the primary organ of gas and ion exchange. Gills are the locus for interference of hydrogen ion and inorganic Al with iono-regulatory exchange.

Woodward et al. (1989) exposed cutthroat trout (*Oncorhynchus clarki*) from the Snake River in Wyoming to pH depressions from pH 4.5 to 6.5 in the laboratory and found that reductions in pH from 6.5 to 6.0 in low-Ca water (70 μeq/L) did not affect survival, but did reduce growth of swim-up larvae. The eggs, alevin, and swim-up larval stages showed significantly higher mortality at pH 4.5 than at pH 6.5. Mortality was also higher at pH 5.0 than at pH 6.5, but only statistically higher for eggs. The authors concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of inorganic Al was pH 5.0 (Woodward, 1991).

In juvenile, young-of-year and adult fish there is an energy cost in maintaining physiological homeostasis; the calories used to respond to stress are a part of the fish's total energy budget and are unavailable for other functions, such as growth and reproduction (Schreck, 1981, 1982; Wedemeyer et al., 1990). Observed differences in condition factor may occur because maintenance of internal chemistry in the more acidic streams would require energy that otherwise would be available for growth and weight gain (Dennis and Bulger, 1999; Sullivan et al., 2003). The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish, 1969; Bulger, 1986).

Prominent physiological disturbances to fish exposed to acid waters are iono- and osmoregulatory failure, acid-base regulatory failure, and respiratory and circulatory failure. Most of these effects can be directly attributed to effects on gill function or structure. The acute toxicity of low pH in acidic waters results in the loss of Ca from important binding sites in the gill epithelium, which reduces the ability of the gill to control membrane permeability (McDonald, 1983; Havas, 1986; Exley and Phillips, 1988). Al has been shown to accumulate on the gill surface when fish are exposed to water having high inorganic Al concentration.

Cumulative sublethal physiological effects can be expressed by changes in condition factor. Condition factor has been developed and applied mainly for blacknose dace. This fish species is widely distributed in Appalachian Mountain streams and is moderately tolerant of low pH and ANC, relative to other fish species in the region. However, the condition factor concept is probably applicable to other species as well. Condition factor may be a useful metric for many species in aquatic ecosystems that are only marginally affected by acidification. Bulger et al. (1999) observed a positive relationship between dace condition factor and pH in streams in Shenandoah National Park. Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. In addition to effects on blacknose dace, condition factor, reduced growth rates have been also attributed to acid stress in a number of other fish species, including Atlantic salmon (*Salmo salar*), chinook salmon (*Oncorhynchus tshawytscha*), lake trout (*Salvelinus namaycush*), rainbow trout (*Oncorhynchus mykiss*), brook trout, brown trout (*Salmo trutta*), and arctic char (*Salvelinus alpines*) (Baker et al., 1990a).

In summary, some studies have been conducted on changes in the health, vigor, and reproductive success of fish exposed to water having low pH and high inorganic Al concentration. Blacknose dace have been most thoroughly studied regarding the sublethal effects of acidity on fish condition. Effects tend to vary by life stage; early life stages tend to be particularly sensitive. Adverse effects often involve disruption of gill function, partly due to Al toxicity.

Fish Biodiversity

Biodiversity loss is a predictable consequence of acidification and there are abundant examples of this in North America and Europe, mostly focused on fish (cf. Bulger, 2000). Population-level fish response to acidification is primarily through recruitment failure, a result of increased mortality of early life stages or indirect effects through the food chain (loss of prey species). Changes in inorganic Al, pH, and Ca most likely have the greatest influence on fish community structure. These changes in water chemistry can alter species composition and species richness, both of which are components of biodiversity.

By 1990, it was well established that changes in pH in the range of 4.0 to 6.5 could cause significant adverse biological effects on fish community composition. As described above, the toxicity of low pH was, in most cases, the result of impaired body salt regulation. Decreased water pH inhibited the active uptake of Na^+ and Cl^- and stimulated the passive loss of these ions from the bloodstream (Baker et al., 1990a). Species vary in terms of their sensitivity to such disruptions of physiological condition.

The response of fish to pH, ANC, and inorganic Al is not uniform across species. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH is lower, there is a greater likelihood that more fish species could be lost without replacement, resulting in decreased richness and diversity. In general, populations of salmonids are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than about 5.2 to 5.5. Bioassay experiments using brook trout eggs and fry have demonstrated greater mortality in chronically acidic stream water as compared to water having higher ANC.

The ASI is an index of acidification that uses fish bioassay survival data fitted to a regression model of exposure to water chemistry (pH, Al, and Ca) to predict the probability of fish survival. Approximate ASI reference levels were reported by Baker et al. (1990c) for various fish species, based on logistic regression of fish presence as a function of the sensitive, intermediate, and tolerant ASI values for brown bullhead (*Ameiurus nebulosus*), brook trout, lake trout, and common shiner (*Luxilus cornutus*).

Fish species richness is an important indicator of acidification response, in part because the public tends to place relatively high value on fisheries. As discussed in the previous section, lakes and streams having pH below about 5.0 or ANC below about 0 generally do not support fish. There is often a positive relationship between pH and number of fish species, at least for pH values between about 5.0 and 6.5, or ANC values between about 0 and 50 to 100 μeq/L (Bulger, 1999; Cosby, 2006)Sullivan et al., 2006a). Such observed relationships are complicated, however, by the tendency for smaller lakes and streams, having smaller watersheds, to also support fewer fish species, irrespective of acid-base chemistry. This pattern may be due to a decrease in the number of available niches as stream or lake size decreases.

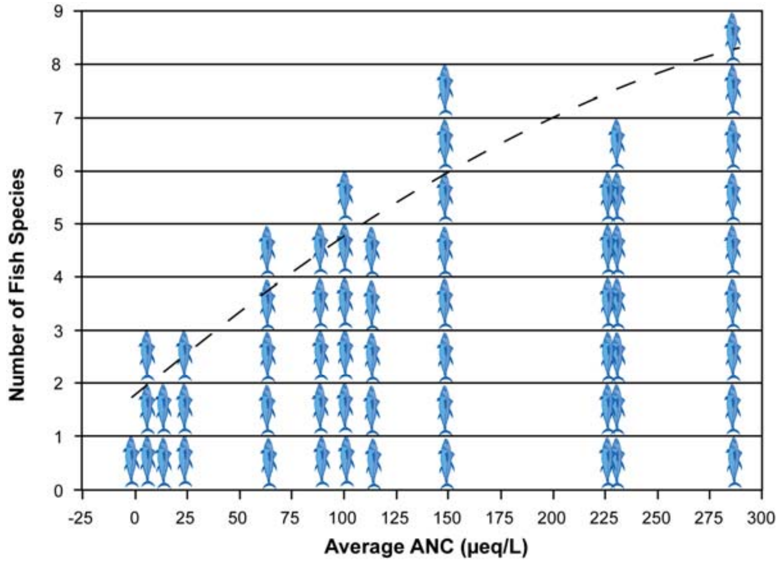
Nevertheless, fish species richness is relatively easily determined and is one of the most useful indicators of biological effects of surface water acidification.

Some of the most in-depth studies of the effects of acid stress on fish species richness have been conducted in the streams in Shenandoah National Park, Virginia and the lakes in the Adirondack Mountains, New York. These regions are examined in detail below. However, note that effects on fish species richness have also been documented in acid-sensitive streams of the Catskill Mountains of southeastern New York (Stoddard, 1991) and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina (SAMAB, 1996; Bulger, 1999; Bulger, 2000).

The Shenandoah National Park Fish in Sensitive Habitats (FISH) Project evaluated the effects of streamwater acidification on fish communities in streams in Shenandoah National Park (Bulger, 1995)Dennis et al., 1995; Dennis, 1995)MacAvoy and Bulger, 1995). A statistically robust relationship between stream ANC and fish species richness was documented. Numbers of fish species were compared among 13 Shenandoah National Park streams spanning a range of pH and ANC conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base status (during the 7–year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 3-15). The 3−year FISH study of stream acidification demonstrated negative effects on fish from both chronic and episodic acidification (Bulger, 1999). Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress from acidification. However, an additional causal factor may have been a decrease in the number of available aquatic niches when moving from downstream locations (which are seldom low in pH and ANC) to upstream locations (which are often low in pH and ANC in this region; Sullivan et al., 2003).

South of Shenandoah National Park, the effects of surface water acidification on fish species richness have been studied in some detail in the St. Marys River in Virginia. Fish species richness was closely associated with surface water acid-base chemistry. The number of fish species in the St. Marys River within the wilderness declined from 12 in 1976 to 4 in 1998. Three of the four species present in 1998 (brook trout, blacknose dace, fantail darter [*Etheostoma flabellare*] are tolerant of low pH and are typically the only fish species present in streams having similar levels of acidity in nearby Shenandoah National Park (Bulger, 1999).

Dynamic water chemistry model projections have been combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the Shenandoah National Park data was used by Sullivan et al. (2003), along with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present and future chemical conditions simulated for each stream. Results suggest that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic bedrock; 1.6 species lost), with fewer lost species on granitic bedrock and basaltic bedrock (average of 0.4 species lost).



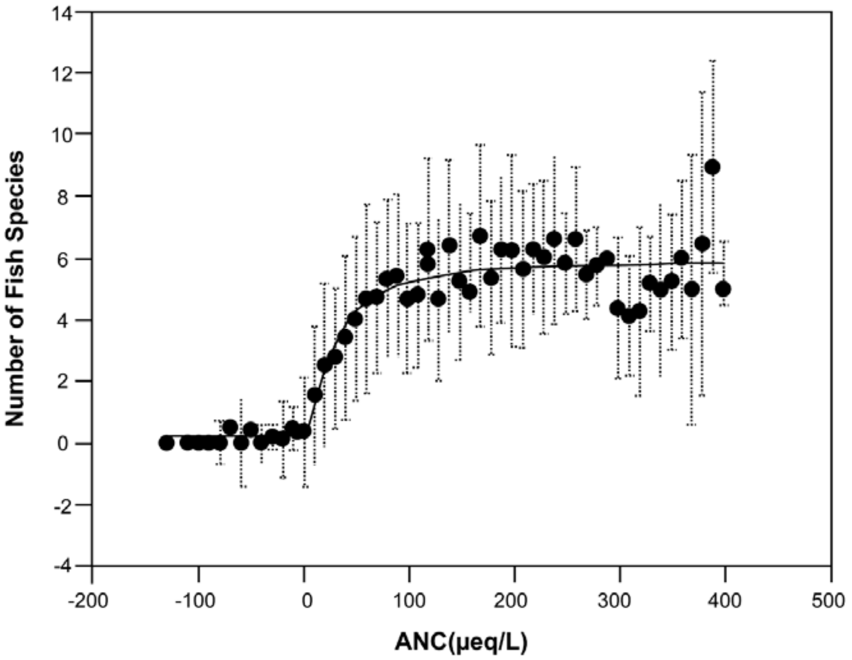
Source: Redrawn from Bulger et al. (1999)

Figure 3-15. Number of fish species as a function of mean stream ANC among 13 streams in Shenandoah National Park, Virginia. Values of ANC are means based on quarterly measurements, 1987–1994. The regression analysis showed a highly significant relationship ($p < 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently < 50 μeq/L had three or fewer species.

In the Adirondack Mountains, lakewater acidification and the associated elevated concentrations of inorganic Al have adversely affected fish populations and communities in sensitive areas (Baker and Schofield, 1982; Johnson, 1987; Schofield, 1987) Baker et al., 1990b; Siminon et al., 1993). Of the 53 fish species recorded in Adirondack lakes by the Adirondack Lakes Survey Corporation, about half (26 species) were absent from lakes with pH below 6.0. Among the absent species were several important recreational species (Baker et al., 1990b), plus ecologically important minnows that serve as forage for sport fish. Fully 346 of 1,469 lakes surveyed supported no fish at all at the time of the survey. These lakes were significantly lower in pH, dissolved Ca, and ANC, and had higher concentrations of inorganic Al than lakes hosting one or more species of fish (Gallagher, 1990). Among lakes with fish, there was an unambiguous relationship between the number of fish species and lake pH, ranging from about one species per lake for lakes having pH less than 4.5 to about six species per lake for lakes having pH higher than 6.5 (Baker et al., 1990b; Driscoll et al., 2001a).

High-elevation lakes are more likely to be fishless than larger lakes at low elevation (Gallagher, 1990). This observation has been attributed to the fact that high elevation lakes tend to have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to periodic winter kills. Small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless high-elevation lakes; acidity is likely to play an important role in the absences of fish from such lakes (Driscoll et al., 2001b).

Sullivan et al. (2006a) developed a relationship between fish species richness and ANC class for Adirondack lakes. Under chronically acidic conditions (summer index or annual average ANC < 0 µeq/L), Adirondack lakes are generally without fish. There was a marked increase in mean species richness with increases in ANC up to values of approximately 50 to 100 µeq/L (Figure 3-16). The asymptote for the fish species equation was 5.7 species. This analysis suggests that there could be loss of fish species with decreases in ANC below approximately 50 to 100 µeq/L. The response functions from Shenandoah National Park (Figure 3-15) and the Adirondack Mountains (Figure 3-16) are generally similar at low ANC values, below about 100 µeq/L. Fish species richness was somewhat higher in Shenandoah National Park at higher ANC values. The reasons for this difference are not known.



Source: Sullivan et al. (2006a)

Figure 3-16. Number of fish species per lake versus acidity status, expressed as ANC, for Adirondack lakes. The data are presented as mean (filled circles) and range (bars) of species richness within 10 µeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

The absence of fish from a given lake or stream in an area that experiences surface water acidification does not necessarily imply that acidification is responsible for the absence of fish. For example, results of fisheries research in the Adirondacks has indicated that many Adirondack lakes always had marginal spawning habitat for brook trout (Schofield, 1993). However, multivariate regression of the presence or absence of brook trout in Adirondack waters produced a ranking of factors that appeared to influence the presence of brook trout when biological factors (stocking, presence of associated species, presence of competitors) were excluded from the analysis. Among contributing factors, including silica (Si), ANC, dissolved OC, substrate type, and distance to the nearest road, pH ranked first as a predictor of brook trout presence (Christensen et al., 1990). The results of this analysis supported the conclusion that 1990 levels of pH and related variables restricted the distribution of fish in some Adirondack lakes.

In summary, acidic conditions characterized by low pH, low ANC, and high inorganic Al exert considerable influence on the fish species composition of sensitive surface waters, particularly in the eastern U.S. Low pH and ANC, and high inorganic Al concentrations, contribute to loss of the most acid-sensitive fish species. Species richness is a common indicator used to reflect the effects of water acidification on aquatic biota. This index is most often applied to fish. Few or no fish species are found in lakes and streams that have very low ANC (near zero) and low pH (near 5.0). The number of fish species generally increases at higher ANC and pH values. This relationship is complicated, to some extent, by the tendency of smaller lakes and streams (which are more likely to have low ANC and pH) to host fewer fish species, regardless of acid-base chemistry. Nevertheless, available data strongly suggest that acid stress is a major factor governing the observed relationship between fish species richness and surface water acidity.

Summary of Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota. The strongest evidence for a causal relationship comes from studies of aquatic systems exposed to elevated levels of acidifying deposition that support fewer species of fishes, macroinvertebrates, and diatoms. Although there are few studies of the response of higher trophic levels to pH changes resulting from acidifying deposition, piscivorous birds are known to be affected by acidifying deposition. Consistent and coherent evidence from multiple species and studies shows that acidification can result in the loss of acid-sensitive species, and more species are lost with greater acidification. Biological effects are linked to changes in water chemistry including ANC, pH, and Al. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur over both long- and short-term time scales, with additional effects on biological systems. Short-term (hours or days) episodic changes in water chemistry can have biological effects, including reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions.

Species

- Logistic regression modeling showed that the occurrence of two piscivorous birds (common loons and common mergansers) is positively related to the pH of lakes in the Algoma region of Ontario. Model estimates suggested that the number of lakes projected to be suitable for supporting breeding pairs and broods of these bird species increased with increasing lake pH.
- High levels of acidification (to pH values below 5) virtually eliminate all mayflies, crustaceans, and mollusks from some streams.
- In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (Micropterus dolomieu) populations are usually not found at pH values less than 5.5 to 5.2.
- Twenty percent mortality of young-of-the year brook trout was documented during a 30–day period with a median inorganic Al concentration of 2 µmol/L (Baldigo, 2007). It was estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

Community

Community-level effects were observed in the Adirondacks and Shenandoah National Park where taxonomic richness is lower in lakes and streams having low ANC and pH.

- Decreases in pH and increases in inorganic Al concentrations have reduced the species richness of plankton, invertebrates, and fish in acid-affected surface waters.
- Invertebrate taxa that are most sensitive to acidification include mayflies, amphipods, snails, and clams.
- In the Adirondacks, a positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes. A number of synoptic surveys indicated suggested loss of species diversity and absence of several sensitive fish species in the pH range of 5.0 to 6.0.

- In Shenandoah National Park streams, the fish species richness decreased with decreasing stream ANC. On average, richness is lower by one fish species for every 21 μeq/L decrease in ANC.

- Short-term episodes of acidification are particularly harmful to aquatic biota. Early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults. Episodes are most likely to affect biota if the water had pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. Episodic acidification can have long-term adverse effects on fish populations.

3.2.4. Most Sensitive and Most Affected Ecosystems and Regions

3.2.4.1. Characteristics of Sensitive Ecosystems

The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification from S and N deposition is geology (particularly surficial geology). Geologic formations having low base cation supply generally underlie the watersheds of acid-sensitive lakes and streams. Bedrock geology has been used in numerous acidification studies (e.g., Bricker, 1989); Stauffer, 1990; Stauffer and Wittchen, 1991; Vertucci and Eilers, 1993; Sullivan et al., 2007). Other factors contribute to the sensitivity of soils and surface waters to acidifying deposition, including topography, soil chemistry, land use, and hydrologic flowpath.

Several studies have confirmed the importance of geology in regulating terrestrial and aquatic ecosystem sensitivity to acidification, and highlighted other key factors responsible for terrestrial and aquatic sensitivity to acidifying deposition throughout the southeastern U.S. Sensitive terrestrial ecosystems include high-elevation spruce-fir forests dominated by relatively nonreactive bedrock in which base cation production via weathering is limited (Elwood, 1991). Soils in such areas tend to have thick organic horizons, high organic matter content in the mineral horizons, and low pH 2. Because of the largely nonreactive bedrock, base-poor litter and organic acid anions produced by the conifers, high precipitation, and high leaching rates, soil base saturation in these high-elevation forests tends to be below about 10% and the soil cation exchange complex is generally dominated by Al (Johnson, 1992)Eagar et al., 1996).

Galloway (Galloway, 1996) further attributed forest soil sensitivity to acidification in the southeastern U.S. to atmospheric deposition level, soil age, weathering rate, and S adsorption capacity. Moncoulon et al. (2004) suggested that forest ecosystem sensitivity to acidification varies mainly with weathering rate. In a review of 241 ecosystem types in France (classified by pedologic and geologic characteristics), the ecosystems most susceptible to acidification were those with low weathering rates and thus limited buffering capacity (Moncoulon et al., 2004).

In hardwood forests, species nutrient needs, soil conditions, and additional stressors work together to determine sensitivity to acidifying deposition. Stand age and successional stage also can affect the susceptibility of hardwood forests to acidification effects. In northeastern hardwood forests, older stands exhibit greater potential for Ca depletion in response to acidifying deposition than younger stands. Thus, with the successional change from pin cherry (*Prunus pensylvanica*), striped maple (*Acer pensylvanicum*), white ash (*Fraxinus americana*), yellow birch and white birch (*Betula papyrifera*) in younger stands to beech and red maple in older stands, there is an increase in sensitivity to acidification (Hamburg et al., 2003).

Land use influences watershed sensitivity to acidification mainly through disturbance and consequent exposure of S-bearing minerals to oxidation, loss of base cations through erosion and timber harvesting, and change in N status of the forest through timber management. Each of these types of activity can influence the relative availability of mobile mineral acid anions (SO_4^{2-}, NO_3^-) in soil solution and base cations (Ca, Mg, K, Na) on the soil ion exchange sites and in drainage water.

The movement of water through the soils into a lake or stream, and the interchange between drainage water and the soils and sediments, strongly regulate the type and degree of watershed response to acidic inputs (Sullivan, 2000). Surface waters in the same setting can have different sensitivities to acidification depending on the relative contributions of near-surface drainage water and deeper groundwater (Eilers et al., 1983; Chen et al., 1984; Driscoll et al., 1991).

Movement of a strong acid anion, such as SO_4^{2-} or NO_3^-, through an acidic soil can mobilize H^+ and Al^{3+} because these cations are available on soil exchange sites. There is no time lag in this exchange reaction and it is instantly reversible if input of strong acid anions is ceased (Turner, 1990). It is necessary, however, for appreciable mobilization of H^+ and Al^{3+} that the soil be acidic, either naturally or because of soil acidification from acidifying deposition.

In summary, lakes and streams in the U.S. that are sensitive to episodic and chronic acidification in response to SO_X, and to a lesser extent NO_X, deposition tend to occur at relatively high elevation in areas that have base-poor bedrock, high relief, and shallow soils. For example, in the Southern Appalachian region, Sullivan et al. (2002a, 2007) determined that underlying bedrock geology dominated by sandstone or related rock types and elevations greater than 1000 m (3250 ft) could be used to identify landscapes in the region most likely to contain acidic streams.

3.2.4.2. Extent and Distribution of Sensitive Ecosystems

Surface Waters

Several regions of the U.S. contain appreciable numbers of lakes and streams with low ANC (less than about 50 μeq/L), including portions of the Northeast (especially New England, the Adirondacks, and the Catskill Mountains), Southeast (the Appalachian Mountains and northern Florida), Upper Midwest, and western U.S. (Charles, 1991). The Adirondack and Appalachian Mountains, and to a lesser extent the Upper Midwest, include many acidified surface waters that have been affected by acidifying deposition. Portions of northern Florida also contain many acidic and low-ANC lakes and streams, although the role of acidifying deposition in these areas is less clear. The Western U.S. contains many of the surface waters most susceptible to potential acidification effects, but with the exception of the Los Angeles Basin and surrounding areas, the levels of acidifying deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has likely been very limited.

Several national assessments were conducted to estimate the distribution and extent of surface water acidity in the U.S. During summer baseflow of 2004, the EPA conducted a National Wadeable Stream Assessment (WSA) survey of 1,392 randomly selected sites across the conterminous 48 U.S. to assess the ecological condition of wadeable streams (EPA, 2006c). Because this sampling was conducted during baseflow in the summer (which exhibits the least acidic conditions of the year) only the most chronically acidified streams were identified as acidic. Therefore, the extent of potential seasonal acidification was underestimated by this approach (Lawrence et al., in press). Overall, less than 1% of the 1,020,000 km of stream in the target population (based on the 1:100,000–scale U.S. Geological Survey (USGS) map blue line network) was acidic due to acidifying deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Acidic streams attributable to acidifying deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0–25 μeq/L) streams likely exposed to episodic acidification were found in the Northern Appalachians (2.7% of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of 204,000 km).

Even though the WSA had over 1,300 sample sites, it was still a very coarse sample of the nation's streams with respect to acidifying deposition effects, which are only observed in spatially restricted subpopulations. More precise survey estimates of the effects of surface water acidification were made in the National Surface Water Survey (NSWS) in the mid 1980s. By statistically selecting representative lakes and streams in each surveyed region, the NSWS estimated chemical conditions of 28,300 lakes and 56,000 stream reaches (Baker et al., 1990c). The NSWS concluded that 4.2% of lakes larger than 4 ha and

2.7% of stream segments in the acid-sensitive regions of the eastern U.S. were acidic. The NSWS documented the status and extent of surface water acid-base chemistry during probability surveys of lakes and streams conducted from 1984 through 1988 in the major acid sensitive regions of the U.S. (Linthurst et al., 1986a; Landers et al., 1987; Kaufmann et al., 1988).

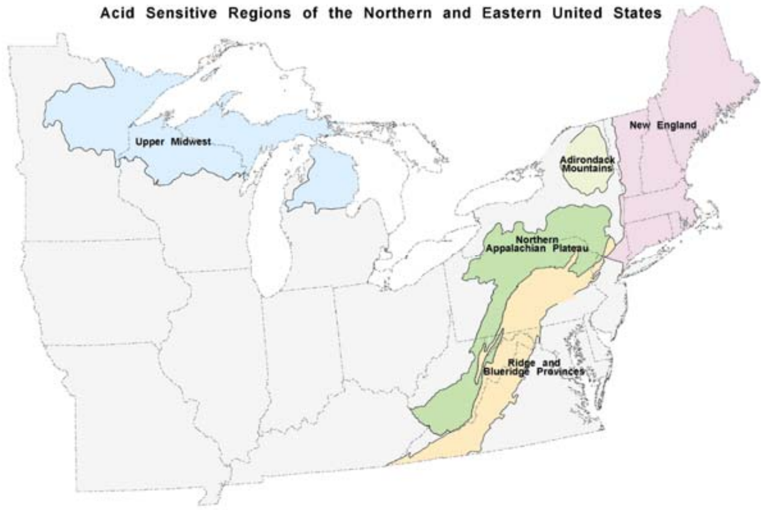
The stream component of the NSWS, the National Stream Survey (NSS), was focused in the northern and southern Appalachians and Coastal Plain of the Eastern U.S. (Kaufmann et al., 1991). The NSS included 500 stream reaches selected from 1:250,000 scale USGS topographic maps using a systematic, randomized sample. Study reaches were sampled at both the upstream and downstream end of each selected reach. Population estimates were made for chemistry at both reach ends and for stream length by interpolating chemical results between reach ends.

Overall, out of the estimated 57,000 stream reaches in the NSS, after excluding streams acidic due to acid mine drainage, 6.2% of the upstream and 2.3% of the downstream reach ends were acidic during spring baseflow (Kaufmann et al., 1991). After interpolation, this corresponded to 2.7% of the 201,000 km of stream in the study region. In acidic and low-ANC NSS reaches, ANC usually increased with downstream distance. Acidic ($ANC \leq 0$) streams were located in the highlands of the Mid-Atlantic Region (southern New York to southern Virginia, 2320 km), in coastal lowlands of the Mid-Atlantic (2530 km), and in Florida (461 km). Acidic streams were rare (less than 1%) in the highlands of the Southeast and Piedmont. Inorganic monomeric Al concentrations were highest in acidic streams of the Mid-Atlantic Highlands, where over 70% of the acidic streams had inorganic Al greater than 3.7 µM (100 µg/L), a concentration above which deleterious biological effects have frequently been reported.

Anion composition of the NSS stream samples was examined to evaluate the most probable sources of stream acidity in acidic and low-ANC sites (Baker et al., 1991; Herlihy et al., 1991). Acidic streams that had minimal organic influence (organic anions constituted less than 10% of total anions), and SO_4^{2-} and NO_3^- concentrations indicative of evaporative concentration of atmospheric deposition, were classified as acidic due to acidifying deposition. These acidic streams were located in small ($< 30\ km^2$) forested watersheds in the Mid-Atlantic Highlands (an estimated 1980 km of stream length) and in the Mid-Atlantic Coastal Plain (1250 km). Acidic streams affected primarily by acidifying deposition but also influenced by naturally occurring organic anions accounted for another 1210 km of acidic stream length and were mainly located in the New Jersey Pine Barrens, plateau tops in the Mid-Atlantic and Southeast Highlands, and the Florida Panhandle. The total length of streams that were identified as acidic due to acid mine drainage in the NSS (4590 km) was about the same as the total length of acidic streams likely affected by acidifying deposition (4455 km). Acidic streams whose acid anion composition was dominated by organics were mainly located in Florida and the Mid-Atlantic Coastal Plain. In Florida, most of the acidic streams were organic-dominated, whereas about half of the acidic streams in the Mid-

Atlantic Coastal Plain were organic-dominated. Organic-dominated acidic streams were not observed in the Mid-Atlantic or Southeast Highlands.

Stoddard et al. (2003) presented a map of acid-sensitive regions of the eastern U.S. where lakes and streams occur that are likely to be affected by acidifying deposition (Figure 3-17). The map shows considerable overlap with the areas of high interest identified by Baker et al. (1990c). Surface waters in most other regions of the U.S. are not sensitive to the effects of acidification due largely to the nature of the local geology (Stoddard, 2003). An exception is the region surrounding the Los Angeles Basin, which receives high N deposition (> 20 kg N/ha/yr in some areas) and includes streams with very high NO_3^- concentrations (> 50 µeq/L; Bytnerowicz and Fenn, 1996; Fenn and Poth 1999, 2001).



Source: Stoddard et al. (2003).

Figure 3-17. Regions of the eastern U.S. that contain appreciable numbers of lakes and streams that are sensitive to acidification from acidifying deposition.

In addition to the large water chemistry databases developed by the EPA that help to identify the spatial distribution of acid-sensitive and acid-affected surface waters in the U.S., there are also some important supplemental regional databases in New England, the Adirondacks, the mid-Appalachian region, the Florida Panhandle, the Upper Midwest, and the Western U.S. Results from these studies are summarized in the following paragraphs.

New England

For the New England region, results from EPA's TIME program indicate that 5.6% of the regional lake population (386 lakes) in New England exhibited ANC < 0 µeq/L during the period 1991 to 1994. This result is similar to the Environmental Monitoring and Assessment Program (EMAP) findings, which indicate that 5% of lakes in New England had ANC values less than 0 μeq/L. The EMAP survey was a probability based survey representative of lakes with surface area greater than 1 ha (1,812 lakes). The survey was conducted during low-flow summer conditions, and the results therefore likely reflect the highest ANC values for the year. The EMAP analysis also estimated that an additional 10% of the population had low ANC values, between 0 and 50 μeq/L, and were probably sensitive to episodic acidification (Driscoll et al., 2001b).

Adirondacks

A study by Driscoll et al. (2001b) used EMAP data from 1991 to 1994 to evaluate the extent of acidic lakes in the Adirondacks for that period. Results from the survey indicate that 10% of the population of Adirondack lakes were chronically acidic (ANC values of less than 0) and 31% were sensitive to episodic acidification (ANC values between 0 and 50) during the study period (Driscoll et al., 2001b).

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

Mid-Appalachian Region

A compilation of survey data from the mid-Appalachians yields a consistent picture of the acid-base status of streams. In the subpopulation of upland forested streams, which comprises about half of the total stream population in the mid-Appalachian area, data from various local surveys showed that 5% to 20% of the streams were acidic and about 25 to 50% had ANC < 50 μeq/L (Herlihy et al., 1993). NSS estimates for the whole region showed that there were 2330 km of acidic streams and 7500 km of streams with ANC < 50 μeq/L. In these forested reaches, 12% of the upstream reach ends were acidic and 17% had pH ≤ 5.5. SO_4^{2-} from atmospheric deposition was the dominant source of acid anions in acidic mid-Appalachian streams.

Cosby et al., (Cosby, 2006) provided a detailed characterization of streamwater acid-base chemistry in Shenandoah National Park, Virginia, which has been the most thoroughly studied area within the mid-Appalachian Mountain region with respect to acidification from acidifying deposition. Based on MAGIC model simulations and extrapolation using landscape characteristics, Cosby et al. (Cosby, 2006) developed maps showing the distribution of streamwater conditions in the Park for the preindustrial past, current conditions, and anticipated future conditions.

Florida Panhandle

According to the EPA's Eastern Lakes Survey conducted in 1984, 75% of the Florida Panhandle lakes were acidic at that time, as were 26% of the lakes in the northern peninsula. Most of the acidic lakes were clear water (dissolved OC < 400 µM) seepage lakes in which the dominant acid anions were chloride and SO_4^{2-}. Most of the acidic and low-ANC lakes were located in the Panhandle and northcentral lake districts. Acidic streams were located in the Panhandle and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-corrected sum of base cations (mean 21 µeq/L) and sea salt-corrected SO_4^{2-} concentrations (mean 16 µeq/L). One-fourth of these acidic Panhandle streams were organic-dominated but the remaining sites all had dissolved OC < 2 mg/L. Inorganic monomeric Al concentrations in these acidic streams were very low (mean 11 µg/L). In these low dissolved OC, low ANC Panhandle streams, it was suggested that the degree of SO_4^{2-} and NO_3^- retention in soil was an important control on streamwater ANC (Baker et al., 1990c).

Upper Midwest

Based on the Eastern Lakes Survey, the Upper Midwest has a large population of lakes having ANC ≤ 200 µeq/L, (Linthurst et al., 1986a,b); only 6% of the lakes had ANC ≤ 50 µeq/L. Groundwater recharge lakes (those having Si concentration less than 1 mg/L, indicating little groundwater input) constituted 71% of the seepage lakes in the Upper Midwest, and were more frequently low in pH and ANC. Five percent were acidic and 9% had pH ≤ 5.5. Nearly 90% of Upper Midwestern lakes that had ANC ≤ 50 µeq/L were in the groundwater recharge category (Baker et al., 1991). Such lakes tend to be susceptible to acidification from acidifying deposition.

Acidic lakes in the Upper Midwest are primarily small, shallow, seepage lakes that have low concentrations of base cations and Al and moderate SO_4^{2-} concentrations. Organic anions, estimated by both the Oliver et al. (1983) method and the anion deficit, tend to be less than half the measured SO_4^{2-} concentrations in the acidic lakes (Eilers, 1988, but much higher in many of the drainage lakes that are less sensitive to acidification from acidifying deposition.

West

Landers et al. (1987) identified subregions in the West with acid-sensitive lakes, based on results of EPA's Western Lakes Survey. The surface water chemistry data for the West indicate that the Sierra Nevada and Cascade Mountains constitute the mountain ranges with the greatest number of sensitive lake resources. Surface waters in this region are among the most poorly buffered surface waters in the U.S. (Landers et al., 1987; Melack and Stoddard, 1991). The hydrologic cycle is dominated by the annual accumulation and melting of a dilute, mildly acidic snowpack.

Many Cascade and Rocky Mountain lakes are highly sensitive to potential acidifying deposition effects (Nelson, 1991; Turk and Spahr, 1991). It does not appear that chronic acidification has occurred to any significant degree, although episodic acidification has been reported for lakes in the Colorado Front Range (Williams and Tonnessen, 2000).

Along the eastern edge of the Continental Divide in Colorado and southeastern Wyoming, Musselman et al. (1996) conducted a synoptic survey of surface water chemistry in the mountainous areas that are exposed to relatively high (by western standards) deposition of N. A total of 267 high-elevation lakes situated in watersheds having a high percentage of exposed bedrock or glaciated landscape were selected for sampling. None of the lakes were chronically acidic (ANC < 0), although several had ANC < 10 μeq/L, and more than 10% of the lakes had ANC < 50 μeq/L.

Forest Ecosystems

No systematic national survey of terrestrial ecosystems in the U.S. has been conducted to determine the extent and distribution of terrestrial ecosystem sensitivity to acidifying deposition. The scarcity of information on sensitive terrestrial ecosystems is due in part to sparse soils data. In general, forest ecosystems of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forests in the southern Appalachians are considered to be the regions most sensitive to terrestrial acidification effects from acidifying deposition.

One national and a few regional efforts have been undertaken to characterize forest sensitivity to acidifying deposition using a critical loads approach. In this context, acid-sensitive soils are those which contain low levels of exchangeable base cations and low base saturation. On a broad national scale, McNulty et al. (McNulty, 2007) used a simple mass balance equation and available national databases to estimate forest soil critical acidic loads (for wet and dry deposition of S and N) and exceedences for forest soils. Exceedences are pollutant loads that are greater than the estimated critical load for that location. They found that approximately 15% of forest soils in the U.S. receive acidifying deposition that exceeds the estimated critical load of wet and dry deposition of S and N by more than 250 eq ha/yr (McNulty, 2007). The areas where exceedences reach this level could be considered to represent those areas that are likely most sensitive to continued high levels of acidifying deposition. Thus, there is not a national survey of soil sensitivity to acidification, but there are approaches available with which to identify areas likely to include sensitive soils.

Note that the McNulty et al. (McNulty, 2007) paper represents the beginning of an iterative process to identify more precise critical loads for terrestrial acidity. The authors note that the actual area in exceedence of the forest soil critical acid load may be higher than the mapped estimates for several reasons (McNulty, 2007). First, their estimated total deposition did not include cloud deposition. Second, base cation deposition to near-coastal areas was not corrected for marine aerosol contributions. Third, the 1–km squared grid size of the mapping resulted in averaging of soil and deposition data, which removed extreme values from the analysis (McNulty, 2007). The authors take care to describe their results as "preliminary" and note that a more systematic analysis of model-predicted and measured forest soil critical acid load exceedance is needed before this approach can be used as a tool for identifying areas of potential forest health concern (McNulty, 2007). For these reasons, and because of the significant uncertainty associated with many of the large national databases used in the analysis, the appropriate use of this information is not for the actual determination of critical loads at specific locations or for predictions of forest health effects, but rather for increased understanding of relative differences in forest soil sensitivity at a national scale. In general, the Northeast, the Southern Appalachians, parts of Florida and the Upper Midwest have the highest proportion of soils that exceed the estimated critical acid loads by at least 250 eq ha/yr and could, therefore, be termed vulnerable. Where the exceedances are highest, forest soils are likely most sensitive to continued effects from acidifying deposition.

At a regional scale, Pardo et al. (Pardo, 2007) calculated critical loads of S and N deposition to forests in Great Smoky Mountains National Park (GSMNP) based on available data. A simple mass balance model and the Very Simple Dynamic model (VSD) were used to calculate a critical load for acidity (N+S) and N nutrient. The authors concluded that current deposition exceeded the critical load at all four sites evaluated (2 high elevation spruce-fir sites, a mid-high elevation beech site, and a lower elevation mixed hardwood site). The exceedance for S + N deposition ranged from 150 eq/ha/yr for the low elevation mixed hardwood site to 2300 eq/ha/yr at the upper spruce-fir site. The maximum acceptable deposition of N ranged from 200 eq/ha/yr (3 kg/ha/yr) for the low elevation mixed hardwood site to 500 eq/ha/yr (7 kg/ha/yr) at the upper spruce-fir site.

Another approach to identification of sensitive forest lands is to map the distribution of tree species thought to be most sensitive to adverse effects. The effects of acidifying deposition are particularly well documented for red spruce trees (Johnson, 1992; Cronan, 1995; Joslin, 1992; Johnson, 1994) that occur in the northeastern U.S. and southern Appalachian Mountains (Table 3-6 shows the distribution). In the Northeast, red spruce grows at elevations from near sea level to about 1,400 m. In the Appalachian Mountains, spruce-fir forests are generally found at relatively high elevation, for example above about 1400 m in the southern portion of the range (SAMAB, 1996). Northern hardwood forests have also been identified as forest resources experiencing air pollution effects. Effects are best documented for sugar maples, which are broadly distributed across the northern hardwood forests in the northeastern U.S. (Figure 3-6 shows the distribution). The areas where sugar maples appear to be at greatest risk are along ridges and where this species occurs on nutrient-poor soils.

Model Simulations

In the eight-state Southern Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC class. The model runs were based on three emissions control strategies (A2, B1, and B3). A2 is the base case that represents best estimates for air emission controls under regulations for which implementation strategies were relatively certain at the time of the study (about the year 2000), including the acid rain controls under Title IV of the 1990 Amendments to the CAA, the 1–h ozone (O_3) standard, NO_X reductions required under EPA's call for revised State Implementation Plans (SIPs), and several highway vehicle and fuel reductions. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight states in the southern Appalachian Mountains region, but covering all emissions sectors.

The results for the portion of the region south of Virginia and West Virginia suggest that the percentages of streams having ANC below zero and below 20 μeq/L will actually increase through the year 2040 under all except the most restrictive emissions control strategies (Sullivan et al., 2005). Most simulated changes in stream water ANC from 1995 to 2040 were rather modest, given the very large estimates of future decrease in S deposition. Few modeled streams showed projected change in ANC of more than about 20 μeq/L (Sullivan et al., 2005). Some of the largest changes were simulated for some of the streams that were most acidic in 1995. For such streams, however, even relatively large increases in ANC would still result in stream water having negative ANC, and therefore little biological improvements would be expected from the simulated improvement in chemistry (Sullivan et al., 2005).

Sullivan et al. (2002b) used the NuCM model to evaluate potential changes in soil chemistry in response to acidifying deposition in the southern Appalachian Mountains. The results suggest that spruce-fir forests in the region are likely to experience decreased Ca:Al ratios in soil solution under virtually all strategies of reduced future acidifying deposition considered. This result was partly because SO_4^{2-} adsorption in soils is likely to decline, even with dramatically reduced S deposition. In addition, many spruce-fir forests in the region are N-saturated, and continued N deposition at moderate or high levels would be expected to contribute to elevated NO_3^- concentrations in soil water, which could further enhance base cation leaching and mobilization of Al from soils to soil solution.

In the Adirondacks, model results produced by several studies suggest that the trend of increasing lakewater ANC for the most acid-sensitive lakes might not continue in coming decades. These results are discussed above in the Adirondack case study.

In a regional application of PnET-BGC, Chen and Driscoll (2005) analyzed 60 DDRP (Direct Delayed Response Project) lake watersheds within northern New England under three future emissions reduction scenarios. Most of the lakes had surface water ANC values greater than 50 μeq/L in 1984 and were therefore not considered chronically acidic. The authors reported that ANC was projected to increase under all three scenarios, with greater rates of recovery occurring with deeper emissions reductions. Soil improvements were slow and modest under all scenarios. Simulations suggested that 80% of the northern New England sites and 60% of the Maine sites will have soil base saturation below 20% in 2050 (Chen and Driscoll, 2005). They concluded that the decreases in SO_4^{2-} and NO_3^- concentrations in surface water were coupled with nearly stoichiometric decreases in base cation concentrations. Simulated improvements in ANC in response to reduced acidifying deposition were minor. Therefore, while further declines in atmospheric deposition in S and N will bring some improvements, most ecosystems in the study were not expected to recover to background conditions by 2050.

Bulger et al. (2000) developed model-based projections using the MAGIC model to evaluate the potential effect of reductions in S deposition of 40% and 70% from 1991 levels using data from streams in and near Shenandoah National Park. Projections were based on four brook trout stream categories: Suitable, ANC > 50 μeq/L; Indeterminate, ANC 20 to 50 μeq/L; Marginal, ANC 0 to 20 μeq/L; and Unsuitable, ANC < 0 μeq/L. Three scenarios of future acidifying deposition were modeled: constant deposition at 1991 levels, 40% reduction from 1991 deposition levels, and 70% reduction from 1991 deposition levels. Based on observed 1991 ANC values, approximately 30% of all trout streams in Virginia were marginal or unsuitable for brook trout because they were either episodically (24%) or chronically (6%) acidic. In addition, another 20% of the streams were classified as indeterminate, and brook trout in these streams may or may not have been affected. Based on the model simulations, 82% of these streams would not have been acidic prior to the onset of acidifying deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidifying deposition would increase the number of streams that were suitable for brook trout above the ambient 50%. In fact, the results suggested that a 70% reduction in deposition would be needed in the long term just to maintain the number of streams that were considered suitable for brook trout. Because of the length of time required to restore buffering capacity in watershed soils, most of the marginal or unsuitable streams were expected to remain marginal or unsuitable for the foreseeable future.

Results of modeling studies for lakes and streams in the Adirondack Mountains and in Shenandoah National Park are presented in the case study sections of this report.

3.2.4.3. Levels of Deposition at Which Effects are Manifested

The effects of S and N deposition are manifested at a range of deposition levels, depending on the inherent sensitivity of the natural resources, as described in the previous sections, and the historical deposition loading. The intersection among current deposition loading, historic loading, and sensitivity defines the ecological vulnerability to the adverse effects of acidification. Few studies in the U.S. have defined deposition levels that are associated with effects over large areas.

Some degree of surface water acidification, and perhaps also of soil acidification, can occur at very low levels of S deposition (only a few kg/ha/yr). These highly sensitive areas are characterized by very low levels of exchangeable base cations and soil base saturation. They provide limited neutralization of acidic drainage water.

Effects levels for N deposition can be established based on changes to stream and soil chemistry that signal alteration of nutrient cycling, causing NO_3^- leaching. Analyses have been conducted in the northeastern U.S. and Europe to examine the relationships between N deposition and NO_3^- leaching to surface waters. The relationship between measured wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The resulting data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N/ha/yr. Aber et al. (2003) concluded that loss of NO_3^- to surface waters during the growing season in forested watersheds often occurs above a threshold of total (wet plus dry) atmospheric N deposition of about 8 to 10 kg N/ha/yr.

The effects of N addition on forests have been shown to be wide-ranging. Additions of 25 kg N/ha/yr to spruce plots in Vermont (ambient bulk deposition 5.4 kg N/ha/yr), in which net nitrification did not occur prior to treatment, triggered net nitrification in the second year of treatment (McNulty et al., 1996). Similar results were seen in Colorado, where additions of 25 kg N/ha/yr to old-growth spruce plots in Loch Vale watershed (ambient bulk deposition 4 to 5 kg N/ha/yr) doubled N mineralization rates and stimulated nitrification. In marked contrast to these results, concentrations of NO_3^- plus NH_4^+ were not detected until the seventh year in hardwood plots in Harvard Forest, Massachusetts, which received additions of 150 kg N/ha/yr (Magill et al., 2004). Concentrations of NO_3^- plus NH_4^+ in hardwood plots receiving 50 kg N/ha/yr were not yet detectable in the 15th year of treatment.

Many of the changes in plant species composition, species diversity, and nitrification and mineralization rates in response to atmospheric N deposition are associated with nutrient N fertilization, rather than acidification. They are discussed in more detail in Section 3.3.

Chemical Response

As discussed in Section 3.2.1.6, surface water chemistry has responded to changes in emissions and deposition of S over the past two to three decades and most recently also decreases in N. Monitoring data collected within EPA's Long-Term Monitoring (LTM) and TIME projects, as well as other monitoring programs, has been key to understanding chemical responses. See discussion of major monitoring programs in Annex B. Surface water chemistry monitoring data generated through TIME and LTM

(Stoddard, 2003) suggest that the following important changes in lake and stream chemistry have occurred over the past one to two decades in the eastern U.S.:

- SO_4^{2-} concentration has decreased as a percentage of total ion concentration in surface waters.
- ANC has increased modestly in three of the five regions studied.
- Dissolved OC and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidifying deposition has decreased.
- Inorganic Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

The significant decreases in surface water SO_4^{2-} concentration which have been observed in many areas have not necessarily brought large changes in the acidity of lakes and streams. For example, the decline in Adirondack lakewater SO_4^{2-} during the 1980s was charge-balanced by a nearly equivalent decrease in concentrations of base cations in many of the low-ANC lakes, and this limited the increase in ANC and pH that occurred in response to lower SO_4^{2-} concentrations. Overall, improvements in lakewater acid-base chemistry since 1990 have been measurable but modest. Similar patterns have been observed in most other regions. There are currently no data in the U.S. that indicate increases in soil pH associated with recent declines in acidifying deposition levels.

Declines in SO_2 and NO_X emissions have brought about measurable improvements in streamwater chemistry in sensitive regions of the U.S. since 1990. However, model forecasts suggest that a reversal in chemical recovery could occur in many sensitive ecosystems under current emissions and deposition levels and that further reductions beyond those required by the 1990 Amendments to the Clean Air Act may be needed to prevent continued adverse effects and to support biological recovery of terrestrial and aquatic ecosystems (see discussion in Section 3.2.4.5.3).

Biological Response

Biological recovery can occur only if chemical recovery is sufficient to allow survival and reproduction of acid-sensitive plants and animals. The time required for biological recovery is uncertain. For terrestrial ecosystems, it may be decades after soil chemistry is restored because of the long life of many plant species and the complex interactions of soil, roots, microbes, and soil biota. For aquatic systems, research suggests that stream macroinvertebrate populations may recover relatively rapidly (within approximately 3 years), whereas lake populations of zooplankton recover more slowly (Gunn and Mills, 1998).

Table 3-8 contains a general summary of pH levels at which biological changes are typically manifested. Nevertheless, for aquatic ecosystems, there is currently no theoretical basis on which to predict the pathway and timing of biological recovery. Biological recovery of previously acidified surface waters can lag behind chemical recovery because of such factors as (1) limits on dispersal and recolonization, (2) barriers imposed by water drainage patterns (Jackson and Harvey, 1995), (3) the influence of predation (h et al., 1995), and (4) other environmental stressors (Gunn et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996a,b). Full biological recovery may take decades from the onset of chemical recovery. The results of biological recovery research from the Sudbury region of Canada and several experimental lakes is summarized below.

Table 3-8. General summary of biological changes anticipated with surface water acidification, expressed as a decrease in surface water pH.

pH Decrease	General Biological Effects
6.5 to 6.0	Small decrease in species richness of plankton and benthic invertebrate communities resulting from the loss of a few highly acid-sensitive species, but no measurable change in total community abundance or production.
	Some adverse effects (decreased reproductive success) may occur for highly acid-sensitive fish species (e.g., fathead minnow, striped bass).
6.0 to 5.5	Loss of sensitive species of minnows and dace, such as fathead minnow and blacknose dace; in some waters, decreased reproductive success of lake trout and walleye, which are important sport fish species in some areas.
	Visual accumulation of filamentous green algae in the near-shore zone of many lakes and in some streams.
	Distinct decrease in species richness and change in species composition of plankton and benthic invertebrate communities, although little if any change in total community abundance or production.
	Loss of some common invertebrate species from zooplankton and benthic communities, including many species of snails, clams, mayflies, and amphipods, and some crayfish.
5.5 to 5.0	Loss of several important sport fish species, including lake trout, walleye, rainbow trout, and smallmouth bass, as well as additional nongame species such as creek chub.
	Further increase in the extent and abundance of filamentous green algae in lake near-shore areas and streams.
	Continued shift in species composition and decline in species richness of plankton, periphyton, and benthic invertebrate communities; decreases in total abundance and biomass of benthic invertebrates and zooplankton may occur in some waters.
	Loss of several additional invertebrate species common in surface waters, including all snails, most species of clams, and many species of mayflies, stoneflies, and other benthic invertebrates.
	Inhibition of nitrification.
5.0 to 4.5	Loss of most fish species, including most important sport fish species such as brook trout and Atlantic salmon. A few fish species are able to survive and reproduce in water below pH 4.5 (e.g., central mudminnow, yellow perch, and in some waters, largemouth bass).
	Measurable decline in the whole-system rates of decomposition of some forms of organic matter, potentially resulting in decreased rates of nutrient cycling.
	Substantial decrease in number of species of plankton and benthic invertebrates and further decline in species richness of plankton and periphyton communities; measurable decrease in total community biomass of plankton and benthic invertebrates of most waters.
	Loss of additional species of plankton and benthic invertebrate species, including all clams and many insects and crustaceans.
	Reproductive failure of some acid-sensitive species of amphibians, such as spotted salamanders, Jefferson salamanders, and the leopard frog.

The Sudbury region of Ontario, Canada has been important for studying both the chemical and biological effects of S deposition. Mining and smelting of copper-nickel ore began in the 1880s. By the 1950s and 1960s, SO_2 emissions from the mining and smelting operations peaked at over 5,000 tons/day and extensive acidification of nearby surface waters was documented (Beamish and Harvey, 1972). Emissions of SO_2 then decreased during the 1970s to less than one-third of the peak values. S emission reductions resulted in improved water quality in many lakes (Keller and Pitblado, 1986; Keller et al., 1986), and some fisheries recovery was also documented (Gunn and Keller, 1990; Keller and Yan, 1991). Griffiths and Keller (1992) found changes in the occurrence and abundance of benthic invertebrates that were consistent with a direct effect of reduced lakewater acidity. A more recent assessment of recovery of ecosystems in Canada provided further evidence of biological recovery, but also showed that the spatial extent of recovery was limited to lakes that had been severely acidified by the Sudbury smelter (Jeffries et al., 2003). Research at Sudbury clearly documented that chemical recovery of lakes was possible upon reduced emissions and deposition of S, and also that biological recovery, involving multiple trophic levels, could follow. Major findings of the research at Sudbury and elsewhere are summarized below.

Phytoplankton

Studies of phytoplankton recovery from experimental acidification indicate that there is an increase in phytoplankton species richness and diversity as pH increases. In Lake 223 in the Experimental Lakes area of Ontario, there was little increase in phytoplankton diversity as pH changed from 5.0 to 5.8 but a strong recovery of diversity at pH above 6 (Findlay and Kasian, 1996). In Lake 302S, profound change began at pH 5.5; phytoplankton assemblages at pH below 5.5 resembled acidified lakes.

Zooplankton

Zooplankton recovery in response to experimental de-acidification has been reported for lakes in Ontario, Canada and Minnesota. Zooplankton recovery in experimentally acidified Lake 223 as pH returned back to 6.1 was reported by Malley and Chang (Malley, 1995). Species diversity that had been reduced during the acidification phase had partially returned to pre-acidification levels. Rotifers had recovered less than crustaceans.

One decade after cessation of the experimental acidification of Little Rock Lake in Wisconsin, recovery of the zooplankton community was complete (Frost et al., 2006). Recovery did not follow the same trajectory as the initial acidification, however, indicating a substantial hysteresis in zooplankton community recovery. About 40% of the zooplankton species in the lake exhibited a lag of 1 to 6 years to recover to levels that occurred in the neutral reference basin.

Benthic Invertebrates

There has been some research conducted on the recovery of benthic invertebrate communities in surface waters exhibiting chemical recovery from acidification. In Scotland, Soulsby et al. (1995) reported an increase in acid-sensitive mayflies in some streams that showed recent ANC increases.

However, no increases in invertebrates were observed in the most acidic streams despite observed increases in ANC. They suggested that further acidifying deposition reductions and sufficient time for reversal of soil acidification may be required before aquatic biotic recovery can occur. The extent to which benthic invertebrates in streams in the U.S. may have recovered in response to any recent increases that may have occurred in stream ANC and pH is not known.

Fish

Fish populations have recovered in acidified lakes when the pH and ANC have been increased through liming or reduction of acidifying deposition (Hultberg and Andersson, 1982; Beggs and Gunn, 1986; Dillon et al., 1986; Keller and Pitblado, 1986; Raddum et al., 1986; Gunn et al., 1988; Kelso and Jeffries, 1988). The timing of fish recovery is uncertain and probably depends heavily on dispersion. Stocking could accelerate fish population recovery (Driscoll et al., 2001b). Limitations on dispersal and recolonization can hamper biological recovery from acidification.

Continued periodic episodic acidification might hamper biological recovery of a lake or stream that is experiencing improvement in chronic chemistry. If fish move into refugia during episodes of low pH and then return, behavioral avoidance would reduce the overall effect of episodic acidification on fish populations. If fish move out of the stream system in response to acidic episodes, as suggested by Baker et al. (1996), and do not return or return in smaller numbers, then the population level effects of episodic acidification would be greater than predicted based on mortality tests alone.

Baker et al. (1990a) used field-based models to test the potential for biological recovery. For each species considered, the current presence or absence of the species was analyzed as a function of the water quality variables associated with acidification (e.g., pH, Al, Ca, ANC, and DOC) using maximum likelihood logistic regression (Reckhow et al., 1987). The results from the various models were compared to their prediction of the change in the number of Adirondack lakes with unsuitable acid-base chemistry, given a 50% decrease or a 30% increase in S deposition relative to the existing conditions at the time of the Eastern Lakes Survey (1984). Most of the models provided similar results and suggest that a 30% increase in S deposition would increase the unsuitable fish habitat in Adirondack DDRP lakes by 15% to 28% for brook trout, lake trout, and common shiner. A 50% decrease in S deposition was projected to increase suitable habitat by 8% to 18%.

Waterfowl

Few studies have been conducted on the recovery of higher trophic level organisms such as birds (Table 3-9). However, breeding distribution for the common goldeneye (Bucephala clangula), an insectivorous duck, may be affected by changes in acidifying deposition (Longcore, 1993). Similarly, reduced prey diversity and quantity have been observed to create feeding problems for nesting pairs of loons on low-pH lakes in the Adirondacks (Parker, 1988).

Table 3-9. Studies that either did or did not yield evidence that acidifying deposition affected certain species of birds.

Species	Diet/ Foraging		Breeding Distribution		Reproductive Measures		Reference
	YES	NO	YES	NO	YES	NO	
Common loon	x		x	x	x	X	Alvo et al. (1988); Parker (1988); Wayland and McNicol (1990); Blancher and McNicol (1991); DesGranges and Houde (1989); Blair (1990)
Arctic loon						X	Eriksson (1987)
Common merganser			x		x		McNicol et al. (1987b)
Belted kingfisher			x				Goriup (1989)
Osprey	x		x		x		Eriksson (1983); Eriksson (1986)
Black duck	x		x		x[b]		Hunter et al. (1986); DesGranges and Darveau (1985); Rattner et al. (1987); Harasmis and Chu (1987)
Common goldeneye			x[b]				McNicol et al. (1987b); DesGranges and Darveau (1985)
Ring-necked duck	x				x		McAuley and Longcore (1988a,b)
Eurasian dipper	x		x		x		Ormerod et al. (1985, 1986); Ormerod and Tyler (1987)
Eastern kingbird				x	x		Glooschenko et al. (1986)
Tree swallow	x			x	x		Blancher and McNicol (1988, 1991); St. Louis et al. (1990)

[b] Effect was beneficial

Logistic regression modeling with measured pH and species occurrence data for acid-sensitive lakes in the Algoma region of Ontario showed that the occurrences of fish, common loons, and common mergansers were positively related to lake water pH (McNicol, 2002). Predictions of common loon and merganser recovery for this area were made using the Waterfowl Acidification Response Modeling System (WARMS) under varying S emissions control scenarios targeted for 2010 (McNicol, 2002). The number of lakes projected to be suitable for supporting breeding pairs and broods increased with Lake pH and stricter emissions controls (McNicol, 2002). Marginal improvements in fish-eating bird habitat were predicted to occur by 2010, with more significant improvements expected under hypothetical S emissions reductions of 50% and 75% for lakes with pH below 6.5 ((McNicol, 2002). Fundamental to the predicted improvement of these fish-eating bird populations is the expected increase in food availability with lake pH recovery.

3.2.4.4. Acidification Case Study #1: Adirondack Region of New York

In this and the following section, case studies are presented for two of the most thoroughly studied regions of the U.S. that are known to have been affected by acidification from atmospheric S and N deposition. Studies in these regions have focused on both chemical and biological effects, and have included extensive model simulations of past acidification and projections of the likelihood of future recovery as deposition levels decline. The Adirondack Mountain region is perhaps the most thoroughly studied region in the world with respect to surface water acidification. Large numbers of Adirondack lakes have been acidified over the past century, and many of those now show signs of chemical recovery. Shenandoah National Park contains many acidified and acid-sensitive streams. Sensitivity in this region is strongly controlled by geology and the extent to which deposited S is adsorbed to soils. These two case studies are intended to be illustrative of the types of research that has been conducted and what that research has revealed.

General Description of Region

The Adirondack Mountains are in northeastern New York State and are densely forested, have abundant surface waters, and have 46 peaks that extend up to 1600 m in elevation. The Adirondack Park has long been a nationally important recreation area for fishing, hiking, boating, and other outdoor activities.

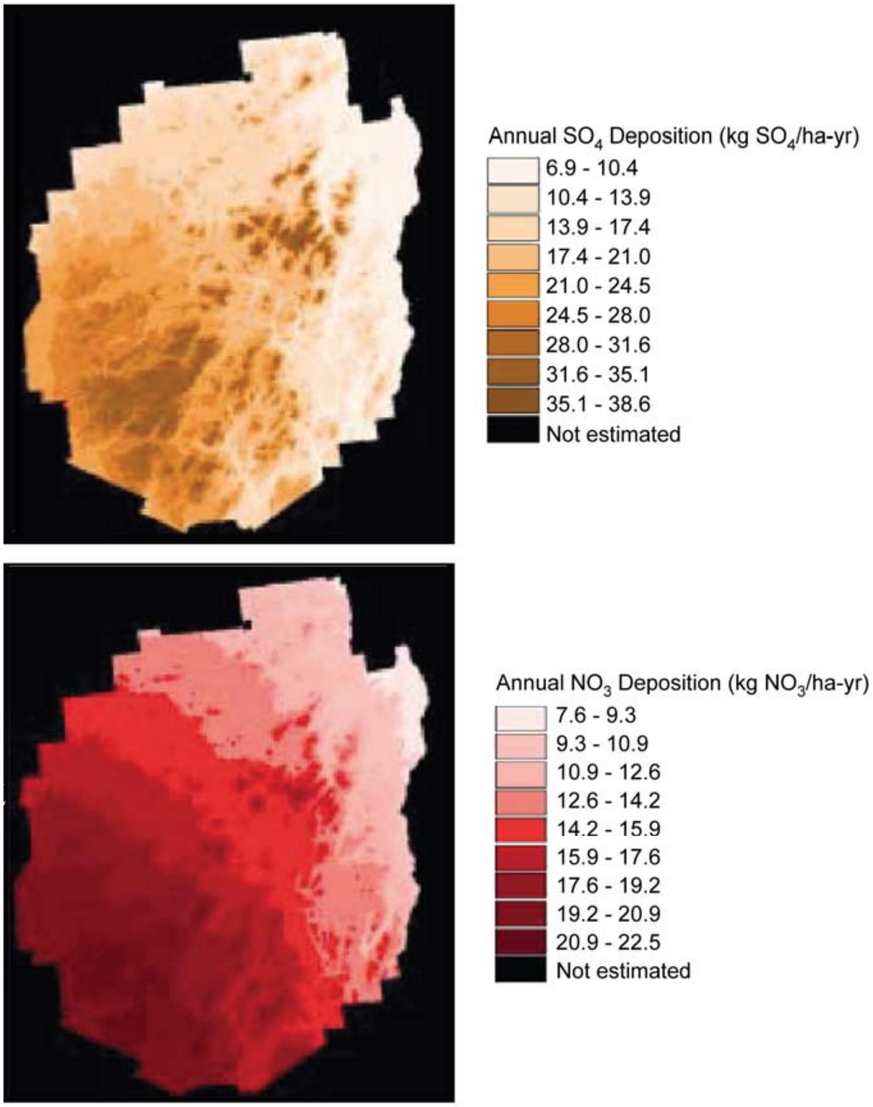
The Adirondacks, particularly the southwestern Adirondacks, are sensitive to acidifying deposition because they receive high precipitation, have shallow base-poor soils, and are underlain by igneous bedrock with low weathering rates (Driscoll et al., 1991). The Adirondacks are among the most severely acid-affected regions in North America (Landers et al., 1988; Driscoll et al., 2003b). It has long been used as an indicator of the response of forest and aquatic ecosystems to U.S. policy on atmospheric emissions of SO_2 and N oxides (EPA, 1995b; NAPAP, 1998; GAO, 2000).

Rates of Acidifying Deposition

Current rates of wet deposition of S and N in the western Adirondacks remain among the highest in the nation. Spatial patterns in wet deposition of S and N from 1988 to 1999 were developed by Ito et al. (2002), using data from 24 precipitation and 4 wet deposition monitoring stations. Results from this effort suggest that wet S deposition ranged from 2.3 to 12.9 kg S/ha/yr and wet NO_3-N deposition rates ranged from 1.7 to 5.1 kg N/ha/yr (Ito et al., 2002) (Figure 3-18). In general, deposition rates are highest in the southwestern Adirondacks and decrease to the northeast. Rates of dry deposition are less well known, but probably constitute 25% to 50% or more of total wet deposition (Sullivan et al., 2006a).`

Deposition trends have changed with the implementation of federal and state emissions control regulations. For example, by 1990 average wet S deposition in the Adirondack region had declined by approximately 30% from its peak in the 1970s (Sullivan, 1990). Deposition of S has continued to decline (Figure 3-19)and (Figure 3-20) in response to implementation of the Clean Air Act Amendments of 1990.

Until recently, wet N deposition had been fairly consistent over the previous two decades. N deposition now appears to be decreasing (http://nadp.sws.uiuc.edu/).



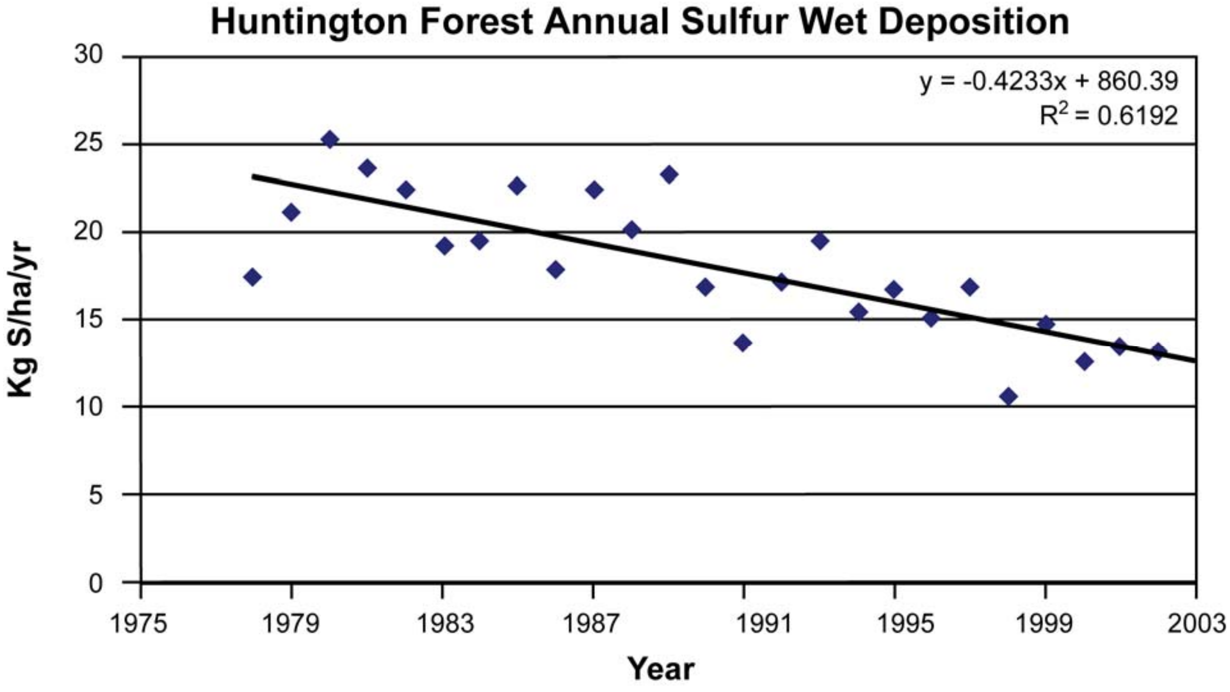
Source: Ito et al. (2002)

Figure 3-18. Spatial patterns in predicted wet SO_4^{2-} and NO_3 deposition in the Adirondack Park during the period 1988 to 1999.

Soil Retention and Leaching of Sulfur and N

As discussed in Section 3.2.4.4, acidifying deposition has resulted in the accumulation of S and N in Adirondack soils. Although input-output budgets for S developed in the 1980s suggested that the amount of S exported was approximately equal to the S inputs from atmospheric deposition, more recent studies show that watershed loss of SO_4^{2-} now exceeds atmospheric S deposition inputs (Driscoll, 1998). This pattern suggests that decades of atmospheric S deposition have resulted in the accumulation of S in forest soils. With recent declines in atmospheric S deposition and a possible warming-induced enhancement of S mineralization from soil organic matter, previously retained S is gradually being released to surface waters (Driscoll, 1998). This release of SO_4^{2-} from soils could contribute to a delay in the recovery of surface waters in response to SO_2 emissions controls.

N dynamics are quite different from those of S. Because N is a growth-limiting nutrient for many forest plants, retention in forest ecosystems under low levels of air pollution is generally high and NO_3^- loss to streams is relatively low (Aber, 2003). However, recent research suggests that N has accumulated in soils over time in the Adirondacks and that some forests have exhibited declining retention of N inputs (Driscoll et al., 2003a,c). The result has been increased leaching of NO_3^- to surface waters. The extent and degree of leaching appear to be linked to climatic variation, land-use history, and vegetation type (see Section 3.2.1.3).



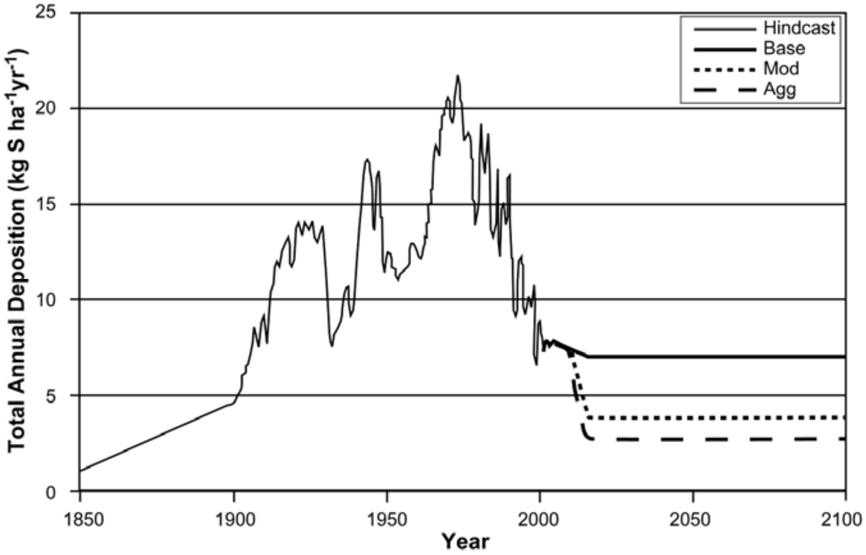
Source: Sullivan et al. (2006a)

Figure 3-19. Measured wet deposition of sulfur at the Huntington Forest NADP/NTN monitoring station.

The leaching of both SO_4^{2-} and NO_3^- into drainage water has contributed to the displacement of cations from soil, acidification of surface waters (Driscoll et al., 2001a), and the associated chemical and biological effects discussed below.

Soil Acidification and Base Cation Depletion

Atmospherically deposited hydrogen ions can directly affect soil pH. Net uptake of nutrient cations by vegetation can also generate acidity within the soil, and a considerable amount of natural organic acidity is produced in the Oa horizon through the partial decomposition of organic matter and uptake of nutrient cations. In the only repeated soil sampling in the U.S. in which the original sampling predated acidifying deposition, Johnson et al. (1994) found significantly higher soil pH values in 1930 than in 1984 in the Oa horizon of Adirondack soils that had an initial pH of 4.0–5.5, but no decrease in pH in soils with an initial pH of < 4.0. Johnson et al. (1994) also documented a decrease in exchangeable Ca concentrations in both the O (combined Oa and Oe horizons) and B horizons from 1930 to 1984. The decrease in soil pH and Ca concentrations was attributed to a combination of acidifying deposition and changing vegetation dynamics.



Source: Sullivan et al. (2006b)

Figure 3-20. Estimated time series of S deposition at one example watershed in the southwestern Adirondack Mountains. Table used by Sullivan et al. (2006b) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidifying deposition. Future deposition estimates were based on three emissions control scenarios (Base Case [solid line], Moderate Additional Controls [dotted line], Aggressive Additional Controls [dashed line]).

In a statistically based regional assessment of changes in soil-exchange chemistry, Sullivan et al. (Sullivan, 2006) found that base saturation and exchangeable Ca concentrations in the Adirondack region appeared to have decreased in the B horizon between the mid 1980s and 2003 in watersheds of lakes with acid-neutralizing capacity less than 200 μeq/L. Although this study did not involve repeated sampling of the same sites, the comparison could be made on a regional basis because the sampling locations were selected randomly in both the mid 1980s and in 2003, and a large and similar number of sites were included in both samplings.

Effects of Acidifying Deposition on Adirondack Surface Water Chemistry

The Adirondack Lake Survey Corporation conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Baker et al., 1990b). Of the 1,489 lakes surveyed, 24% had summer pH values below 5.0, 27% were chronically acidic (ANC < 0) and an additional 21% were probably susceptible to episodic acidification (ANC between 0 and 50; Driscoll et al., 2007a).

In addition to low pH and ANC, many acidic surface waters in the Adirondacks are characterized by high concentrations of inorganic Al. For example, a study of 12 sub-basins in the watershed of the North Branch of the Moose River by Driscoll et al. (1987b) determined that the concentration of inorganic Al in lakewater was higher in lakes having pH below 6.0. Recently, Lawrence et al. (2007) determined that 66% of 188 streams sampled in the western Adirondack region during snowmelt in 2004 had measurable concentrations of inorganic Al, an indicator of acidification by acidifying deposition.

Historical changes in lakewater chemistry from the mid-1800s to recent times have been estimated for the Adirondacks using paleolimnological techniques. Fossil remains of diatoms and chrysophytes in sediment cores have been used to reconstruct chemical histories. The PIRLA I and II projects (Paleoecological Investigation of Recent Lake Acidification) used the remains of diatoms preserved in lake sediments to estimate historical changes in lakewater chemistry across the Adirondack region. The PIRLA-II project focused on lakes that are 4 ha or larger that represented a subpopulation of 675 Adirondack lakes. The results from these analyses suggest that nearly all lakes with estimated preindustrial pH less than 6.0 had acidified between 0.3 and 1.0 pH units during the 20th century. Based on an analysis of data from Cumming et al. (1992) and Baker et al. (1990b), low-pH lakes were uncommon or rare in the preindustrial Adirondacks; the number of lakes with pH less than 5.5 had at least doubled by the mid 1980s and the number with pH less than 5.0 had increased by 5 to 10 times.

The PIRLA results are generally consistent with projections from model hindcasts. Sullivan et al. (2006a) modeled past changes in the acid-base chemistry of 70 Adirondack lake watersheds, including 44 that were statistically selected to be representative of the approximately 1,320 Adirondack lake watersheds that have lakes larger than 1 ha and deeper than 1 m and that have ANC ≤ 200 μeq/L. Model hindcasts were constructed using both the MAGIC and PnET-BGC models. Based on MAGIC model outputs, maximum past acidification occurred by about 1980 or 1990, with a median ANC for the study population of about 61 μeq/L (reduced from a median of 92 μeq/L estimated for the preindustrial period). By 1990, 10% of the population target lakes had decreased in ANC to below -16 μeq/L and 25% had ANC < 28 μeq/L. The model simulations coupled with population-level extrapolations suggest that none of the target lakes were chronically acidic (had ANC < 0 μeq/L) under preindustrial conditions, but that by 1980 there were about 204 chronically acidic Adirondack lakes.

PnET-BGC model simulations generated output that was generally similar to results provided by MAGIC model simulations. Results from PnET-BGC suggest that none of the lakes in the Adirondack population had preindustrial ANC below 20 μeq/L. By 1990, there were 289 lakes having ANC < 20 μeq/L and 217 chronically acidic (ANC ≤ 0 μeq/L) lakes according to PnET-BGC simulations. There were 202 lakes in the population simulated to have had preindustrial ANC below 50 μeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations.

Zhai et al. (2008) reported PnET-BGC hindcasts for the 44 EMAP lakes. They report that simulated median values of pH, ANC, and soil percent base saturation were 6.63, 67.7 μeq/L, and 12.3%, respectively, in 1850 compared to current measured values of 5.95, 27.8 μeq/L, and 7.9%. They also calculated F factors for the PnET-BGC model projections of historical acidification. The F-factor (Henriksen, 1984; Husar et al., 1991) reflects the proportion of the increase in lakewater SO_4^{2-} plus NO_3^- concentration that is charge balanced by an equivalent increase in base cation concentrations. The remaining proportion (1–F) is attributed to increase in the potentially toxic cations, hydrogen ions and inorganic Al. Based on PnET-BGC hindcast simulations, F-factors for the EMAP lakes ranged from 0.3 to slightly over 1.0, with a mean value of 0.7 (Figure 3-13). The F-factor increased with ambient lakewater ANC. These results are in close agreement with paleolimnological analyses reported by Sullivan et al. (Sullivan, 1990), which showed historic F-factors for Adirondack lakes ranging from about 0.5 to above 1.0.

Biological Effects

The Adirondack region has a rich aquatic biota dataset from which to examine relationships among lake water chemistry and species abundance, composition, and richness. In general, there tends to be a negative relationship in Adirondack lakes between pH, ANC, and inorganic Al chemical variables and the diversity and abundance of fish (Baker and Laflen, 1983; Baker et al., 1990c; Havens et al., 1993) Figure 3-16 phytoplankton, and zooplankton (Confer et al., 1983; Siegfried et al., 1989) (Table 3-10).

Table 3-10. Observed relationships between zooplankton species richness and lakewater ANC in the Adirondack Mountains.

Taxonomic Group	Equation	R^2	p
Total zooplankton	Richness = 15.65 + 0.089 ANC	0.46	0.001
Crustaceans	Richness = 6.35 + 0.028 ANC	0.47	0.001
Rotifers	Richness = 9.04 + 0.053 ANC	0.30	0.001

Through the Adirondack Lakes Survey, 1,469 lakes were sampled between 1984 and 1987, representing 80% of the estimated population of Adirondack lakes larger than 1 ha in area (Whittier et al., 2002). The goal of the survey was to characterize the biological, physical, and chemical characteristics of the lakes and evaluate the relationships between fish communities and water chemistry. The major results were reported by Baker et al. (1990b). Key findings are:

- Seventy-six percent of the lakes had fish; 24% (346 lakes) were fishless.
- The most common fish caught were native acid-tolerant species: brown bullhead, brook trout, and white sucker.
- As pH decreases, fish diversity also decreases. The average number of fish species declines from six fish species in lakes with pH higher than 6.5 to two or fewer fish species in lakes with pH of 5.0 or less.
- As pH decreases, the number of fishless lakes increases. Few lakes with pH of 5.5 or higher are fishless. Below pH 5.0, approximately 75% of the lakes are fishless.

Researchers in the Adirondacks were among the first in the U.S. to demonstrate that fish mortality increases during acid episodes, which are common to lakes and streams in the Adirondacks during spring runoff. Driscoll et al. (Driscoll, 1987) documented surface water chemistry changes associated with periods of high flow. They found that pH and ANC decreased substantially during hydrological episodes and inorganic Al concentrations commonly exceeded thresholds harmful to fish. These relationships were further documented by the Episodic Response Project as shown in the example for Bald Mountain Brook in the Adirondacks (Wigington Jr., 1996). Work by Van Sickle et al. (1996) and others linked these chemical changes to fish mortality in small streams. They determined that blacknose dace were highly sensitive to low pH and could not tolerate inorganic Al concentrations above about 3.7 µM for extended periods of time. After 6 days of exposure to high inorganic Al, dace mortality increased rapidly to nearly

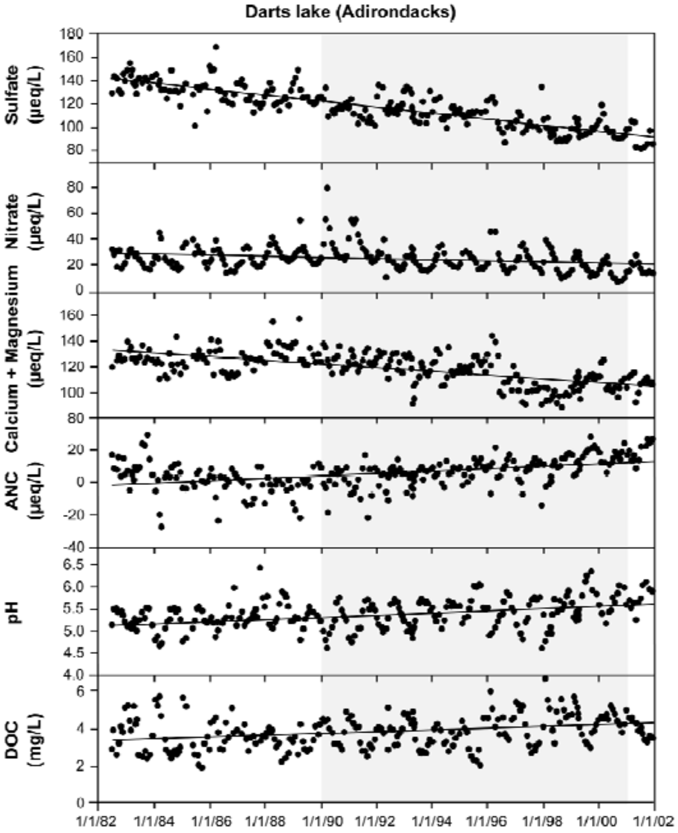
100% (Van Sickle et al., 1996). Brook trout were less sensitive, but still showed high mortality during many acid episodes.

Several efforts have been made to link changes in fish populations with historical changes in water chemistry associated with acidifying deposition. Among the most widely cited is the work of Baker et al. (1990b; Baker, 1996). They analyzed 988 Adirondack Lake Survey lakes for which data existed for the period before 1970 and for the 1980s. Of the 2,824 fish populations confirmed by pre-1970 surveys, 30% had apparently been lost by the 1980s (Baker et al., 1990b). An estimated 23% of the fish population losses were related to acidifying deposition. This relationship was strengthened by evidence from the PIRLA projects. In the 32 lakes that had both historic fish data and paleolimnological chemical reconstructions, the lakes that had acidified the most or that were originally the most acidic were the same ones that were judged to have lost fish populations (Baker et al., 1996).

Recent Trends in Surface Water Chemistry and Projections of Future Change

Several studies have been conducted to analyze trends in lake chemistry in the Adirondacks. Driscoll et al. (Driscoll, 2003) evaluated changes from 1982 to 2000 in the original 16 Adirondack LTM lakes and from 1992 to 2000 in the complete set of 48 Adirondack LTM lakes. They found that nearly all study lakes showed marked decreases in SO_4^{2-} concentration over the period of record and several lakes showed declines in NO_3^- concentration. Data for one example monitoring lake are given in Figure 3-21. They found that 7 of the 16 original monitoring lakes showed a statistically significant increase in ANC (Figure 3-22), with a mean rate of increase of 0.78 μeq/L/yr (Driscoll, 2003). Twenty-nine of the group of 48 lakes showed increasing ANC trends from 1992 to 2000 with a mean rate of increase of 1.60 μeq/L/yr (Driscoll, 2003). The authors attributed this recent increase in ANC to declines in both SO_4^{2-} and NO_3^- concentrations (Driscoll, 2003).

Despite these recent improvements in lake water chemistry in the Adirondack Long-Term Monitoring lakes, 34 of the 48 lakes still had mean ANC values less than 50 μeq/L in 2000, including 10 lakes with ANC less than 0 μeq/L. Thus, current chemistry data suggest that most of these lakes exhibit chemical conditions that continue to pose a risk to aquatic biota. Model projections of future acid-base chemistry of lakes in the Adirondack Mountains under three scenarios of future atmospheric emissions controls were presented by Sullivan et al. (2006b) to evaluate the extent to which lakes might be expected to continue to increase in ANC in the future. Estimated levels of S deposition at one representative watershed are shown in Figure 3-20 for the hindcast period and in the future under the three emissions control scenarios. Model simulations for 44 statistically selected Adirondack lakes using the MAGIC and PnET-BGC models were extrapolated to the regional lake population. Cumulative distribution frequencies of ANC response projected by MAGIC are shown in Figure 3-23 for the past (1850), peak acidification period (approximately 1990), and future (2100). Results for the future are given for each of the scenarios.

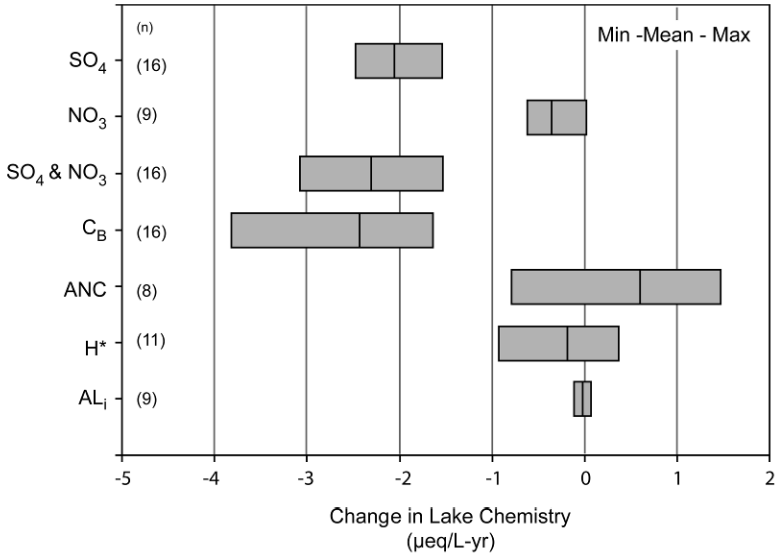


Source: Stoddard et al. (2003)

Figure 3-21. Time series data for SO_4^{2-}, NO_3, base cations [Ca plus Mg], Gran ANC, pH, and dissolved OC in one example Long-Term Monitoring Lake in the Adirondack Park. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Forecasting results suggested that the ongoing trend of increasing lakewater ANC for the most acid-sensitive lakes would not continue under future emissions and deposition levels anticipated as of 2003 (Base Case Scenario). The numbers of Adirondack lakes having ANC below 20 and below 50 µeq/L were projected to increase between 2000 and 2100 under that scenario, and the number of chronically acidic Adirondack lakes (i.e., ANC less than 0) was projected to stabilize at the level reached in 2000. This projected partial reversal of chemical recovery of acid-sensitive lakes was due to a continuing decline in the simulated pool of exchangeable base cations in watershed soils. Simulations suggested that re-acidification might be prevented with further reductions in emissions and deposition.

Chen and Driscoll (2004) applied the PnET-BGC model to DDRP lake watersheds in the Adirondacks. The model was applied to three future emissions scenarios: base case, moderate emissions reductions, and aggressive emissions reductions. A case study for Indian Lake in the Adirondacks illustrated that larger reductions in deposition caused greater decreases in SO_4^{2-} and base cation concentrations in lake water and greater recovery in pH and ANC. Within the full population of lake-watersheds, some showed decreasing ANC and pH values from 1990 to 2050 even under the moderate and aggressive reduction scenarios. By 2050 to 2100, however, nearly all lakes were simulated to experience increasing ANC and pH. The modeled soil base saturation increased very slowly over the modeled time period compared to changes in surface water chemistry. For 95% of the lake-watersheds studied, simulated soil base saturation remained below 20% in 2100 under all emissions scenarios.

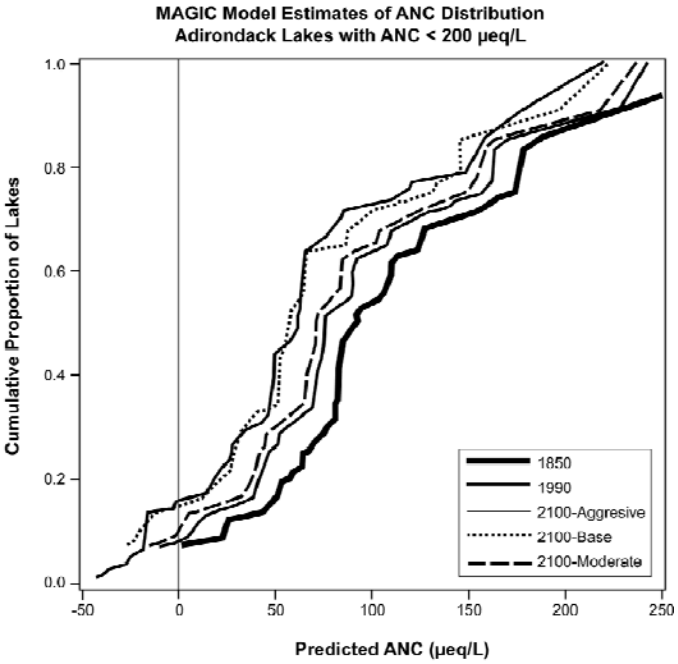


Source: Driscoll et al. (Driscoll, 2003)

Figure 3-22. Mean rates of change in solute concentration in 16 lakes of the Adirondack Long-Term monitoring (ALTM) program from 1982 to 2000. Minimum, mean, and maximum changes in concentrations and number of lakes showing significant trends are shown. All values are in µeq/L/yr, except for concentrations of inorganic monomeric aluminum (Al_i), which are expressed in µM/yr.

Multipollutant Interaction: Biological Mercury Hotspots in the Adirondacks

The Adirondacks has been identified as a region at risk from the combined effects of acidifying deposition and Hg deposition (Driscoll, 2007). The relationship between atmospheric deposition of S and enhanced Hg methylation is discussed in Section 3.4. In general, the solubility of Hg increases with increasing sulfide concentrations in anoxic waters through complexation reactions, potentially increasing the pool of Hg available for methylation (Benoit et al., 2003; Driscoll, 2007). Evers et al. (2007) identified a biological Hg hotspot in the western Adirondacks based on Hg concentrations in yellow perch and common loons. Mean yellow perch Hg concentrations in the Adirondack hotspot were 1.5 to 2.5 times higher than the EPA and U.S. Food and Drug Administration’s reference dose used for fish consumption advisories (Evers et al., 2007). The authors hypothesized that the occurrence of the biological hotspot was due in part to the combination of high Hg deposition and sensitive water chemistry, such as low ANC and pH, which is associated with both natural acidity and the long-term effects of acidifying deposition (Evers et al., 2007). Driscoll et al. (Driscoll, 2007) concluded that watersheds sensitive to Hg deposition tend to be forested, have an abundance of wetlands, contain shallow hydrologic flow paths and low nutrient concentrations, and are affected by acidifying deposition.



Source: Sullivan et al. (Sullivan, 2006)

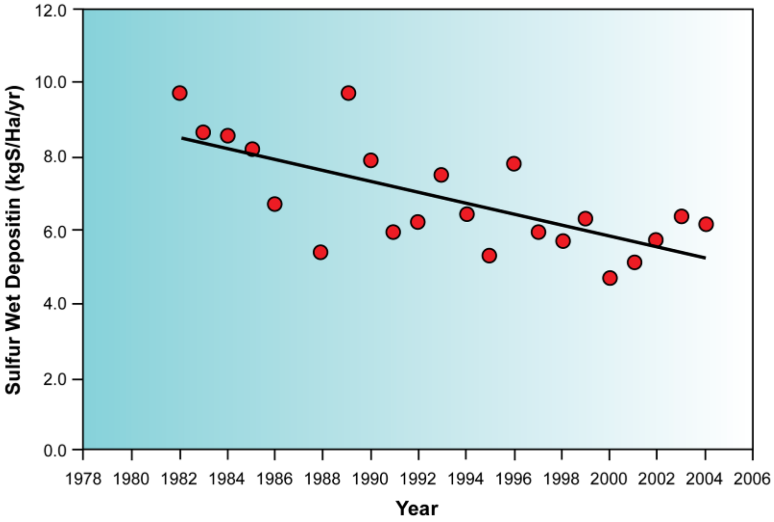
Figure 3-23. Simulated cumulative frequency distributions of lakewater ANC at three dates for the population of Adirondack lakes, based on MAGIC model simulations reported by Sullivan et al., 2006. Conditions for the year 2100 are presented for three emissions control scenarios: Base Case, Moderate Additional Controls, and Aggressive Additional Controls. (See Figure 3-15)

3.2.4.5. Acidification Case Study #2: Shenandoah National Park, Virginia

Shenandoah National Park is located along the crest of the Blue Ridge Mountains in Virginia. Air pollution within Shenandoah National Park, including S and N deposition and O_3 concentration, is higher than in most other national parks in the U.S. Measured wet S deposition in the park has ranged from 8 to 10 kg S/ha/yr in the early 1980s to near 6 kg S/ha/yr since 2000 (Figure 3-24). Dry S deposition may be nearly as high as wet deposition (Sullivan, 2003). Most acidification effects in the park have been linked with S deposition.

The sensitivity of streams in the park to acidification from acidifying deposition is determined mainly by the types of rocks found beneath the stream and the characteristics of the watershed soils that surround it. If the underlying geology is Si-based (siliclastic lithology), the soil and water in the watershed generally have poor ability to neutralize acids deposited from the atmosphere. About one-third of the streams in the park are located on this type of geology. Model estimates using the MAGIC model suggest that such streams have typically lost most of their natural ANC, largely in response to a century of industrial emissions and acidifying deposition. As a consequence, stream pH values in many streams are low, especially during winter and spring. Prior to human-caused air pollution, most streams in Shenandoah National Park probably had pH above about 6. Many park streams on siliclastic lithology currently have pH as low as about 5 (Sullivan, 2003; Cosby, 2006). Other predominant lithologies in the park include granite-based (granitic) lithologies typically characterized by intermediate ANC streams, and basalt-based (basaltic) lithologies typically characterized by relatively high stream ANC (Cosby, 2001)Sullivan et al., 2004, 2007, (Sullivan, 2008).

The effects of acidifying deposition on Shenandoah National Park streams have been studied for over 25 years by the Shenandoah Watershed Study, the longest-running watershed study program in any of the national parks (Cosby, 2006) see http://swas.evsc.virginia.edu). This program has determined that the high rate of atmospheric deposition of S, combined with naturally low contributions from some rock types of Ca and other base cations (that serve to neutralize acidity), are the most important causes of low streamwater ANC in many park streams. Some park streams can also become temporarily acidic for short periods (hours to days) during rainstorms or snowmelt.



Source: Sullivan et al. (Sullivan, 2003).

Figure 3-24. Wet sulfur deposition for the period of record at the Big Meadows NADP/NTN monitoring station in Shenandoah National Park.

The acidification of streams in the Park is linked to effects that are occurring in the watershed soils. Over time, the ability of soils to adsorb S, thereby effectively negating S's potential to acidify water, is decreasing due to the long term accumulation of SO_4^{2-} on soil adsorption sites in response to a legacy of acidifying deposition. In addition, the amount of stored Ca and Mg in the soil is gradually declining in response to acidifying deposition. Therefore, streams are expected to acidify more in the future than they have so far, relative to the amount of acidifying deposition received. This prognosis is consistent with recent analysis of national lake and stream response to reductions in air pollution emissions (Stoddard, 2003). Unlike a number of other regions of the country, streams in the region that includes Shenandoah National Park are generally not recovering from acidification.

A great deal of research has been conducted in the park on the effects of S and N deposition on soil and water acidification. This park was a major site of early research on acidification processes (cf. Galloway, 1983). This early work provided much of the foundation for development of the MAGIC model (Cosby et al., 1985), which has been the most widely used dynamic watershed acid-base chemistry model worldwide for the past two decades.

Although research on many aspects of acidification effects science has been conducted in the park, it has been particularly noteworthy for studies on episodic acidification; biological effects of stream acidification; and dynamic modeling of acidification, recovery, and critical loads. Research within Shenandoah National Park on each of these topics is discussed below.

Episodic Acidification

A number of studies of episodic acidification have been conducted in streams within Shenandoah National Park. Eshleman and Hyer (2000) estimated the contribution of each major ion to observed episodic ANC depressions in Paine Run, Staunton River, and Piney River during a 3−year period. During the study, 33 discrete storms were sampled and water chemistry values were compared between antecedent baseflow and the point of minimum measured ANC (near peak discharge). The relative contribution of each ion to the ANC depressions was estimated using the method of Molot et al. (1989), which normalized the change in ion concentration by the overall change in ANC during the episode. At the low-ANC (~0 μeq/L) Paine Run site on siliciclastic bedrock, increases in NO_3^- and SO_4^{2-}, and to a lesser extent organic acid anions, were the primary causes of episodic acidification. Increases in base cations tended to compensate for most of the increases in acid anion concentration. ANC declined by 3 to 21 μeq/L (median 7 μeq/L) during the episodes studied.

At the intermediate-ANC (~60 to 120 μeq/L) Staunton River site on granitic bedrock, increases in SO_4^{2-} and organic acid anions, and to a lesser extent NO_3^-, were the primary causes of episodic acidification. Base cation increases compensated these changes to a large degree, and ANC declined by 2 to 68 μeq/L during the episodes (median decrease in ANC was 21 μeq/L).

At the high-ANC (~150 to 200 μeq/L) Piney River site on basaltic (69%) and granitic (31%) bedrock, base cation concentrations declined during episodes (in contrast with the other two sites where base cation concentrations increased). SO_4^{2-} and NO_3^- concentrations usually increased. The change in ANC during the episodes studied ranged from 9 to 163 μeq/L (median 57 μeq/L) (Eshleman and Hyer, 2000). Changes in base cation concentrations during episodes contributed to changes in the ANC of Paine Run, had little effect in Staunton River, and contributed to decreases in ANC in Piney River.

The most acidic conditions in Shenandoah National Park streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. There are several different mechanisms of episodic acidification in operation in these streams, depending at least in part on the bedrock geology of the stream watershed. The relative importance of the major processes that contribute to episodic acidification varies among the streams, in part as a function of baseflow streamwater ANC which is largely controlled by bedrock geology. S-driven acidification was an important contributor to episodic loss of ANC at all three study sites, probably because S adsorption by soils occurs to a lesser extent during high-flow periods. This is due, at least in part, to diminished contact between drainage water and potentially adsorbing soil surfaces along the shallow flow paths. Dilution of base cation concentrations during episodes, which is an acidifying process, was most important at the high-ANC site.

Thus, episodic acidification of streams in Shenandoah National Park can be attributed to a number of causes, including dilution of base cations and increased concentrations of sulfuric, nitric, and organic acids (Eshleman et al., 1995; Hyer et al., 1995). For streams having low pre-episode ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse effects on fish populations. However, not all of the causes of episodic acidification are related to acidifying deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of N, indicated by increased NO_3^- concentrations, has evidently been (at least for streams in the park) related to forest defoliation by the gypsy moth (Webb et al., 1995; Eshleman et al., 1998). Significant contributions of H_2SO_4, indicated by increased SO_4^{2-} concentrations during episodes in some streams, is an effect of atmospheric deposition and the dynamics of S adsorption on soils (Eshleman and Hyer, 2000).

A recent study by Deviney et al. (Deviney, 2006) used hourly ANC predictions over short time periods to compute recurrence intervals of annual water-year minimum ANC values for periods of 6, 24, 72, and 168 h. They extrapolated the results to the rest of the catchments using catchment geology and topography. On the basis of the models, they concluded that many streams in the park have 6– to 168–h periods of low ANC values, which may stress resident fish populations (Deviney, 2006). Specifically, on the basis of a 4–year recurrence interval, approximately 23% of the land area (44% of the catchments) can be expected to have conditions for 72 continuous hours that are indeterminate with respect to brook trout suitability (ANC 20 to 50), episodically acidic (ANC 0 to 20), or chronically acidic (ANC less than 0). Many catchments were predicted to have successive years of low-ANC values potentially sufficient to extirpate some species (Deviney, 2006). The authors of the study reported that smaller catchments are more vulnerable to adverse effects of episodic acidification than larger catchments underlain by the same bedrock. Catchments with similar topography and size are more vulnerable if underlain by less basaltic and carbonate bedrock.

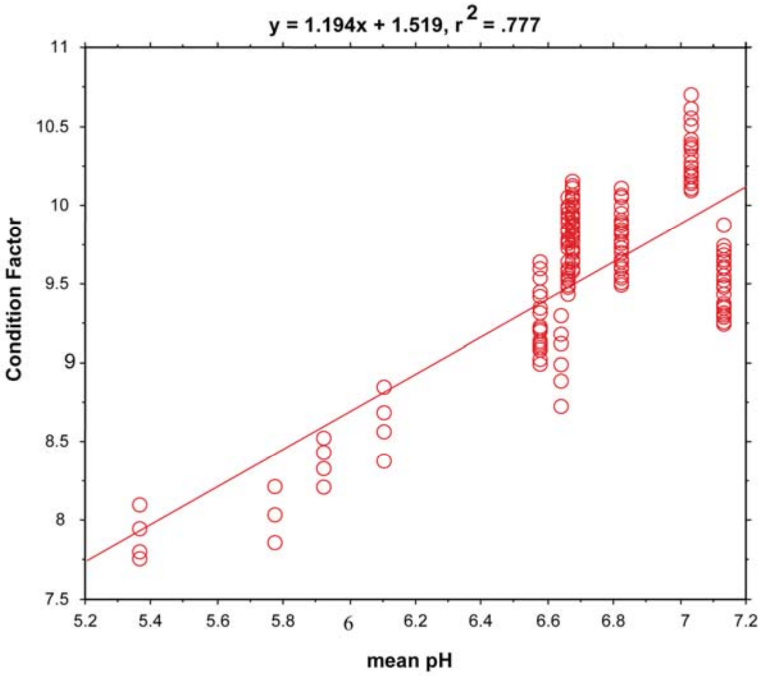
Biological Effects of Acidification

A robust relationship between acid-base status of streams and fish species richness was documented in Shenandoah National Park in the 3−year Fish in Sensitive Habitats (FISH) study

(Bulger, 1999). Numbers of fish species were compared among 13 streams spanning a range of pH and ANC conditions. There was a highly significant ($p < 0.0001$) relationship between stream acid-base status (during the 7–year period of record) and fish species richness among the 13 streams. The streams with the lowest ANC hosted the fewest species (Figure 3-15). This study demonstrated biological differences in low- versus high-ANC streams, including species richness, population density, condition factor, age, size, and field bioassay survival. Of particular note was that both episodic and chronic mortality occurred in young brook trout exposed in a low-ANC stream, but not in a high-ANC stream (MacAvoy and Bulger, 1995), and that blacknose dace (*Rhinichthys atratulus*) in low-ANC streams were in poor condition relative to blacknose dace in higher-ANC streams (Dennis, 1995).

Bulger et al. (Bulger, 1999) observed a positive relationship between condition factor and pH in streams in Shenandoah National (Figure 3-25). Dennis and Bulger (1995) also found a reduction in condition factor for blacknose dace in waters near pH 6.0. The four populations depicted in (Figure 3-25) with the lowest condition factor had mean habitat pH values within or below the range of critical pH values at which Baker and Christensen (1991) estimated that negative population effects for blacknose dace are likely for the species. The mean condition factor of fish from the study stream with the lowest ANC was about 20% lower than that of the fish in best condition. Comparisons with the work of Schofield and Driscoll (1987) and Baker et al. (1990b) suggest that pH values in the low-pH streams are also near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan, 2003).

MacAvoy and Bulger (1995) used multiple bioassays over 3 years in one of the low-ANC streams as part of the FISH project to determine the effect of stream baseflow and acid episode stream chemistry on the survival of brook trout eggs and fry. Simultaneous bioassays took place in mid- and higher-ANC reference streams. Acidic episodes, with associated low pH and elevated inorganic Al concentrations and high streamwater discharge, caused rapid fish mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger, 1999).



Source: Bulger et al. (Bulger, 1999)

Figure 3-25. Length-adjusted condition factor (K), a measure of body size in blacknose dace (Rhinichthys atratulus) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991–94; K was measured in 1994. The regression analysis showed a highly significant relationship (p < 0.0001) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams.

Modeling of Acidification, Recovery, and Critical Loads

Dynamic models have been used in Shenandoah National Park to help determine whether the changes in surface water chemistry that have occurred over the past one to two decades will continue and whether they will reach levels needed to support biological recovery. The most commonly used models are described in Annex B, and details of these analyses are discussed below. In general, model forecasts indicated that under base case conditions (those expected under existing or anticipated emissions controls) surface water ANC in the southern Appalachians (and also in parts of the Adirondacks) would be likely to decline in the future. In terms of soil chemistry, projected future improvements in both regions appear to be slow and in most cases do not reach a base saturation of 20% or more within the next 100 years.

MAGIC model simulations for streams in Shenandoah National Park by Sullivan et al. (Sullivan, 2003) suggested that acidifying deposition would have to be decreased substantially to improve and maintain acid-sensitive streams at levels of ANC that would be expected to protect against ecological harm. In addition, it took a long time for these streams to acidify in the past; because of complexities related to soil conditions, it will take even longer for them to recover in the future. To protect against chronic acidity in the year 2100, with associated probable lethal effects on brook trout, S deposition to the most geologically sensitive siliciclastic lithology watersheds in the park will have to be kept below about 9 kg/ha/yr for the next 100 years (Sullivan et al., 2007a). Prior to the Industrial Revolution, most streamwater in the Park had ANC higher than about 50 μeq/L. To promote ANC recovery to 50 μeq/L in the future, to protect against general ecological harm, S deposition to Si-based (siliciclastic) watersheds in the park will have to be kept below about 6 kg/ha/yr. Some watersheds will likely not recover streamwater ANC to values above 50 µeq/L over the next century even if S deposition is reduced to zero (Sullivan et al., 2007a).

Simulation and mapping of watershed responses to historical changes in acidifying deposition (from preindustrial to current) by Cosby et al. (Cosby, 2006) suggest that large areas of Shenandoah National Park have suffered deterioration of both soil and stream conditions. The changes in soil condition have been relatively modest up to the present time, with areas in the southern district of the park moving from classification of “moderate concern” (watershed average mineral soil percent base saturation 10% to 20%; the historical baseline) to “elevated concern” (average mineral soil percent base saturation 5% to 10%) as a result of leaching of base cations from the soils in response to S deposition. Simulation results indicated that deterioration in stream conditions has been more severe than for soil conditions, with large areas in the southern district and some smaller areas in the central and northern districts moving from “moderate concern” (average stream ANC 50 to 100 µeq/L) to “elevated concern” (average stream ANC 0 to 50 µeq/L). Neither soil nor stream conditions have shown any improvement from 1980 to the present in response to the decline in acidifying deposition over the last 25 years.

Simulation and mapping of watershed responses to predicted future changes in acidifying deposition by Cosby et al. (Cosby, 2006) were developed following EPA methods for preparation of emissions inventory inputs into air quality modeling for policy analysis and rule making purposes. These alternate emissions scenarios were based on existing emission control regulations and several proposed alternatives. The model output suggested that the responses of soil conditions to changes in S deposition are expected to be relatively slow. In the short term (by the year 2020), neither improvement nor further deterioration is likely to be observed in soil condition regardless of the future deposition scenario considered. However, model results suggested that constant deposition at 1990 levels would produce worsening soil conditions in the park by the year 2100 with the development of areas of “acute concern” (average percent soil base saturation below 5%) in the southern district. Although the scenarios of possible reduced future deposition did not produce worsening soil conditions, neither did they indicate any improvement in soil condition, even in the long term.

Simulated responses of stream conditions were more rapid than those of soils. In the short term (by the year 2020), constant deposition at 1990 levels would likely produce further deterioration in stream condition. The scenarios of future deposition reductions failed to reverse the deterioration of stream condition that has occurred during the last century. In the long term (by year 2100), the effects of the deposition reduction scenarios begin to diverge. The moderate S deposition reduction scenario (69% reduction from 1990 values) did not produce improvement in stream chemistry relative to current conditions. The larger deposition reduction scenario (75%), by contrast, produced modest improvements in stream chemistry by 2100. However, even the relatively large S deposition reductions of this scenario did not result in a simulated return of stream conditions to the preindustrial state.

To develop projections of probable past and future responses of aquatic biota to changing S deposition in Shenandoah National Park, the MAGIC model was coupled by Sullivan et al. (2003) with several empirical models that linked biological response to past and future model projections of water quality. Unlike MAGIC, which is a geochemical, process-based model, the biological effects estimates were based on observed empirical relationships rooted in correlation and expressed as linear relationships. Correlation does not necessarily imply causality, but an observed pattern of covariation between variables does provide a quantitative context for extrapolation. In this case, the projections did not require extrapolation beyond the observed ranges of observations, and therefore the projections were statistically robust. To the extent that the observed empirical relationships used in the coupled models do in fact reflect the effects of acid stress on aquatic biota, the projections were also biologically robust.

Dynamic water chemistry model projections were combined with biological dose-response relationships to estimate declines in fish species richness with acidification. A relationship derived from the data in Figure 2-107 was used by Sullivan et al. (2003) with stream ANC values predicted by the MAGIC model to provide estimates of the expected number of fish species in each of the modeled streams for the past, present, and future chemical conditions simulated for each stream. The coupled geochemical and biological model predictions were evaluated by comparing the predicted species richness in each of the 13 streams with the observed number of species that occur in each stream. The agreement between predicted and observed species numbers was good, with a root mean squared error in predicted number of species across the 13 streams of 1.2 species. The average error was 0.3 species, indicating that the coupled models were unbiased in their predictions. Model reconstructions of past species richness in the streams suggested that historical loss of species had been greatest in the streams located on the most sensitive geological class (siliciclastic). The average number of species lost from streams on the three bedrock types examined were estimated as 1.6 species on siliciclastic bedrock; 0.4 species on granitic bedrock; and 0.4 species on basaltic bedrock. In the case of the siliciclastic streams, the projected past changes were much larger than the average error and root mean squared error of the coupled models, suggesting that the projections were reasonably robust.

3.3. Nutrient Enrichment Effects from N Deposition

The ecological effects caused by atmospheric deposition of reactive N (N_r) are the main focus of this section. As discussed previously, the scope of this ISA includes assessment of evidence for all forms of N compounds that contribute to nutrient enrichment. The present context, the various chemical forms of N can be divided into two groups: nonreactive (N_2 gas) and N_r. Nonreactive N_2 gas composes 80% of the total mass of the Earth's atmosphere, but it is not biologically available until transformed into to reactive forms of N. Reactive N includes all biologically and chemically active N compounds in the Earth's atmosphere and biosphere (Galloway, 2003). The N_r group includes inorganic reduced forms (e.g., NH_3 and NH_4^+), inorganic oxidized forms (e.g., NO_X, HNO_3, N_2O, NO_3^-), and organic N compounds (e.g., urea, amine, proteins, nucleic acids) (Galloway, 2003). Atmospheric N deposition may be composed of numerous chemical species besides oxides, all of which contribute to ecosystem nutrient enrichment. The ISA evaluates the nutrient effects of nitrogen oxides in combination with all other forms of N_r deposition.

This assessment focuses on the effects of atmospheric N deposition. Agricultural lands are excluded from this discussion of ecosystems sensitive to nutrient enrichment effects of N deposition because crops are routinely fertilized with amounts of N (100 to 300 kg/ha) that far exceed air pollutant inputs even in the most polluted areas (EPA, 1993). These high rates of fertilization can contribute to ground water NO_3^- contamination and eutrophication of some surface waters, especially estuaries. However, assessment of the environmental effects of agricultural N fertilization is beyond the scope of this assessment.

Organisms in their natural environment are commonly adapted to a specific regime of nutrient availability. Change in the availability on one important nutrient, such as N, may result in imbalance in ecological stoichiometry, with effects on ecosystem processes, structure and function (Sterner, 2002). In general, ecosystems that are most responsive to nutrient enrichment from atmospheric N deposition are those that receive high levels of deposition relative to non-anthropogenic N loading, those that are N-limited, or those that contain species that have evolved in nutrient-poor environments.

The following discussion of N-nutrient deposition begins with the N cascade, which provides a conceptual foundation for discussing the effects of N_r on the structure and function of ecosystems. Subsequent sections include the effects of N deposition on: N cycling, C cycling, biogenic GHG emissions, and biodiversity effects, and as well as the characterization of sensitive ecosystems and regions in the U.S. Information is presented for ecosystems in which atmospheric deposition dominates total N_r input (i.e. many terrestrial ecosystems) and ecosystems in which atmospheric deposition constitutes a small proportion of total N_r load (e.g. some wetlands and estuarine ecosystems).

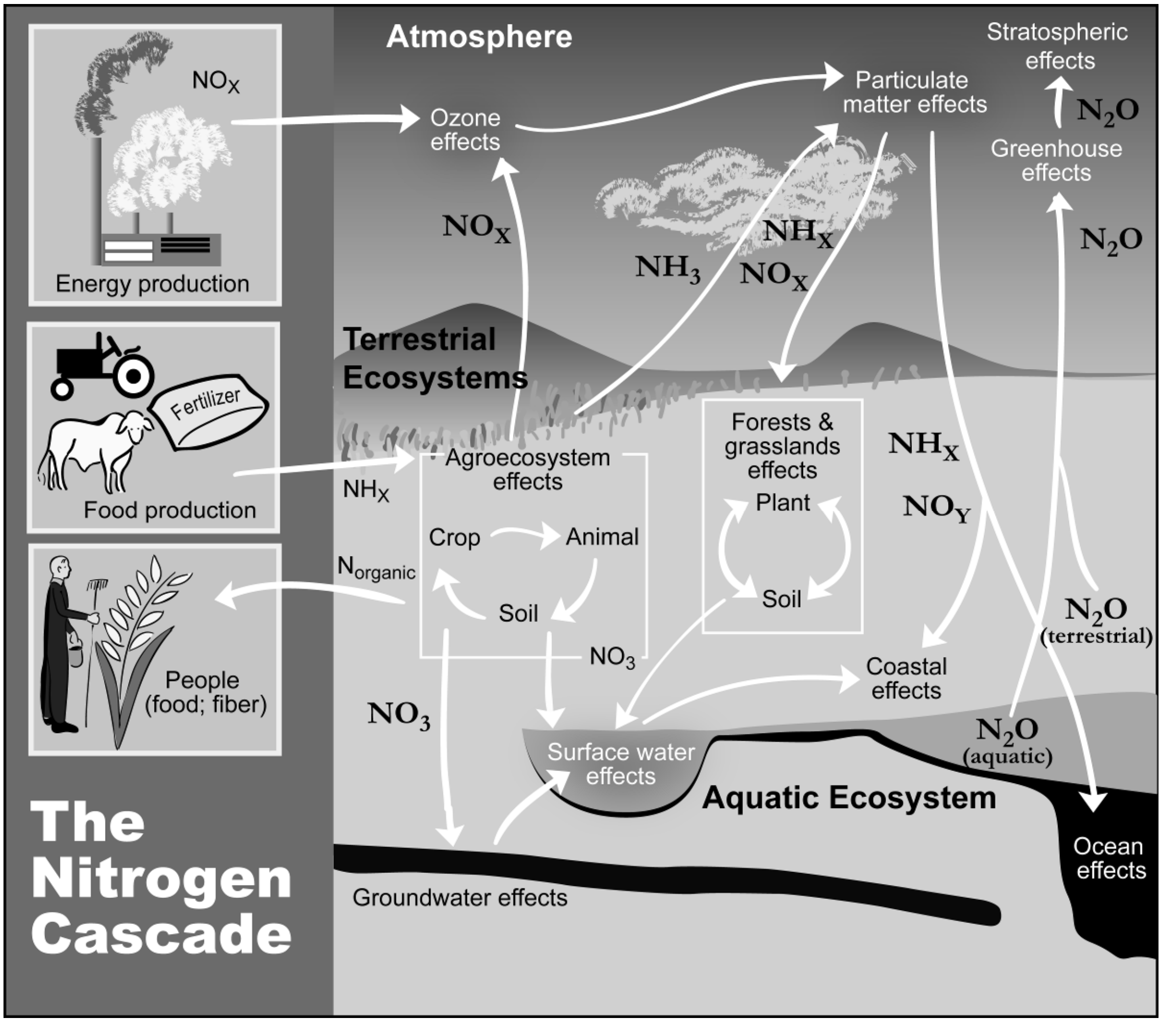
3.3.1. Reactive Nitrogen and the N Cascade

N is one of the most important nutrients in practically all ecosystems (Vitousek, 1991, and is often limiting. It is mainly because of its importance as a limiting nutrient that N deposition from air pollution causes ecological problems. N is required by all organisms because it is a major constituent of both the nucleic acids that determine the genetic character of all living things and the enzymes and proteins that drive the metabolism of every living cell (Sterner, 2002; Galloway, 1998; Galloway, 2002). It is of critical importance in plant metabolism and it often governs the utilization of phosphorus (P), potassium (K) and other nutrients.

An increase in global N_r has occurred over the past century, largely due to three main causes: (1) widespread cultivation of legumes, rice, and other crops that promote conversion of N_2 gas to organic N through biological N fixation; 2) combustion of fossil fuels, which converts both atmospheric N_2 and fossil N to NO_X; and (3) synthetic N fertilizer production via the Haber-Bosch process, which converts nonreactive N_2 to N_r to sustain food production and some industrial activities (Galloway, 2002; Galloway, 2003). Food production accounts for much of the conversion from N_2 to N_r, and accounts for geographic redistribution of N as food is shipped to meet population demands and often returned to the environment via waste water.

Reactive N accumulates in the environment on local, regional, and global scales (Galloway, 1998) (Galloway, 2002; Galloway, 2003). This accumulation occurs in the atmosphere, soil, and water (Galloway, 2002, with a multitude of effects on humans and ecosystems (Galloway, 1998; Rabalais, 2002)Van Egmond et al., 2002; Townsend et al., 2003). The sequence of transfers, transformations, and environmental effects is referred to as the “N cascade” (See Figure 3-26) (Galloway, 2002, 2003).

In general, the results of the N cascade and the various transformations in the N cycle can be both beneficial and detrimental to humans and to ecosystems (Galloway, 2002; Galloway, 2003). Among the most important effect of atmospheric N deposition are aquatic eutrophication and changes in the structure of terrestrial plant communities, disruptions in nutrient cycling, increased soil emissions of nitrous oxide (N_2O; a potent greenhouse gas), accumulation of N compounds in the soil, soil-mediated effects of acidification (see Section 3.2), and increased susceptibility of plants to stress factors (Aber, 1989; Aber, 1998; Bobbink, 1998; Driscoll, 2003; Fenn, 1998).

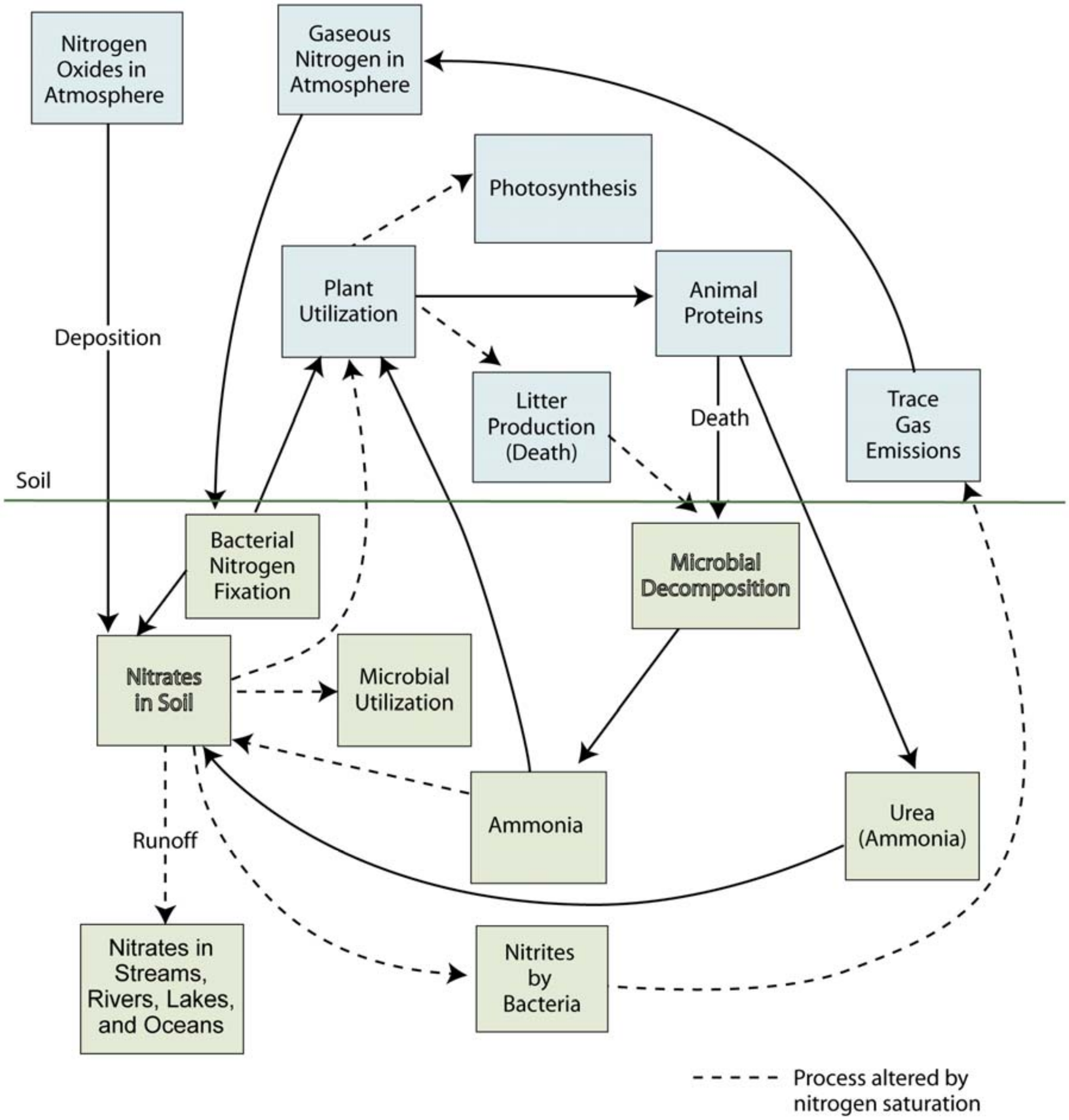


Source: Galloway et al. (Galloway, 2003)

Figure 3-26. Illustration of the N cascade showing the movement of the human-produced reactive nitrogen (N_r) as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and aquatic ecosystems.

3.3.2. N Enrichment Effects on N Cycling

Given the complexity of the N cycle, the goal of creating a broadly applicable and well-tested predictive model of these interactions has not yet been fully achieved. There is scientific information with which to make generalizations about how ecological and biogeochemical processes respond to N_r deposition. Significant scientific advancements in recent years have included refinement of theoretical foundations of nutrient limitation, development and improvement of analytical technologies, and improved understanding of the role of N_r in regulating or influencing the cycling of other elements, especially C (see Section 3.3.3). Central to this understanding is the basic process of N cycling in terrestrial, transitional, and aquatic ecosystems.



Source: Garner (1994)

Figure 3-27. N cycle (dotted lines indicated processes altered by N saturation).

The key steps in the N cycle are outlined in Figure 3-27 include N fixation, assimilation, mineralization (conversion of organic N to simple inorganic forms), nitrification (conversion of reduced inorganic N to oxidized inorganic N), and denitrification (the reduction of NO_3^- to NO, N_2O, and N_2 gas by microbes under anaerobic conditions). These steps generally require biologically mediated transformations. Key organisms involved in transforming N from one form to another include plants and microbes.

In addition to direct effects on the ecosystem where it is deposited, N can be exported from the system and cause environmental effects (eutrophication or acidification) in other ecosystem compartments. The two principal mechanisms for N export or loss from ecosystems are leaching and denitrification. Leaching removes N from terrestrial or transitional ecosystems, but adds it to aquatic ecosystems. Thus, an export from one ecosystem becomes an import to another. Denitrification removes N from terrestrial, transitional, and aquatic ecosystems and adds it to the atmosphere (Davidson, 2000; Seitzinger, 2006). Although denitrification provides a pathway for removing excess N_r from ecosystems, incidental production of NO and N_2O during denitrification is of concern due to the roles of NO as a precursor in the production of ozone (O_3), and N_2O as a potent greenhouse gas (see Section 3.3.4 for N deposition effects on biogenic N_2O flux). Here we discuss leaching and denitrification in addition to other fundamentals of N cycling in terrestrial, transitional, and aquatic ecosystems.

3.3.2.1. Terrestrial Ecosystems

N_r deposition has a potentially important effect on terrestrial ecosystems throughout large areas of the U.S. The availability of N to plants in soil is largely controlled by the process of N mineralization, or the microbial conversion from organic N to simple amino acids and then to inorganic forms such as NH_4^+ and NO_3^- (Schimel and Bennett, 2004). The two-step, aerobic, microbial process of autotrophic nitrification converts NH_4^+ to NO_3^-. Nitrification is an acidifying process, releasing 2 mol hydrogen ion (H^+) per mol NH_4^+ converted to NO_3^- (Reuss, 1986) see Section 3.2 and Annex C for the effects of acidifying deposition). As the N cycle becomes enriched through cumulative N addition, N becomes more abundant, competition among organisms for N decreases, net nitrification rates often increase, and NO_3^- can leach from the ecosystem (Aber, 1989; Aber, 2003).

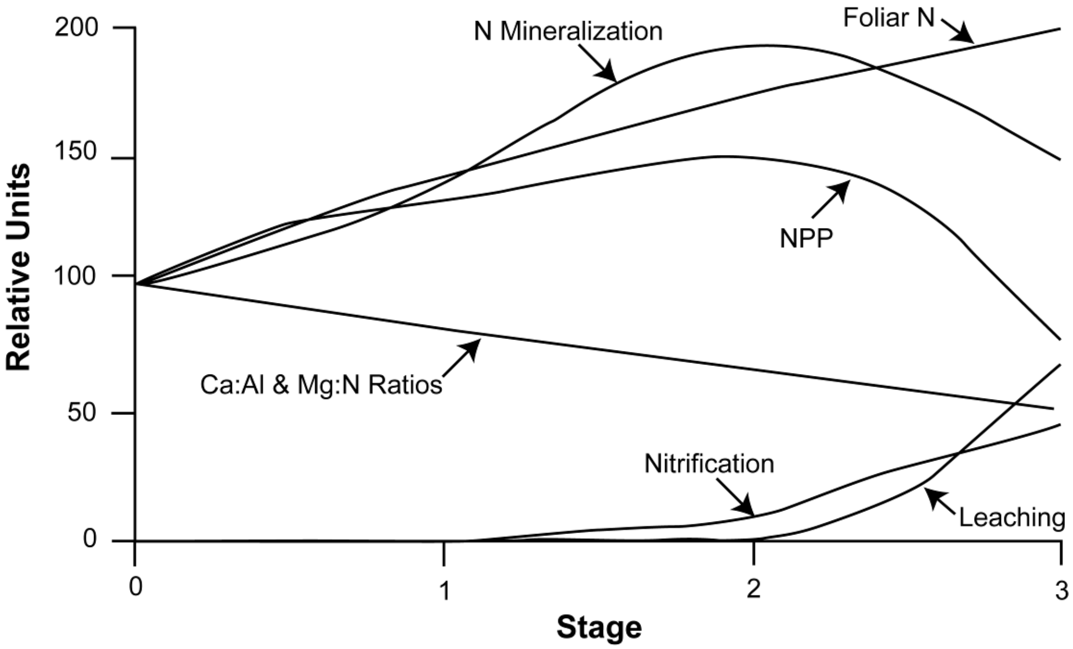
Numerous experimental ^{15}N-addition studies have been conducted as a way of understanding how N cycles through terrestrial ecosystems. These studies have shown that trees typically take up only a small fraction of added ^{15}N; the vast preponderance is retained in the soil (e.g., Tietema et al., 1998; Nadelhoffer et al., 1999; Providoli et al., 2005; Templer et al., 2005). This pattern persists even a decade after ^{15}N application (Nadelhoffer et al., 2004), but these experiments have been criticized for applying ^{15}N directly to the soil surface, thereby precluding direct canopy uptake of N from wet, dry, or gaseous deposition (Sievering, 1999; Sievering et al., 2000). Canopy ^{15}N experiments are now underway, but have not yet been published. Comparisons of rates of N deposition in throughfall and in total deposition suggest that forest canopies can take up an average of 16% of total atmospheric N input (Lovett, 1992), but this interception can be considerably higher (up to 90%) in some N-limited forests with large epiphyte loads (e.g., Klopatek et al., 2006). Of that N from deposition that is retained in vegetation, it remains unclear how much of it is used in photosynthetic enzymes (e.g., Bauer et al., 2004).

N in forest ecosystems is stored primarily in the soil, and soil N often exceeds 85% of the total ecosystem N (cf. Bormann et al., 1977; Cole and Rapp, 1981). Most soil N is contained in organic matter, typically bound in humic material or organo-mineral complexes that are resistant to microbial degradation. This N is not directly available for biological uptake by plants or microbes or for leaching loss into ground water or surface water.

Only what is termed the mineralizable, or labile, pool of N in the soil is considered to be biologically active (Aber, 1989). Bioavailable N often controls photosynthesis and net primary productivity (NPP) (e.g., Field and Mooney, 1986). Plants obtain N from the soil by absorbing NH_4^+, NO_3^-, or simple organic N compounds through their roots, or N is taken up by symbiotic organisms (e.g., fungi, bacteria, cyanobacteria) in plant roots (cf. Lilleskov et al., 2001; Schimel and Bennett, 2004). Plant roots, nitrifying bacteria, and microbial decomposers within the soil utilize, and compete for, this available soil N pool. Plant uptake of N can be energetically costly, as NO_3^- must be reduced to NH_4^+, and NH_4^+ fixed into amino acids before N can be used in plant processes. Some species reduce NO_3^- in their leaves, taking advantage of excess energy from photosynthesis, whereas other species are restricted to the more energy expensive approach of reducing NO_3^- in their roots.

N Saturation

The term N-saturation refers to the condition whereby the input of N to the ecosystem exceeds the requirements of terrestrial biota, and consequently an elevated fraction of the incoming N leaches from soils to surface waters. The original description of N saturation by Aber et al. (Aber, 1989) described four stages. It was revised by Stoddard (1994) and Aber et al. (1998) Figure 3-28. In Stage 0, N inputs are low and there are strong N limitations on growth. Stage 1 is characterized by high N retention and a fertilization effect of added N on tree growth. Stage 2 includes the induction of nitrification and some NO_3^- leaching, though growth may still be high. In Stage 3 tree growth declines, nitrification and NO_3^- loss continue to increase, but N mineralization rates begin to decline. While not all terrestrial ecosystems move through the stages of N saturation at the same rate or in response to the same N loading, several experimental N addition studies and a survey of 161 spruce-fir stands along a N deposition gradient support the concept of N saturation progressing from the onset of increase in net nitrification and NO_3^- leaching loss to the eventual decline in tree growth and increase in tree mortality (Aber, 1998).



Source: Aber et al. (1998)

Figure 3-28. Schematic illustration of the response of temperate forest ecosystems to long-term, chronic N additions. Changes from initial hypotheses of Aber et al. (Aber, 1989) include the reduction in N mineralization in stage 3 and the addition of foliar Ca:Al and Mg:N ratios.

Decades of atmospheric deposition of N have increased the availability of NO_3^- and NH_4^+ in some terrestrial ecosystems to levels where excess N availability results in net nitrification and associated NO_3^- leaching in drainage water. Severe symptoms of N saturation have been observed (1) in the northern hardwood watersheds at Fernow Experimental Forest near Parsons, West Virginia (Peterjohn, 1996), (2) in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains (Cook, 1994), (3) throughout the northeastern U.S. (Aber, 1989; Aber, 1998) and (4) lower-elevation eastern forests (Edwards and Helvey, 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000).

Mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North America (Bytnerowicz and Fenn, 1996; Fenn, 1998). In general, it is believed that deciduous forest stands in the eastern U.S. have not progressed toward N-saturation as rapidly or as far as coniferous stands. Deciduous forests may have a greater capacity for N retention than coniferous forests. In addition, deciduous forests tend to be located at lower elevation and receive lower atmospheric inputs of N. Many deciduous forests have higher rates of N uptake and greater N requirement than coniferous forests (Aber, 1998).

NO_3^- Leaching

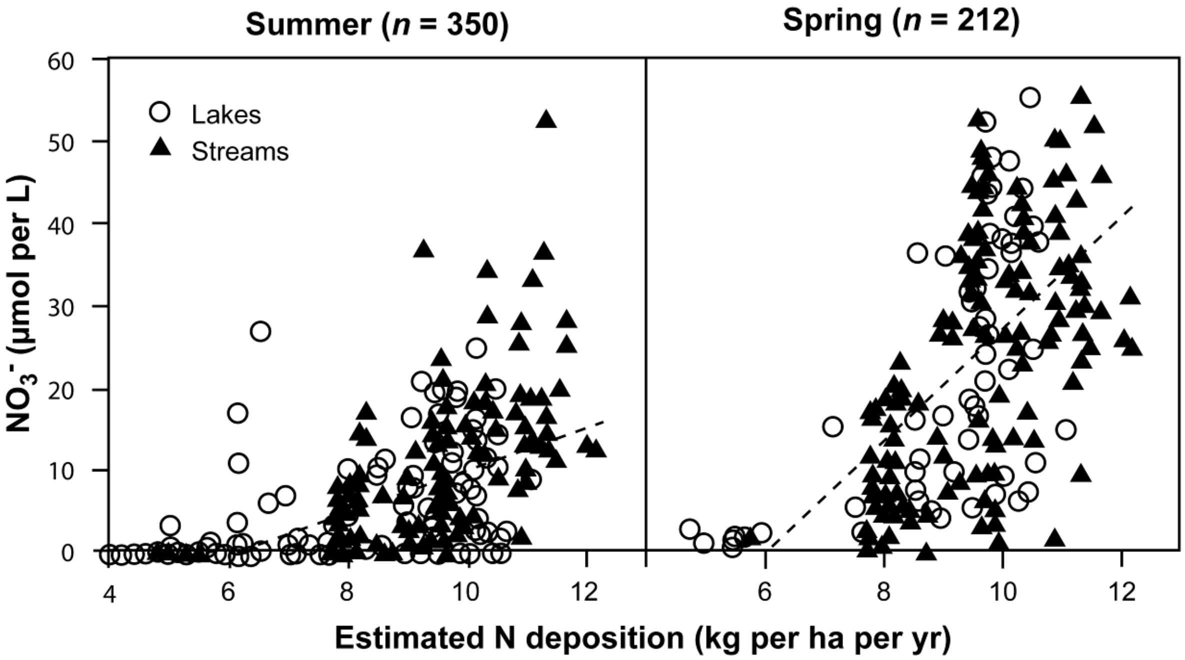
Two of the primary indicators of N enrichment in forested watersheds are the leaching of NO_3^- in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season (2. The concentration of NO_3^- in surface water provides an indication of the extent to which N deposited atmospherically or otherwise leaches from the terrestrial ecosystem.

In most upland forested areas in the U.S., most N received in atmospheric deposition is retained in soil (Nadelhoffer et al., 1999). Several different data compilations indicate that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems that receive less than about 10 kg N/ha/yr (Dise and Wright, 1995; Sullivan, 2000; MacDonald et al., 2002; Aber, 2003; Kristensen et al., 2004). In general, because much of the atmospherically deposited N is retained within the terrestrial ecosystem or denitrified during export, a relatively small fraction of this N reaches downstream estuaries (Castro, 2001)Alexander et al., 2002; Seitzinger, 2002; van Breemen, 2002).

Despite retention of most atmospheric N deposition within the terrestrial environment, N-related adverse effects on aquatic life do occur (Driscoll, 2003). For example, although 70% to 88% of atmospheric N deposition was retained in the Catskill Mountains watersheds in upstate New York, fish populations could not be sustained because high NO_3^- concentrations in stream water during high flows caused the concentrations of inorganic Al to exceed the toxicity threshold (Lawrence, 1999).

In an analysis of data collected during the mid- to late 1990s from lakes and streams throughout the northeastern U.S., Aber et al. (2003) suggested that nearly all N deposition is retained or denitrified in northeastern watersheds that receive less than about 8 to 10 kg N/ha/yr. An analysis of N deposition to forestland in the northeastern U.S. based on Ollinger et al. (1993) suggested that approximately 36% of the forests in the region received 8 kg N/ha/yr or more and may therefore be susceptible to elevated NO_3^- leaching (Driscoll, 2003).

Aber et al. (2003) further found that surface water NO_3^- concentrations exceeded 1 μeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition Figure 3-29. The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition (Figure 3-30) (Aber, 2003).

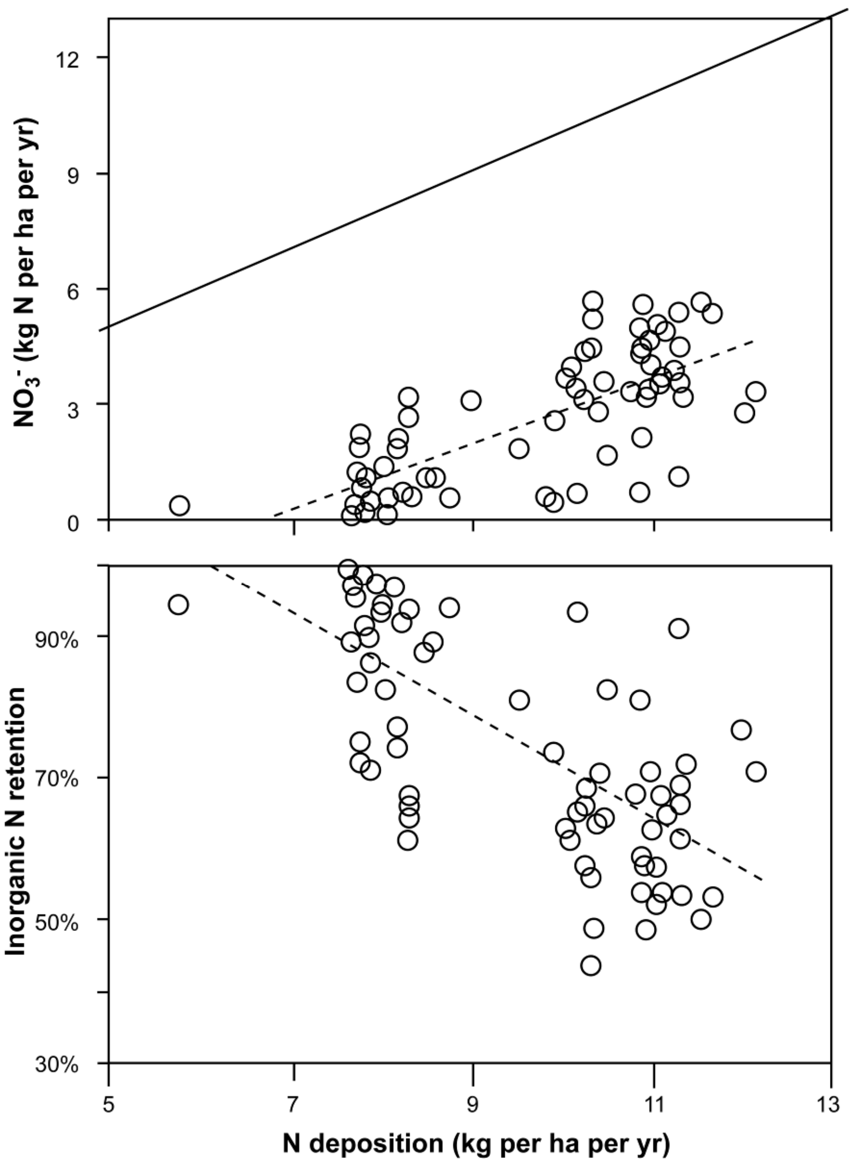


Source: Aber et al. (2003).

Figure 3-29. Surface water NO$_3^-$ concentrations as a function of N deposition at the base of each watershed in summer and spring. N deposition to the whole watershed may be 2 to 6 kg N/ha/yr greater than at the base.

In other studies, the isotopic signature of ^{18}O in streamwater NO$_3^-$ indicates that only a small percentage of the incoming NO$_3^-$ from atmospheric deposition leached directly to drainage waters (e.g., Spoelstra et al., 2001; Burns and Kendall, 2002; Pardo, 2004). The rest of the NO$_3^-$ that leached from the terrestrial ecosystem was cycled by biota in soils or streams prior to being exported. That cycled N may have originated in atmospheric deposition, but its first origin was not identified.

In general, field experiments have shown that NO$_3^-$ leaching can be induced by chronic addition of N (Edwards et al., 2002; Kahl et al., 1999; Norton et al., 1999; Kahl et al., 1993; Peterjohn et al., 1996; See Table 3-11). Several N-exclusion studies in Europe demonstrated that decreases in N deposition produced immediate reductions in NO$_3^-$ leaching from forest stands (Gundersen et al., 1998; Quist et al., 1999). At a regional scale, the leaching transport of N from terrestrial to freshwater systems has important implications beyond its impact on upland lakes and streams, because N exports can ultimately also contribute to the eutrophication of coastal ecosystems (Howarth, 1996)Driscoll et al., 2003c).



Source: Aber et al. (2003)

Figure 3-30. a) N export in stream water as a function of N deposition at the base of sampled watersheds. N export is represented by the equation $NB_{exp} = 0.85\ N_{dep} - 5.8$; $r^2 = 0.56$; $p < 0.001$. (b) Watershed N retention decreases as N deposition at the base of the watersheds increases (N retention = −0.07 N deposition + 1.44; $r^2 = 0.50$).

Denitrification

The role of denitrification in terrestrial ecosystems is important to understand the fraction of the atmospheric deposition that is returned to the atmosphere and therefore does not have direct effects on terrestrial and aquatic ecosystems. Denitrification has been difficult to measure directly in most ecosystems, due to the difficulty of measuring small changes in N_2 and to the great degree of spatial and temporal heterogeneity inherent in the denitrification process (Davidson and Seitzinger, 2006). Additional information on measurement techniques is available in Annex C.

Denitrification is accomplished by facultative anaerobic denitrifying bacteria, and occurs only under anaerobic conditions, in the presence of sufficient NO_3^- and organic C. Hence, most terrestrial denitrification occurs in "hotspots," that is, in sporadically wet places or times or in anaerobic soil microsites (McClain et al., 2003; Seitzinger, 2006). The high organic matter content of terrestrial soils provides an ample supply of C, and so the factors that typically limit rates of denitrification in terrestrial ecosystems are rates of NO_3^- supply and the occurrence of anaerobic conditions. (See Annex C for additional studies and Section 3.3.4 for an analysis of N deposition effects on N_2O flux from terrestrial and wetland ecosystems)

Using a simple model of the fate of global N inputs to terrestrial ecosystems, Seitzinger et al. (Seitzinger, 2006) estimated that denitrification in terrestrial soils removed 46% (124 Tg/yr) of global N inputs from all sources (N deposition, fertilizer, and N fixation). Half of this denitrification (66 Tg/yr) was estimated to have occurred in agricultural systems. However, this model assumed that all N entering terrestrial systems was leached as NO_3^- if it was not taken up by plants. Hence, the model overestimated the potential for denitrification by the extent to which N accumulated in soils or ground water (Seitzinger, 2006).

Foliar N Concentration

The concentration of N in plant foliage, especially in forest trees, can provide an indicator of nutrient enrichment (McNeil et al., 2007; Table 3-11). This indicator may be especially relevant because there is a potential to acquire regional-scale data on foliar N through remote sensing techniques. This allows rapid assessment of N status across large land areas. The N content in tissue of some plant species varies in proportion to N inputs (Baddeley et al., 1994; Hyvarinen and Crittenden, 1998; Pitcairn et al., 2003). Similarly, species typical of nutrient-poor environments tend to accumulate the amino acid arginine in plant tissue (van Dijk and Roelofs, 1988), and arginine concentration therefore varies in proportion to N inputs. Foliar N and foliar arginine concentrations both provide good indices of N deposition effects.

There is an interaction between N content and insects, increases N content has been shown to increase palatability to defoliating insects and therefore increasing the extent of defoliation (Nordin et al., 1998; Forkner and Hunter, 2000).

Soil Carbon-to-N Ratio

The N and C cycles are tightly coupled in forest soils. For example, NO_3^- leaching has been correlated with forest floor C:N. Nitrification and NO_3^- leaching rates are generally low on sites having soil C:N ratios above about 22 to 25 (Lovett et al., 2002; Ross, 2004). The C:N ratio of the forest floor can be changed by N deposition over time, although it is difficult to detect a change over time against background spatial heterogeneity (Aber, 2003). The forest floor C:N ratio has been used as an indicator of ecosystem N status in mature coniferous forests (Table 3-11).

Table 3-11. Summary biogeochemical indicators of N addition to terrestrial ecosystems.

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
White Mountains of New Hampshire	Soil C:N Ratio Nitrification	Observational: field relationships between soil C:N ratio and canopy lignin:N ratio and high spectral resolution remote sensing data to predict spatial patterns in C:N. Remote-sensed data were obtained from NASA's Airborne Visible and Infrared Imaging Spectrometer (AVIRIS) instrument. Preliminary regional estimates of soil C:N ratio suggested that 63% of the land area in the region had C:N below 22, which was suggested as a critical threshold for the onset of nitrification. Below C:N = 22, increasing, but variable, rates of nitrification were found		Ollinger et al. (2002)
Europe	Soil C:N Ratio NO_3^- Leaching	Observation and Modeling: data from 160 sites across Europe was used to determine that NO_3^- leaching occurs in n with soil C:N ratio above 30	Coniferous Forests	Kristensen et al. 2004
Northeast US	Soil C:N Ratio Nitrification	Observational: in a compilation of soil C:N and nitrification data from 250 plots showed a statistically significant but weak correlations between either soil C:N or nitrification and annual N deposition rate. However, across plots, nitrification increased sharply as C:N ratio (by mass) decreased below about 22.		Aber et al. 2
Continental Divide in Colorado	Soil C:N Foliar C:N Mineralization Soil %N Foliar N:Mg Foliar N:P	Deposition Gradient: Comparison of Engleman spruce (Picea englemanii) forest stands east (3 to 5 kg N/ha/yr) and west (1 to 2 kg N/ha/yr) slopes of the Continental Divide in Colorado. The higher N deposition on the east slope was due to agricultural and urban areas of the South Platte River Basin. East slope sites showed lower soil organic horizon C:N ratio, lower foliar C:N ratio, higher potential net mineralization, and higher percent N, N:Mg ratio, and N:P ratio in foliage. These results suggested that even moderate levels of N deposition input can cause measurable changes in spruce forest biogeochemistry.	Engleman Spruce (*Picea Englemanii*)	Rueth and Baron (2002)
Europe	Foliar [N]	Observation and Modeling: data from 160 sites across Europe was used to determine NO_3^- leaching occurs with foliar N <13 mg N/g	Coniferous Forests	Kristensen et al. 2004
Adirondacks	Foliar [N]	Deposition gradient: observe that eight of nine major canopy tree species had increased foliar N in response to a gradient of N deposition. Species specific differences were strongly related to two functional traits that arise from within-leaf allocations of N resources: leaf mass per area and shade tolerance.	Northern Hardwood	McNiel et al. 2007
Scotland	Foliar [N]	Deposition gradient: Total tissue N and arginine concentrations were closely correlated with both atmospheric NH_3 concentration and estimated N deposition ($r^2 > 0.97$ and > 0.78, respectively)	Three Moss Species In A Mixed Woodland	Pitcairn et al. (2003)
Vermont	Nitrification	Field addition: Additions of 25 kg N/ha/yr to spruce plots (ambient bulk deposition 5.4 kg N/ha/yr), in which net nitrification did not occur prior to treatment, triggered net nitrification in the second year of treatment, whereas nitrification was not triggered until the third year in plots receiving 19.8 kg N/ha/yr	Spruce Forest	(McNulty et al., 1996).
Colorado	Mineralization Nitrification Foliar [N] Organic Soil Horizon [N]	Field addition: Additions of 25 kg N/ha/yr to plots in Loch Vale watershed (ambient bulk deposition ~4–5 kg N/ha/yr) doubled N mineralization rates and stimulated nitrification, while the addition of the same amount to plots receiving ambient bulk deposition of ~2.0 kg N/ha/yr in Fraser Experimental Forest elicited no microbial response but significantly increased foliar and organic soil horizon N	Old-Growth Spruce	Rueth et al (Rueth, 2003)
Colorado	Mineralization Nitrification	Deposition gradient: A comparison study of plots across a depositional gradient found mineralization rates to be higher where N deposition ranged from 3 to 5 kg N/ha/yr than where N deposition ranged from 1 to 2 kg N/ha/yr, with measurable nitrification rates at sites with the highest deposition amounts	Old-Growth Spruce	Rueth and Baron, (2002).
Harvard Forest, MA	Soil [NO_3^-] Soil [NH_4+]	Field Addition: which exhibited elevated concentrations of NO_3^- plus NH_4^+ in soil water after 1 year of 150 kg N/ha/yr doses, and after 5 years of 50 kg N/ha/yr doses	*Pinus Resinosa*	Magill et al., 2004
Harvard Forest, MA	Soil [NO_3^-] Soil [NH_4^+]	Field Addition: In plots that received additions of 150 kg N ha-1 yr^{-} , elevated concentrations were detected on the seventh year. In plots receiving 50 kg N/ha/yr, elevated soil concentrations were not observed after 15 years of treatment.	Hardwood Plots	Magill et al., 2004
Maine and West Virginia	NO_3^- Leaching	Field Addition: Additions of N to watersheds in Maine (25 kg N/ha/yr) and West Virginia (35.5 kg N/ha/yr), which were releasing NO_3^- to surface waters prior to the additions, resulted in substantial increases in NO_3^- concentrations in soil water and stream water within the first treatment year	Hardwood	(Kahl et al., 1993; Peterjohn et al., 1996).

Region/Country	Endpoint	Observations	Forest Type/ Species	Reference
Fernow Experimental Forest, WV	NO_3^- Leaching Ca Leaching	Observational: N saturation observed. Progressive increases in streamwater NO_3^- and Ca concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s). This watershed has received higher N deposition (average throughfall input of 22 kg ha/yr of N in the 1980s) than is typical for low-elevation areas of the eastern U.S., however (Eagar et al., 1996), and this may help to explain the observed N saturation.	Lower-Elevation Eastern Forests, Especially In West Virginia	(Edwards and Helvey, 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000)
Bear Brook, ME	NO_3^- Leaching N Retention	Field Addition: Ammonium SO_4^{2-} ($[NH_4]_2SO_4$) fertilization of a forested watershed resulted in long-term increases in NO_3^- concentration in stream water and high annual export of N, although the fertilized catchment retained 80% of N inputs, mostly in soil		(Kahl et al., 1999; Norton et al., 1999).
Fernow Experimental Forest, WV	NO_3^- Leaching	Field Addition: to $(NH_4)_2SO_4$ fertilization caused NO_3^- leaching		(Edwards et al., 2002)
greater Los Angeles area, CA	N Saturation	Observational: plant communities exposed to air pollution received sufficiently high levels of atmospheric N deposition to be N saturated. Symptoms of N saturation were evident in mixed conifer or chaparral sites receiving atmospheric deposition of 20 to 25 kg N/ha/yr or higher.	Chaparral And Mixed Conifer	Fenn et al. (1996)
Sierra Nevada and San Bernardino, CA	NO_3^- Leaching	Critical load for increased NO_3^- leaching calculated as 17 kg N/ha/yr	Mixed Conifer Forests	Fenn et. al. (Fenn, 1998)
San Bernardino Mountains, CA	N Saturation	Deposition gradient: over the range of 12.1–31.7 kg N/ha/yr, the ecosystem was N saturated, as evidenced by high streamwater NO_3^- concentration (151 and 65 µeq/L at upper and lower ends, respectively, of Devil Canyon West Fork	Coniferous Forest	Fenn et al., 2000
San Bernardino Mountains, CA	DIN Export	Deposition gradient: over the range of 11–40kg N/ha/yr , dissolved inorganic N (DIN) export was scale dependent, with highest export occurring in watersheds of ~ 150/ha. Differences attributed to temporal asynchrony between N availability and biological demand	Mixed Forest-Chaparral, Hardwood, Coniferous	Miexner and Fenn, 2004
Rocky Mountain alpine catchments	N Retention	Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at input levels less than 10 kg N/ha/yr		Baron et al. (Baron, 1994) Williams and Tonnessen, 1999

Disturbance and stand age effects on N retention

The varying degree of N assimilation, leaching and microbial transformation often reflect differences in N status among treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more (Goodale, 2001). Sites which have undergone disturbances that cause loss of soil N, such as logging, fire, and agriculture, tend to be most effective at retaining atmospheric and experimental inputs of N. Fire causes substantial N losses from ecosystems (see Table 3-12). Timber harvest contributes to nutrient removal from the ecosystem via biomass export and acceleration of leaching losses (Bormann et al., 1968; Mann et al., 1988). In particular, logging contributes to loss of N and Ca^{2+} from the soil (Tritton et al., 1987; Latty, 2004). N retention capability often decreases with stand age, which suggests that older forests are more susceptible than younger forests to becoming N-saturated (Hedin et al., 1995). Aber et al. (1998) surmised that land use history may be more important than cumulative atmospheric deposition of N in determining the N status of a forest ecosystem. See Annex D for a more detailed discussion of how disturbance affects N cycling.

Table 3-12. Effects of fire on nutrient concentrations in forests in Nevada and California

Region/Country	Endpoint	Observations	Grassland type/ species	Reference
Lake Tahoe Basin, Nevada	nutrient concentration in runoff	Field measurement: Compared runoff from fixed plots within wildfire-burned and unburned areas in both summer and winter seasons. Wildfire increased the frequency and magnitude of elevated nutrient in discharge runoff for all 3 parameters studied: NO_3 N, ammonium nitrogen, phosphate P. The mobilization of nutrients was increased due to wildfire, but the lack of O horizon material (surface organic layer of mineral soils) after burning may ultimately reduce discharge concentrations over time	Jeffery pine, white fir, sugar pine, Sierra chinquapin, currant, and snow brush, bitterbrush Soils: Cagwin series	Miller et al. (2006)
Lake Tahoe, Nevada	leaching, N concentrations in forest floor and soil	Field measurement: Fire and post-fire erosion caused large and statistically significant losses of C, N, P, S, Ca, and Mg from the forest floor; Before the burn, there were no significant differences in leaching, but during the first winter after the fire, soil solution concentrations of NH_4^+, NO_3^-, ortho-P, and (especially) SO_4^{2-} were elevated in the burned area, and resin lysimeters showed significant increases in the leaching of NH_4^+ and mineral N. The leaching losses of mineral N were much smaller than the losses from the forest floor and A11 horizons. The major short-term effects of wildfire were on leaching, whereas the major long-term effect was the loss of N from the forest floor and soil during the fire.	Sierra Nevada mixed conifer forest: Jeffrey pine (*Pinus jeffreyi*), white fir (*Abies concolor*), sugar pine (*Pinus lambertiana*) and incense-cedar (*Calocedrus decurrens*). Understory vegetation: green leaf manzanita (*Arctostaphylos patula*), snowbrush (*Ceanothus velutinus*). Soils-Cagwin series: coarse, loamy sand	Murphy et al. (2006)
Sierra Nevada, California	forest floor and nutrient content, soil chemical properties, and soil leaching	Field experiment: investigated the effect of forest thinning treatments and prescribed burning on carbon, N, ortho-P, and SO_4^{2-} in the forest floor organic layer and surface soil mineral horizons. The study included a prescribed fire and three timber harvest treatments: whole-tree thinning (WT) cut-to-length thinning (CTL), and no harvest (CONT). There were no statistically significant effects of burning on soil C, N, C:N ratio, Bray-extractable P, exchangeable Ca^{2+}, K^+, or $Mg^{2+.}$ Burning had no significant effect on soil solution pH, ortho-P, SO_4^{2-}, NO_3^-, or NH_4^+ as measured by ceramic cup lysimeters and no effect on the cumulative leaching of ortho-P, NO_3^-, or NH_4^+ as measured by resin lysimeters. Prescribed fire had little impact on total and soluble nutrients in the upper mineral soil layer. Loss of N capital from the forest floor appears to be the major effect of prescribed burning.	Jeffery pine (*Pinus jeffreyi*) forest	Murphy et al. (2006a)
Sierra Nevada, California	nutrient budget of C, N, Ca, P, K, S, Mg	Field measurement/Modeling: effects of fire, post-fire salvage logging, and revegetation on nutrient budgets were estimated for a site that burned in a wildfire in 1981. 2 decades after the fire, the shrub ecosystem contained less C and more N than the adjacent forest ecosystem. C was exported in biomass during salvage logging and will not be recovered until forest vegetation occupies the site again. Most N was lost via volatilization during the fire rather than in post-fire salvage logging (assuming that foliage and O horizons were combusted). Comparison of the pre-fire and present day N showed the lost N was rapidly replenished in O horizons and mineral soils, probably due to N-fixation by snowbush. No differences in ecosystem P, K, or S contents or in soil extractable P or S between the shrub and forested plots. K^+, Ca^{2+}, and Mg^{2+} were greater in shrub than in adjacent forested soils. The large increase in Ca resulted from either the release of Ca from non-exchangeable forms in the soil or the rapid uptake and recycling of Ca by post-fire vegetation.	110–130 year old Jeffery pine (*Pinus jeffreyi*)	Johnson et al. (2005)
Little Valley, Nevada	C and N loss	Field measurement/ Modeling: On an ecosystem level, the fire consumed approximately equal percentages of C and N (12 and 9%, respectively), but a greater proportion of aboveground N (71%) than C (21%). Salvage logging was the major factor of C lost, and C lost will not be replenished until forest vegetation is reestablished. N_2 fixation by *Ceanothus velutinus* in the post-fire shrub vegetation appears to have more than made up for N lost by gasification in the fire over the first 16 yr, and may result in long-term increases in C stocks once forest vegetation takes over the site. N loss from the fire equaled > 1,000 years of atmospheric N deposition and > 10,000 years of N leaching at current rates. Calculations of C and N losses from theoretical wildfires in the IFS sites show similar patterns to those in Little Valley. Calculated losses of N in most of the IFS sites would equal many centuries of leaching. Conceptual models of biogeochemical cycling in forests need to include episodic events such as fire.	Jeffery pine (*Pinus jeffreyi*) Mesic forests in the Integrated Forest Study (IFS).	Johnson et al. (2004)
N. Lake Tahoe, Nevada; Truckee, California (Tahoe National Forest); Glenbrook, Nevada (Lake Tahoe Basin)	C and N loss	Field measurement: The quantities of C and N volatilized from the forest floor by prescription fire in the Sierra Nevada were measured at three sites: Marlene, Sawtooth and Spooner. C losses calculated by the weight method were 6.12, 7.39, and 17.8 mg C/ha at the Sawtooth, Marlene, and Spooner sites. N losses calculated by the weight method were 56.2, 60.8, and 362 kg N/ha, at the Sawtooth, Marlene, and Spooner sites, respectively. N volatilization during prescribed fire is the dominant mechanism of N loss from these systems.	Marlene: Jeffery pine, white fir, snowbrush, squawcarpet, greenleaf manzanita, pinemat manzanita, soil: Cagwin series Sawtooth: Jeffery and Ponderosa pine, soil: Kyburz series Spooner: mixed confer, red fir, white fir, snowbrush and manzanita, soil: Tahoma series	Caldwell et al. (2002)

3.3.2.2. Wetland Ecosystems

N dynamics in wetland ecosystems vary in time, with type of wetland and with environmental factors, especially water availability (Howarth, 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito, 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source and sink N dynamics in wetlands (Devito, 1989; Koerselman, 1993) Arheimer and Wittgren, 1994; Mitchell, 1996).

N Fixation and Mineralization

N fixation and mineralization are two mechanisms by which N becomes available for plants. It is documented that ecosystems may derive substantial amounts of new N inputs via N_2-fixation (Hurd et al. 2001). N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). Drought has been shown to inhibit mineralization and nitrification in soils leading to a decrease in NO_3 concentration (Foster et al. 1992). However, drying may stimulate mineralization upon re-wetting (Keift et al. 1987). A laboratory study showed that within 24 h of re-wetting, extractable NO_3^- concentration in dried peat increased approximately 7–fold as compared to continuously moist peat (Watmough et al. 2004).

NO_3^- Leaching

Leaching losses from wetlands are rarely considered separately from leaching losses from upland terrestrial environments and the wet environments that occur in upland catchments. That is, when leaching losses from terrestrial ecosystems are quantified based on stream exports, estimated leaching losses implicitly include the net loss of NO_3^- from both terrestrial ecosystems and adjacent wetlands. Leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. However, hydrologic flowpaths that deliver water to streams by bypassing wetland soils can deliver substantial quantities of NO_3^--rich water from terrestrial uplands.

Denitrification

Transitional ecosystems can remove significant quantities of NO_3^- from water because they represent a convergence of conditions of NO_3^-, O_2, and C that are requisite for denitrification. Denitrification is frequently optimized when NO_3^- from more oxic upland areas passes through wet, often C-rich and anoxic wetlands. In some cases NO_3^- concentration was found to be a better predictor of denitrification rates than soil moisture (Groffman 1994), and there is evidence that in some cases denitrification is limited by C and NO_3^- supply in wetlands(Ashby et al. 1998).

Denitrification has been studied in riparian zone ecosystems (Lowrance, 1992; Pinay et al., 1993, 2000; Watts and Seitzinger, 2001; Hefting et al., 2003) and seems to be related to C availability. Generally, riparian soils that are both rich in organic matter and anaerobic have high denitrification potential. Where riparian soils are aerobic, however, nitrification, rather than denitrification, can be the dominant process (Stevens et al., 1997).

Table 3-13. Summary of N cycling studies for wetlands.

Region/Country	Endpoint	Observations	Wetland Type / Species	Reference
Adirondack Mountains, NY	N sources used by vegetation	Isotopic tracer: Surface waters in forested watersheds. The study estimated N_2 fixation by speckled alder in five wetlands by the ^{15}N natural abundance method and by acetylene reduction using a flow-through system. The study of alder-dominated wetlands showed that alder derived >85% of leaf N from N-fixation at an estimated rate of 43 kg N/ha/yr Conclusion: speckled alder in wetlands of northern New York State relies heavily on N_2 fixation to meet N demands, and symbiotic N_2 fixation in speckled alders adds substantial amounts of N to alder-dominated wetlands in the Adirondack Mountains. These additions may be important for watershed N budgets, where alder-dominated wetlands occupy a large proportion of watershed area	*Alnus incana*	Hurd et al. (Hurd, 2001)
Rhode Island	Denitrification	Observational: the highest rates of denitrification (4 to 135 kg N/ha/yr) were observed in very poorly drained soils on nutrient-rich parent material, with lower rates (1.2 to 5.3 kg N/ha/yr) in soils that were better drained or less nutrient-rich.		Groffman (1994)
Catskill Mountain soils	denitrification	Field Addition: Higher rates of denitrification per unit area associated with soils with higher organic matter content and water-filled pore spaces. Instantaneous NO_3^- concentration did not correlate with denitrification rate, suggesting that the rates of NO_3^- supply through microbial production or hydrologic transport were more important than in situ NO_3^- concentration. Denitrification was most stimulated by amendments with glucose alone or glucose plus NO_3^-, suggesting limitation by labile C and NO_3^- supply.		Ashby et al. (1998)
Adirondack Mountains, NY, Archer Creek Watershed	denitrification	Ecological gradient: Changes in stream N were measured in one riparian wetland and one beaver meadow: Strong effects of peatlands on local N concentrations, but little effect of peatlands on adjacent stream chemistry, since peatland ground water contributed little to streamflow.	peatlands	McHale et al. (2004)
Michigan, Smith Creek	denitrification	Field additions/measurement Over a two-year period > 1400 individual samples of subsurface waters were analyzed. Both spatial patterns of water chemistry and additions of labile C to demonstrate that the supply of degradable C from shallow flowpaths limited rates of NO_3^- removal via denitrification in near-stream zones. Thus, the immediate near-stream region may be especially important for determining the landscape-level function of many riparian wetlands.	Riparian wetlands	Hedin et al. (1998)

N deposition may stimulate biogenic emissions if the N supply is limiting the rate of denitrification in wetland soils via (2006 and Ross, 2005). Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process increases the contribution of nitrous greenhouse gasses to the atmosphere, but limits other environmental effects that are typically associated with increased N supply to soils and drainage waters.

In a review of the effects of riparian zones on NO_3^- removal from ground water, Hill (1996) concluded that there are large losses of NO_3^- to denitrification within riparian zones. However, there are important limitations to the generalization that riparian wetlands prevent the leaching of NO_3^- to streams. Not all water entering streams passes directly through adjacent riparian zones, and denitrification in deep subsurface flowpaths is often limited by the supply of labile C. In addition, not all streamwater passes through riparian zones, and large amounts of water may follow flowpaths beneath organic-rich riparian zones, allowing significant transport of NO_3^- to streams (McHale et al. 2004). The supply of degradable C from shallow flowpaths has been shown to limit rates of NO_3^- removal via denitrification in near-stream zones (Hedin et al. 1998).

In summary, wetland soils can be hotspots of NO_3^- removal by denitrification in anoxic sites rich in NO_3^- and labile C, but denitrification rates can be limited by suboptimal conditions of any single biogeochemical factor, and deep water flowpaths can bypass wetland denitrification altogether (see Table 3-13).

3.3.2.3. Freshwater Aquatic Ecosystems

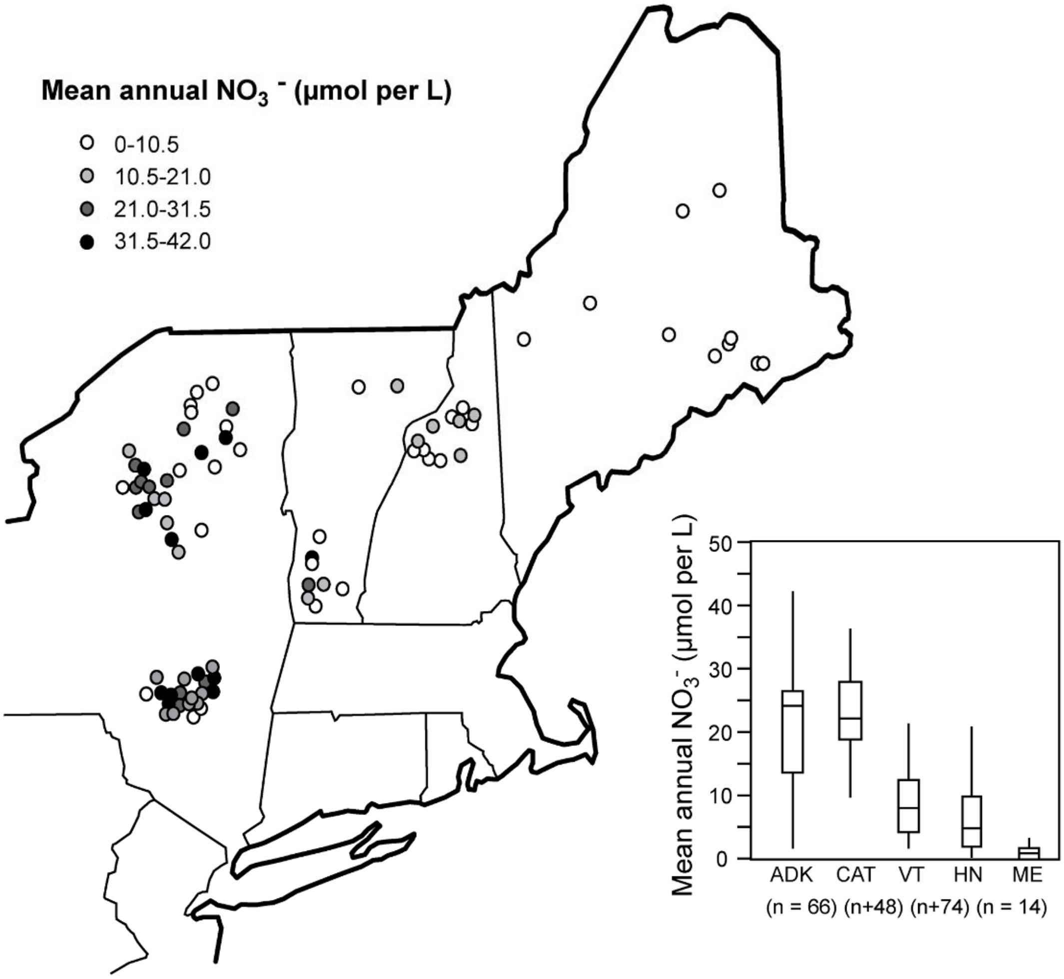
As previously noted, a large fraction of atmospheric N deposition is retained in most forests. Nevertheless, the fraction that does leach to streams can make a substantial contribution to total N inputs to downstream rivers and estuaries, especially in the eastern U.S. (Driscoll et al. 2003).

NO_3^- Leaching

The predominant chemical consequences of excess atmospheric and non-atmospheric N loading to the watershed of fresh surface waters are: (1) elevated NO_3^- concentration in surface water; and (2) NO_3^- leaching downstream. The concentration of NO_3^- in surface water can serve as a chemical indicator of N input in excess of ecosystem requirements, and has relevance with respect to acidification and eutrophication effects on surface water.

The relationship between wet deposition of N and streamwater output of NO_3^- was evaluated by Driscoll et al. (Driscoll, 1989) for sites in North America (mostly eastern areas), and augmented by Stoddard (1994). The data showed a pattern of N leaching at wet inputs greater than approximately 5.6 kg N/ha/yr, which probably corresponds with a total N deposition input of about 8 to 10 kg/ha/yr. In the Northeast, a survey of 230 lakes and streams documented NO_3^- concentrations ranging from less than 2 up to 42 μeq/L, with the highest median values occurring in the Adirondacks (Aber, 2003) (Figure 3-31).

In the western U.S., NO_3^- concentrations of freshwater ecosystems have been shown to increase with proximity to urban areas. Results from the Western Lake Survey (WLS) (Eilers, 1987), document enhanced N concentrations in high elevation lakes adjacent to and downwind of urban centers (Fenn et al., 2003a), such as those found in the Sierra Nevada and Colorado Front Range (see Figure 3-32). For example, NO_3^- concentrations in streamwater during the growing season in the Sierra Nevada were reported to range from 4 to 19 μeq/L (Fenn et al., 2003b). Concentrations above 10 μeq/L are generally considered high.

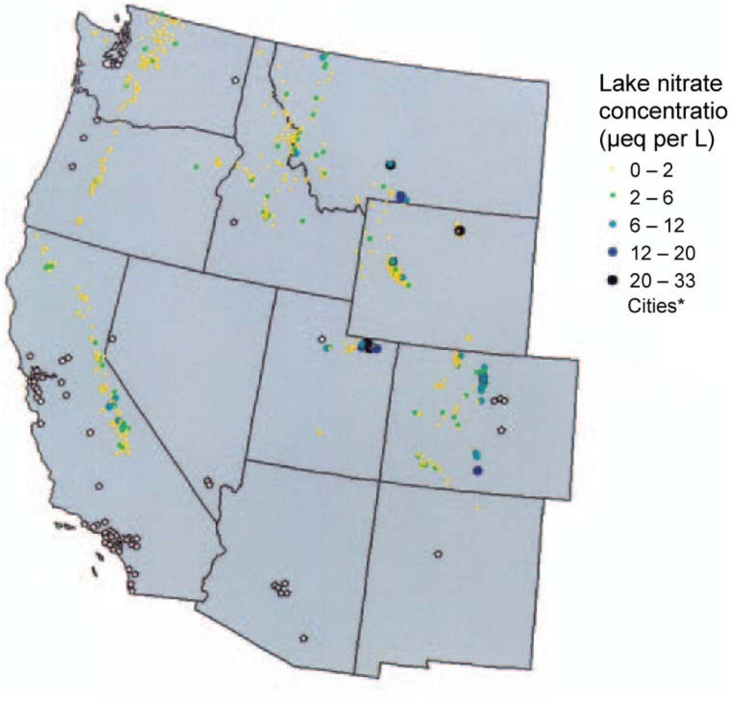


Source: Aber et al. (2003).

Figure 3-31. Mean annual NO_3^- concentrations in 230 lakes and streams across the northeastern U.S. Inset indicates the median, quartile, and 90% range of mean annual NO_3^- in the Adirondacks (ADK), the Catskills (CAT), Vermont (VT), New Hampshire (NH), and Maine (ME).

An interesting example from the Colorado Front Range indicates that lakes on the eastern and western slopes can experience significantly different levels of NO_3^-. A survey of 44 lakes east and west of the Continental Divide indicated that lakes on the western side of the Continental Divide averaged 6.6 µeq/L of NO_3^-, whereas lakes on the eastern side of the divide averaged 10.5 µeq/L of NO_3^- concentration. NO_3^- concentrations above 15 µeq/L have commonly been measured in lakes on the eastern slope of the Front Range, suggesting some degree of N saturation (Baron, 1992), and extreme values as high as 40 µeq/L have also been reported (Campbell et al., 2000). Williams et al. (1996b) concluded that N-saturation is occurring throughout high-elevation catchments of the Colorado Front Range. Many lakes in the Colorado Front Range have chronic NO_3^- concentrations greater than 10 µeq/L and concentrations during snowmelt are frequently much higher, due at least in part to leaching from tundra, exposed bedrock, and talus areas.

In the Unita Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of the lakes included within the Western Lakes Survey had NO_3^- concentrations greater than 10 μeq/L. This pattern suggests that N deposition in these areas may have exceeded the capability of these lakes to assimilate N. It is unknown if these concentrations of NO_3^- represent effects from anthropogenic sources or if this constituted a natural condition associated with inhibited NO_3^- assimilation in cold alpine environments.



Source: Fenn et al. (2003a)

Figure 3-32. NO_3^- concentrations in high-elevation lakes in western North America. Stars represent cities with a population greater than 100,000.

Denitrification

Denitrification in freshwater aquatic ecosystems has been studied in small streams most intensively, though some work has also been done at larger scales. N is cycled rapidly within streams, especially small streams with large relative areas for contact with benthic surfaces and hyporheic zones. For example, Peterson et al. (2001) found that $^{15}N\text{-}NH_4^+$ added to streams of various sizes was taken up most rapidly in the smallest streams, and that these headwater streams exported less than 50% of their added NH_4^+. Nevertheless, the long-term fate of this removed or transformed and recycled N is more difficult to assess. Mulholland et al. (2004) found that addition of $^{15}N\text{-}NO_3^-$ to a headwater stream at Walker Branch, TN, indicated a mean uptake length of 35 m under ambient conditions. The uptake length extended three-fold (i.e., reduced uptake) under a modest fertilization treatment, which employed NO_3^- addition of approximately 500 μg N/L. Direct measurements of denitrification of added ^{15}N indicated that denitrification accounted for 16% of the NO_3^- loss under the ambient treatment, and only 1% of NO_3^- uptake under the fertilized treatment. Nearly all of the denitrification occurred as reduction to N_2 gas rather than to N_2O.

Hyporheic losses of NO_3^- to denitrification may be largely controlled by supplies of labile dissolved organic carbon (DOC). Bernhardt and Likens (2002) found that adding 6 mg/L of DOC as acetate to a small stream at Hubbard Brook, NH, reduced stream NO_3^- concentrations from ~5 to < 1 μmol/L. In experimental mesocosms designed to mimic hyporheic flowpaths of a small river in the Catskill Mountains, NY, Sobczak et al. (2003) found that adding just 0.5 to 1.0 mg/L DOC from leaf litter resulted in the net consumption of nearly all of the 40 μmol/L NO_3^- in solution. Acetylene block measurements indicated that the majority of this NO_3^- loss was due to microbial assimilation rather than denitrification, consistent with the isotopic tracer results of Mulholland et al. (2004).

At large spatial scales, water residence time is the variable most frequently identified as a controller of N loss from aquatic ecosystems examined. Examples include lakes of various sizes (Howarth, 1996) and large river basins spanning the northeastern U.S. (Seitzinger, 2002). Compiling N loss data sets from a wide range of aquatic ecosystems, Seitzinger et al. (Seitzinger, 2006) found that water residence time alone explained 56% of the variance in rates of N loss across lakes, rivers, estuaries, and continental shelves, from fast-flowing river reaches (residence time of h) with 0% to 15% N loss to century-scale turnover lakes that eventually incur 80% to 100% N loss.

N Transport Downstream: Urbanization and Determination of N Sources

The transport of N via rivers and streams represents an important source of N to downstream ecosystems. The transport and loss of N is determined by the net balance of delivery of N by direct atmospheric deposition and from upland terrestrial and associated transitional ecosystem sources, minus the uptake and gaseous loss of that N during transport. Alexander et al. (Alexander, 2002) and 2007) showed ~70% of the N in headwater streams in from N deposition and the net transport of N from headwater streams is between 40–65% of the total N flux to lower order streams. Numerous studies have illustrated correlations between water quality or ecological conditions and various measures of the extent of urbanization, such as human population density or percent impervious surface (Hachmoller et al., 1991; Charbonneau and Kondolf, 1993; Johnson et al., 1997; Thorne et al., 2000; Alberti et al., 2007; see additional discussion of urbanization in Annex C). In many higher order streams and estuaries, atmospheric N combines with fertilizer N in agricultural areas and with N from wastewater treatment facilities in urban areas, and the role of atmospheric deposition in residential and urban ecosystems is rarely addressed (see Section 3.3.2.4 for additional discussion of inputs to estuaries).

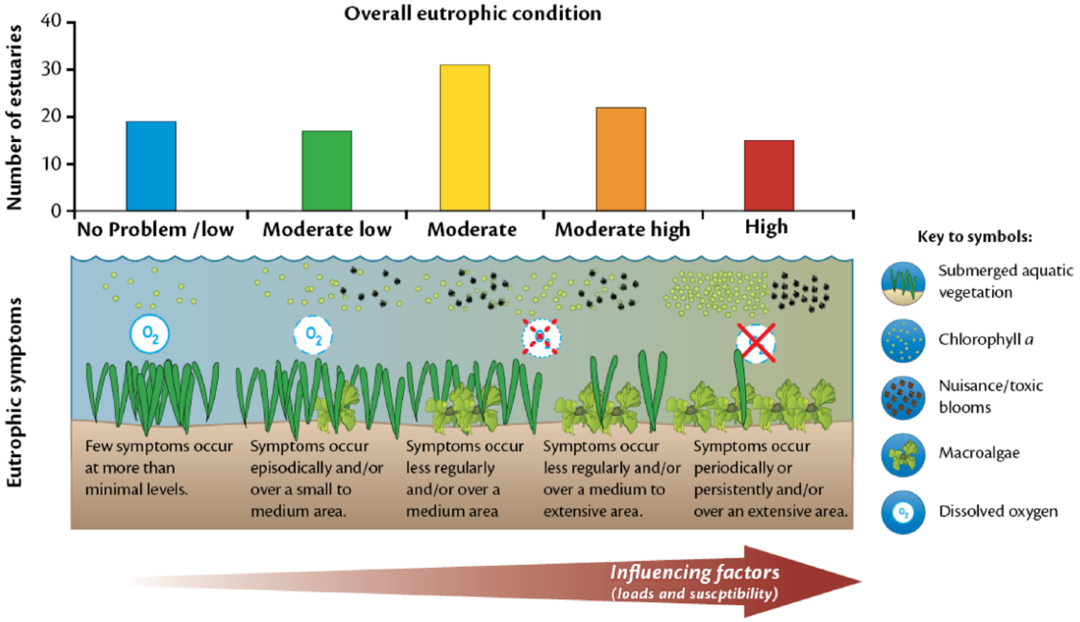
In lowland areas, other terrestrial sources of N, such as fertilizer, livestock waste, septic effluent, and wastewater treatment plant outflow, are often become much more important than in upland areas. In lowland areas, it is difficult to determine the percent of atmospheric N that leaches to drainage water because there are other ill-defined sources of N to drainage waters. In Table 3-14 studies are summarized that address how atmospheric deposition of N to the estuary surfaces and to the terrestrial watershed interact with the other anthropogenic sources of N to make up the total anthropogenic N load to the system.

Table 3-14. Summary of N deposition effects on leaching in freshwater aquatic ecosystems.

Region/Country	Endpoint	Observations	Ecosystem Type/ Species	Reference
New England	N sources in rivers and streams	Modeling: Application of the statistical model SPARROW (SPAtially Referenced Regression On Watershed attributes) showed that first-order headwaters contributed 65%, 55%, and 40% of the N flux to 2nd, 4th, and higher-ordered catchments, respectively. Atmospheric deposition accounted for almost 70% of the total simulated N load to these headwater streams.	Rivers	Alexander et al. (2002, 2007)
Neuse Estuary, NC	water [N] N sources	Observational: trends in N and P concentrations from 1998 to 2002 could be explained mainly by a combination of climate, management policies, and urban/agricultural development. Nutrient loading reductions did occur in response to imposed management practices in the watershed, but they were affected by increases in human and livestock population in the watershed. Thus, goals for estuarine and coastal nutrient loading reduction must consider the influence of within-watershed development	Watershed/ estuary	Burkholder et al. (2006)
Chesapeake Bay system	Watershed N sources	Modeling: The Choptank tributary of the Chesapeake Bay had become eutrophic over the last 50–100 years. Systematic monitoring of nutrient inputs began in 1970, and there have been 2–5–fold increases in nitrogen (N) and P inputs during 1970–2004 due to sewage discharges, fertilizer applications, atmospheric deposition, and changes in land use. Hydrochemical modeling and land-use yield coefficients suggest that current input rates are 4– 20 times higher for N and P than under forested conditions existing 350 yr ago. The Choptank watershed (1756 km^2) is dominated by agricultural land use (62%), with only 5% urban development. O_2 concentration in bottom waters of the Patuxent estuary is consistently below 3 mg/L in summer; O_2 levels have been steadily decreasing in the Choptank estuary over the past two decades and now approach 3 mg/L in wet years	Watershed/ estuary	Fisher et al. (Fisher, 1998) 2006
Chesapeake Bay system	Watershed N sources	Modeling: The Patuxent watershed (2260 km^2) is dominated by forest (64%), with significant urban land use coverage (16%) and less intensive agricultural development (20%). Sewage is a major cause of nutrient enrichment. The low N: P of sewage inputs to the Patuxent results in an N-limited, P-saturated system, whereas the Choptank is primarily limited by N, but with P limitation of phytoplankton during spring river flows. Reduced eutrophication in dry years suggests that both estuaries will respond to significant decreases in nutrients	Watershed/ estuary	Fisher et al. (Fisher, 1998), 2006

3.3.2.4. Estuarine and Coastal Marine Ecosystems

Estuaries and coastal marine environments tend to be N-limited, and many currently receive high levels of N input from human activities (Vitousek, 1991; Howarth, 1996). The nature and extent of the impacts on estuarine and coastal environments is, in part, related to the export of N from upland systems to coastal environments, as discussed in previous sections. Denitrification is the primary mechanism of N output from the estuary and back to the atmosphere (See Annex C). Important environmental effects include increased algal blooms, depletion of dissolved O_2 in bottom waters, and reduction in fisheries and sea grass habitats (Valiela and Costa, 1988; Valiela et al., 1990; Boynton et al., 1995; Paerl, 1995, 1997; Howarth, 1996). The general process of estuarine eutrophication is depicted in Figure 3-33.



Source: Bricker et al. (2007)

Figure 3-33. A conceptualization of the relationship between overall eutrophic conditions, associated eutrophic symptoms, and influencing factors (N loads and susceptibility). Overall eutrophic condition was assessed for estuaries throughout the U.S.

There is broad scientific consensus that N-driven eutrophication of shallow estuaries in the U.S. has increased over the past several decades and that environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl, 2001). For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer, 1984) Pamlico estuary in North Carolina (Paerl et al., 1998), and along the continental shelf adjacent to the Mississippi and Atchafalaya River discharges to the Gulf of Mexico (Eadie et al., 1994). A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions (Bricker, 2007). Estuaries with high overall eutrophic conditions were generally those that received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker, 2007). The relative importance of the various N sources varies from estuary to estuary. Atmospheric sources are proportionately more important to estuaries that exhibit large surface area relative to watershed drainage area, and in those estuaries that drain watersheds dominated by natural ecosystems rather than agricultural or urban lands (Boyer et al., 2002).

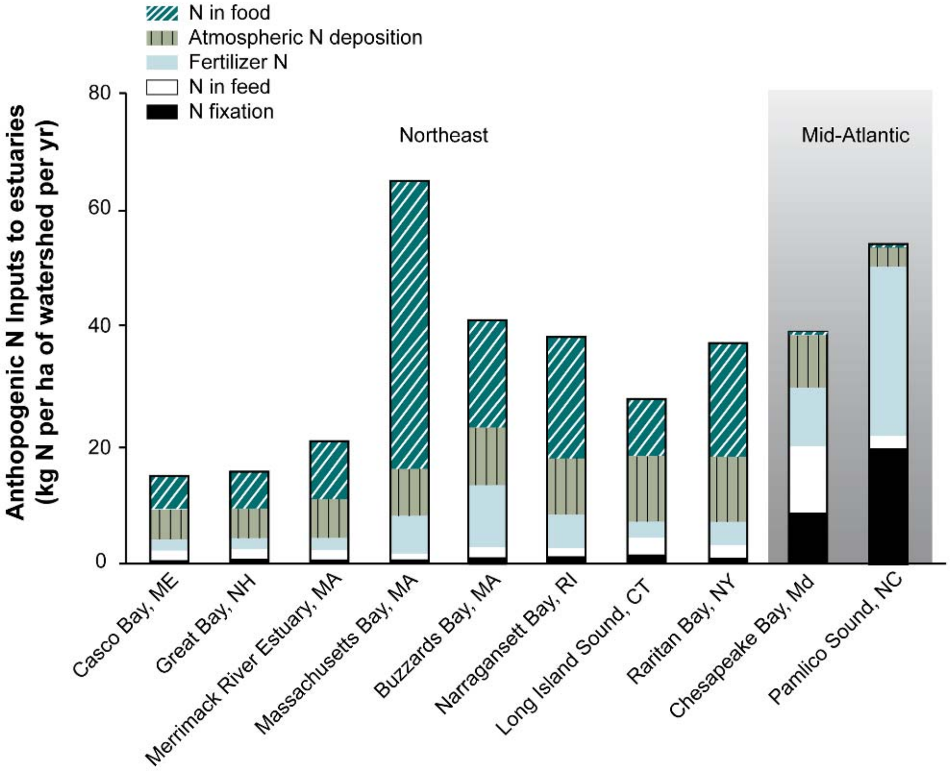
Assessing the contribution of atmospheric N_r deposition to total N_r loading

In the estuaries and coastal ecosystems in the U.S. that experience varying levels of N over-enrichment, the importance of atmospheric deposition as a cause of eutrophication is determined by the relative contribution of atmospheric versus non-atmospheric sources of N input.

Anthropogenic sources of N to estuarine and coastal ecosystems include atmospheric deposition, wastewater discharge, agricultural runoff, and urban runoff. Valigura et al. (2000) estimated that direct atmospheric deposition to the estuary surface generally constitutes at least 20% of the total N load for estuaries that occupy more than 20% of their watershed. EPA (1999b) estimated that between 10% and 40% of the total N input to estuaries in the U.S. is typically derived from atmospheric deposition. NRC (2000) concluded that EPA (1999a) underestimated the importance of atmospheric deposition as a contributor to the total N load.

Estimates of the relative contribution of each major source have been developed by using the Watershed Assessment Tool for Evaluating Reduction Scenarios for Nitrogen (WATERS-N) model (Castro, 2002; Castro, 2002). Driscoll et al. (Driscoll, 2003) estimated annual net anthropogenic N inputs to eight large watersheds in the Northeast for the year 1997. Input values of total atmospheric plus non-atmospheric anthropogenic N ranged from 14 kg N/ha/yr in the watershed of Casco Bay in Maine to 68 kg N/ha/yr in the watershed of Massachusetts Bay (Driscoll, 2003). In all eight watersheds, net import of N in food for humans (input into estuaries as wastewater) was the largest anthropogenic input. Atmospheric deposition was estimated to be the second largest anthropogenic N input, ranging from 5 to 10 kg N/ha/yr, or 11% to 36% of the total inputs, with four watersheds ranging from 34% to 36% (Driscoll, 2003). These results are broadly consistent with estimates by Boyer et al. (2002), who used a similar N budgeting approach for 16 large northeastern U.S. river basins and reported that N deposition contributes approximately 31% of the total N load to large river basins, although this fraction varies regionally (Boyer et al., 2002). Boyer et al. (2002) considered only the portions of each basin above USGS gauging stations, which often occurred above large population centers. Hence, the Driscoll et al. (Driscoll, 2003) budgets included regions with greater human food consumption than those considered by Boyer et al. (2002).

Castro and Driscoll (2002) studied 10 estuaries along the U.S. east coast and found total atmospheric N inputs (watershed runoff plus direct deposition to the surface of estuary) accounted for 15–42% of the total N inputs. Simulated reductions of atmospheric N deposition by 25% and 50% of current deposition rates reduced the contribution made by atmospheric N deposition to the total N loads by 1–6% and 2–11%, respectively. Overall, results from the simulated reductions suggested that considerable reductions (> 25%) in atmospheric N deposition were needed to significantly reduce the contribution made by atmospheric N deposition to the total N loads. In a later study, Driscoll et al. (Driscoll, 2003) estimated that the implementation of aggressive controls on both mobile N emissions sources and electric utilities would produce an estimated reduction in estuarine loading in Casco Bay, ME of 13% (Driscoll, 2003).



Source: Driscoll et al. (Driscoll, 2003)

Figure 3-34. Estimated anthropogenic N inputs to the estuaries of the northeastern U.S., in kg/ha/yr.

One the challenges in determining the contribution of atmospheric N deposition to estuaries is estimating the inputs from upstream river basins. Smith et al. (1997) applied the SPAtially Referenced Regressions on Watershed Attributes (SPARROW) model to streamwater chemistry data from the National Stream Quality Accounting Network in order to evaluate NO_3^- leaching in large river basins. Leaching losses of N in large river systems provide important sources of N to estuaries and coastal marine waters. Smith et al. (1997) concluded that much of the U.S. probably exports less than 5 kg N/ha/yr, but that N export in watersheds of the northeastern U.S. is probably higher. For the watersheds that export more than 10 kg N/ha/yr, Smith et al. (1997) concluded that fertilizer was the largest source of N (48%), followed by atmospheric deposition (18%). In this analysis, fertilizer used for human food production was considered to be the ultimate source of N contributed to waterways through waste water treatment plants. If the analysis of N sources to estuarine water is restricted to only nonpoint sources of N, atmospheric deposition is often considered to be the largest individual source ((Howarth, 1996; Jaworski, 1997)Smith et al., 1997; NRC, 2000; Howarth, 2007).

Overall, these estimates of the relative importance of atmospheric deposition, compared to non-atmospheric sources of N, typically involve many assumptions regarding dry deposition, riverine fluxes, and the relationship between human populations and wastewater inputs. Thus, such estimates entail considerable uncertainty. It is clear, however, that the relative contribution of atmospheric deposition to total N loading varies with the atmospheric N deposition level, land use, watershed and estuary areas, and hydrological and morphological estuarine characteristics. It is also clear that atmospheric deposition is generally an important contributor to the overall N load that stimulates eutrophication of estuaries in the eastern U.S. (Paerl, 2001; Boyer et al., 2002; Driscoll, 2003). See Annex C for an additional discussion of estuarine N budgets.

3.3.2.5. Summary of N_r Effects on Biogeochemical Cycling of N and Associated Chemical Indicators

Terrestrial Ecosystems

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of N in terrestrial ecosystems. The main source of new N_r to ecosystems is atmospheric deposition. N_r deposition disrupts the nutrient balance of ecosystem. The chemical indicators that are typically measured are summarized in Table 3-11 and include: NO_3 leaching, C:N ratio, N mineralization, nitrification, denitrification, foliar N and soil water NO_3^- and NH_4^+. Values for these indicators that represent a threshold for the onset of a related biogeochemical or biological effect are also summarized. Note that N saturation does not need to occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation is a plausible mechanism of net nitrification and associated NO_3^- leaching in drainage water. Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (see Section 3.2) and deplete soils of nutrient base cations, especially Ca and Mg (Likens, 1998).

Aber et al. (2003) suggested that nearly all N deposition is retained or denitrified in northeastern watersheds that receive less than about 8 to 10 kg N/ha/yr. Aber et al. (2003) further found that surface water NO_3^- concentrations exceeded 1 μeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition (see Section 0). The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition (see Section 3.3.2.4) (Aber, 2003).

Wetlands

The evidence is sufficient to infer a casual relationship between N_r deposition and the alteration of biogeochemical cycling of N in wetlands. N_r deposition contributes to total N load in wetlands. The chemical indicators that are typically measured include: NO_3 leaching, N mineralization, and denitrification. N dynamics in wetland ecosystems are variable in time and with type of wetland and environmental factors, especially water availability (Howarth, 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito, 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands (Devito, 1989; Koerselman, 1993) Arheimer and Wittgren, 1994; Mitchell, 1996).

N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). In general, leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. Previous studies suggest that elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg and Brezonik, 1983; Broderick et al., 1988; Cooper, 1990). This process limits environmental effects that are typically associated with increased N supply to soils and drainage waters; but increases the contribution of greenhouse gasses to the atmosphere. Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

Freshwater aquatic

The evidence is sufficient to infer a casual relationship between Nr deposition and the alteration of biogeochemical cycling of N in freshwater ecosystems. N_r deposition is the main source of N to headwater streams, higher order streams and high elevation lakes. The predominant chemical indicator is NO_3^- concentration in surface waters. Recent evidence documents examples of lakes and streams that are limited by N and show symptoms of eutrophication in response to N addition. Elevated surface water NO_3^- concentrations occur in both the eastern and western U.S.

Estuaries and coastal marine

The reviewed evidence is sufficient to infer a casual relationship between N_r deposition and the biogeochemical cycling of N in estuaries and coastal marine waters. The contribution of atmospheric N_r deposition to total N load is calculated for some estuaries and can be greater than

40%. It is unknown if atmospheric deposition alone is sufficient to cause eutrophication. In general, estuaries tend to be N-limited, and many currently receive high levels of N input from human activities to cause eutrophication (Vitousek, 1991; Howarth, 1996). The most widespread chemical indicator of eutrophication is dissolved O_2.

3.3.3. N Deposition Effects on Productivity and C Budgets

3.3.3.1. Terrestrial Ecosystems

The following section discusses the mechanisms by which atmospheric N deposition alters C cycling in terrestrial ecosystems. Although predicted values of atmospheric [CO_2] in the future may alter the interaction between N and terrestrial C cycling (Hyvönen, 2007);Norby et al. 1988; Schindler and Bayley 1993), this topic is beyond the scope this review.

Because N availability often limits rates of net primary production in temperate terrestrial ecosystems (Vitousek, 1991, there is an implicit link between the C and N cycles (Figure 3-35). Over 50% of plant N is used for photosynthetic enzymes. Because N is necessary for photosynthesis, rates of photosynthesis and net primary productivity (NPP) typically correlate with metrics of N availability such as leaf N content and net N mineralization rate (Field, 1986) ; Reich et al., 1997a, b; Smith et al., 2002). A meta-analysis of 126 N addition experiments evaluated N limitation of NPP in terrestrial ecosystems by evaluating aboveground plant growth in fertilized to control plots (LeBauer, 2008). The results showed that most ecosystems are N limited with an average 29% growth response to N. The response ratio was significant within temperate forests, tropical forests, temperate grasslands, tropical grasslands, wetlands, and tundra, but not deserts (LeBauer, 2008).

However, it can be difficult to directly apply the results of fertilizer studies to the question of chronic N deposition effects on ecosystems. Most fertilization studies do not mimic the long-term N loading profile of atmospheric N additions. Most studies add N in a large pulse at one time, rather than chronic N loads of smaller amounts over time as are delivered by atmospheric deposition. Ecosystem growth response to a pulse of 100 kg N/ha at one time may not the be same as 10 kg N/ha/yr for 10 years, although the net load is the same. In addition, climate, ozone and even atmospheric CO_2 concentrations can also affect ecosystem C dynamics (Ollinger, 2002) Nowak et al. 2003).

Unfortunately, few studies have isolated the effect of chronic N deposition on plant growth and ecosystem C balances. It is difficult to untangle the effects of climate, disease and land use from N deposition effects. Therefore to address this question, we rely on fertilization studies, modeling, gradient studies, and time-trend analyses.

Carbon accumulation in terrestrial ecosystems occurs in the plants and in the soil. C cycling is a complex process that can be quantified into ecosystem C budgets on the basis of net ecosystem productivity (NEP), defined as gross primary productivity (GPP) after subtracting the ecosystem respiration (vegetative + heterotrophic respiration). Factors that may increase terrestrial CO_2 sinks on a regional scale are increased NPP, and decreased respiration of CO_2 from leaf or soil processes. These two mechanisms may be altered by atmospheric deposition of N, tropospheric ozone exposure, increased CO_2 concentrations, land-use change and factors associated with climate warming (Myneni et al., 1997; Melillo et al., 2002, Beedlow et al. 2004, Schimel et al. 2001, Caspersen et al. 2001). This adds to the uncertainty regarding the sources and sinks in the terrestrial biosphere (Houghton 2003). It should be noted that it is not known whether present terrestrial C sequestration can be sustained, in view of limits of forest re-growth, nutrient availability and uncertainty about changes in the frequency of disturbances such as fire (Scholes and Noble 2001; Schimel et al. 2001).

Forests

C Allocation Interactions with Stressors

Addition of N_r is believed to decrease resistance to drought stress because plants balance their allocations of sunlight and nutrients in order to grow above ground to maximize light and C capture and to grow below ground to maximize capture of water and other nutrients, including N (Sterner and Elser, 2002). Fertilization with N often causes trees to allocate less photosynthate to roots than shoots (Minnich et al., 1995). Because shoot growth is more enhanced than root growth, the water supply from the roots can become insufficient during periods of drought to support water loss via transpiration (Fangmeier et al., 1994; Krupa, 2003). Smaller root systems also cause greater susceptibility to windthrow. For example, in Switzerland, the amount of trees uprooting during a strong storm event was significantly correlated with base saturation and N concentration in the leaves (positively) in Beech trees (Braun et al. 2003). Across Europe, soil acidification and soil N content since the 1980s have accentuated the storm sensitivity due to changes in root architecture, including more superficial roots and loss of root ramification (Nilsson et al. 2004; Godbold et al., 2003; Puhe, 2003; Braun, 2003).

Deposition of N_r is also believed to reduce frost hardiness of plants (Dueck et al., 1990). This is likely because the addition of N_r prolongs the growth phase of the plants during autumn and delays winter hardiness. This can cause detrimental effects if the first frost occurs early in the autumn period (Cape et al., 1991). Plant shoots also appear to be more susceptible to pathogenic fungal infection under high N status or changed nutrient balance such as an increase in the ratio of N to K^+ (Ylimartimo, 1991; Krupa, 2003). As opposed to shoot diseases, addition of N_r has been found to reduce mycorrhizal fungus colonization of roots (see more detailed discussion in Section 3.3.5.1).

Above-ground processes

There is substantial evidence that N additions to trees cause increased leaf-level photosynthetic rates. However, the potential for N deposition to increase above-ground C biomass it is limited for reasons related to the biogeochemical cycling of N (see more detailed discussion in Section 3.3.2.1). Briefly, C:N stoichiometry of the forest ecosystem compartments determines the C response to N deposition. Only a small portion of added N is taken up by vegetation, thus only a small portion of N contributes to C capture by trees (Nadelhoffer et al., 1999). A recent study reported that tree biomass (e.g., foliage, woody tissue, and fine roots) accumulated 7 to 16% of N additions (Nadelhoffer et al., 2004). N may be immobilized in the soil, leached out before biological assimilation, or, upon the addition of N, some other factor may become limiting to growth (e.g., water or other nutrients). Even though only a portion of N deposition is incorporated into vegetation, the general result of additional N is an increase in leaves, wood, and root biomass (Nilsson and Wiklund, 1995).

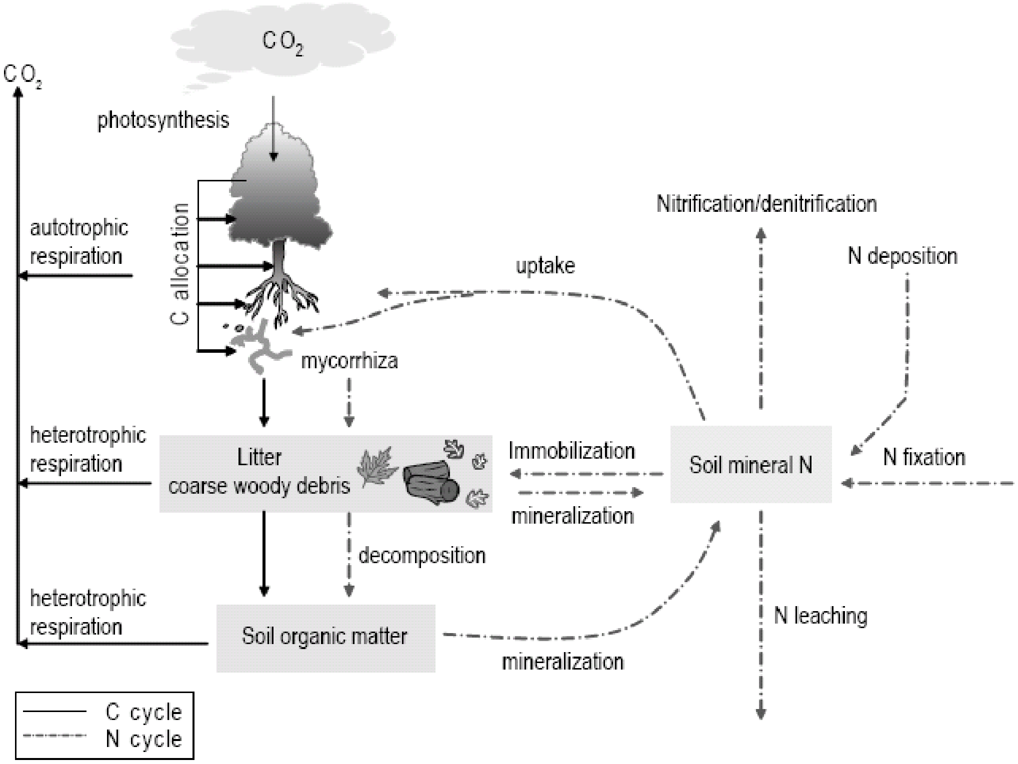


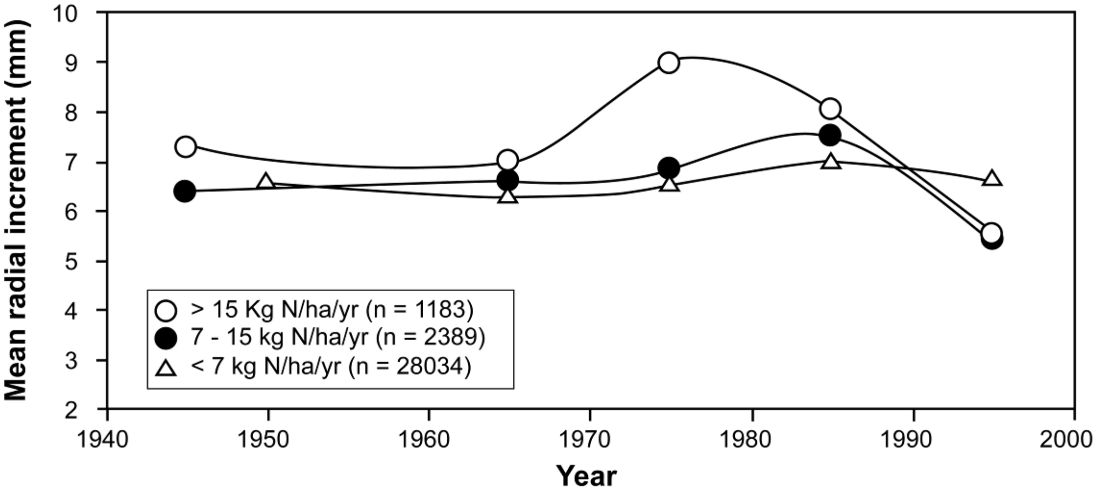
Figure 3-35. Interactions between the carbon and N cycles.

Table 3-15. Summary of N effects on forest carbon cycling.

Region/Country	Endpoint	Observations	Forest type/ species	Reference
Europe	forest Biomass	Modeling: using growing stock of large forest regions over an entire country as empirical data, the authors determine forest biomass is accumulating, largely in response to increases in forest area and improved management, but other possible mechanisms of growth enhancement (including N) cannot be ruled out	Forests from Austria, Finland, Sweden, France, Germany , and Switzerland	Kauppi et al., 1992; Spiecker et al., 1996
Norway	growth (tree ring increments)	Deposition gradient: A comprehensive analyses of regional forest growth trends analyzed tree increment cores from more than 31,000 plots. In this study, growth increased during the 1960s and 1970s and then declined in the 1990s, especially in southern regions exposed to the highest rates of N deposition	boreal forest (*Picea abies* and *Pinus sylvestris*)	Nellemann and Thomsen, 2001
Sweden	growth (stem volume)	Field addition: chronic fertilization at 30 kg N/ha/yr continued to stimulate stemwood production even after 30 years, whereas a higher application (90 kg N/ha/yr) decreased stem volume growth, and an intermediate application (60 kg N/ha/yr) had little positive or negative effect relative to the control plots	Boreal forest Scots pine forest	Högberg et al., 2006
Bear Brook, ME, U.S.	growth (basal area)	Field Addition: basal area increment of sugar maple was enhanced 13 to 104% by addition of 25 kg N/ha/yr as ammonium SO_4^{2-} ($(NH_4)_2SO_4$), whereas red spruce was not significantly affected.	sugar maple and red spruce	Elvir et al., 2003
Fernow Experimental Forest, WV, U.S.	growth	Field addition: The application of 35 kg N/ha/yr as $(NH_4)_2SO_4$ enhanced growth of (Prunus serotina) and yellow poplar (Liriodendron tulipifera) during the first 7 years, but led to reduced growth of these species relative to control trees in years 9 through 12, with no change in red maple or sweet birch (Betula lenta)	black cherry, yellow poplar, red maple, sweet birch	DeWalle et al., 2006
Harvard Forest, MA, U.S.	mortality	Field addition: chronic N addition levels of 50 and 150 kg N/ha/yr for 15 years caused a 31% and 54% decrease, respectively, in red pine growth. As red pine has died, striped maple (Acer pensylvanicum), black cherry, and black birch (Betula lenta) have increased their contributions to annual litterfall production.	red pine, striped maple, black cherry, black birch	Magill et al., 2004
northeastern U.S.	live basal area	Field addition: In a high-elevation red spruce-balsam fir (Abies balsamea) forest in the, N fertilization over 14 years led to a decrease in live basal area (LBA) with increasing N additions. In control plots, LBA increased by 9% over the course of the study, while LBA decreased by 18% and 40% in plots treated, respectively, with 15.7 kg N/ha/yr and 31.4 kg N/ha/yr.	red spruce-balsam fir	(McNulty et al., 2005)
Harvard Forest, MA, U.S.	growth mortality root production	Field addition: N fertilization of a 50–year-old red-oak/red maple stand largely stimulated productivity, although the drought in 1995 induced significant mortality in small red maple trees. Fine root biomass was slightly, but not significantly, lower in highly fertilized stands relative to controls in both red pine and oak/maple ecosystems	old red-oak, red maple	Magill et al., 2004
Ysselsteyn, The Netherlands	growth root production	Field addition and deposition exclusion: improvements in wood accumulation rate, root production, and mycorrhizal associations occurred when a “clean roof” was installed at the site receiving the highest rate of N deposition (>40 kg N/ha/yr). Decreased production of fine roots may predispose N-fertilized plants to be more sensitive to intermittent drought, as well as to nutrient depletion exacerbated by acid deposition.	Coniferous- *Picea abies*, *Picea sitchesis*, *Pseudotsuga menziesii*, *Pinus sylvestris*	Boxman et al., 1998b Emmett et al. (Emmett, 1998)
Southern CA, U.S.	N- saturation-reduced soil base saturation, and lack of a growth response	Observational: Areas of chaparral and mixed conifer forests that receive very high levels of dry N deposition in southern California have experienced significant environmental change over the past several decades	chaparral and mixed conifer	Fenn et al., 1996, 2003a
CA, U.S.	Growth	Observational: Some southern California forests experience N deposition up to 45 kg N/ha/yr, and that increased N deposition caused increased growth of Jeffrey and ponderosa pine stands.	mixed conifers; jeffrey and ponderosa pine	Takemoto et al., 2001
CA, U.S.	growth (productivity) and mortality	Observational: high inputs of reactive N appear to exhibit decreases in productivity and increases in mortality (Fenn, 1998).	Conifer forests	(Fenn, 1998)
California	litter accumulation, above-ground woody biomass, fire susceptibility	Field addition: N fertilization has been shown to cause increased litter accumulation and C storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires.	Ponderosa pine	Fenn et al., 2003a
California	growth	increased N deposition caused increased growth for Jeffrey (*Pinus jeffreyi*) and ponderosa pine (*Pinus ponderosa*) stands,	mixed conifers	Takemoto et al. (Takemoto, 2001)
North Carolina and Virginia	growth (basal area), foliar chemistry, nitrification and mineralization	Deposition gradient: Results from a study of 46 forest plots on six sites in North Carolina and Virginia dominated by American beech, sugar maple, and yellow birch suggested that N deposition is associated with changes in basal area, foliar chemistry, and nitrification and mineralization rates. Growth rates for the three tree species were similar at the lowest rates of N deposition, and then diverged as N deposition increased, with growth of yellow birch and American beech decreasing at the high N deposition loads. These differential growth rates have the potential to affect forest structure and biodiversity	American beech, sugar maple, and yellow birch	Boggs et al., 2005

Region/Country	Endpoint	Observations	Forest type/ species	Reference
California, Sequoia National Park	growth	Field addition: Aspen (Populus tremuloides) have been reported to show positive growth effects from fertilization at N deposition rates as low as 10 kg N/ha/yr	Aspen	Bytnerowicz (Bytnerowicz, 2002)
Michigan	ANPP and surface soil organic matter	Field addition: Chronic N fertilization (30 kg N/ha/yr) for 20 years caused significant increases in ANPP by 10% and surface soil organic matter (0–10 cm) by 26%	Sugar maple	Pregitzer et al. 2008

In order to understand the effects of added N to forest ecosystems, it is helpful to examine the results of modeling projects and experimental N additions. Experimental N additions to forest ecosystems have elicited positive growth responses in some, but certainly not all, organisms (Emmett, 1999; Elvir et al., 2003; DeWalle et al., 2006; Högberg et al., 2006). Forest growth enhancement, to the extent that it occurs, can potentially exacerbate other nutrient deficiencies, such as Ca, Mg, or K. Multiple long-term experiments have demonstrated transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006).



Source: Nellemann and Thomsen (2001)

Figure 3-36. Mean 5–year radial increment from 31,606 core samples from Picea abies during the period 1945 to 1996 for three atmospheric N deposition zones (high, medium, and low wet N-deposition in 1990), respectively. Note that the decline in radial increment after 1975 corresponds with the peak in exceedances for critical loads for the same areas. The increase and subsequent decline from 1965–1996 is significant ($p < 0.01$) using Kruskal-Wallis analysis with Dunn's tests. S.E.s are all below 5% or 1–3.5 mm increment.

Experimental N addition studies on forest ecosystems show a range of responses in terms of mortality and productivity. In general, moderate to high additions of N led to either no significant change in growth rates or transient growth increases followed by increased mortality, especially at higher rates of fertilization (Elvir et al., 2003; Magill et al., 2004; McNulty et al., 2005; Högberg et al., 2006; Table

3-15). An additional line of evidence comes from the experimental N removal studies: removal of N and S from throughfall increased tree growth in Europe (Beier et al., 1998; Boxman et al., 1998).

Decreased growth and increased mortality have more commonly been observed in high-elevation coniferous stands than in lower elevation hardwood forests, and these differences have been partially attributed to higher inputs of N at higher elevation and to response characteristics of coniferous, as opposed to deciduous, trees (Aber et al., 1998). Conifer forests that receive high inputs of N_r appear to exhibit decreases in productivity and increases in mortality (Fenn, 1998). For example, fertilization experiments at Mount Ascutney, VT suggested that N saturation may lead to the replacement of slow-growing spruce-fir forest stands by fast-growing deciduous forests that cycle N more rapidly (McNulty et al., 1996, 2005).

Below-ground processes

Soils contain the largest near-surface reservoir of terrestrial C, with more than 50% of C captured annually by plants may be allocated below ground (Kubiske and Godbold, 2001). Therefore, understanding the factors that control soil C storage and turnover is essential for understanding the C cycle and sequestration. Although there remains considerable uncertainty in the potential response of soil C to increases in reactive N additions (Neff et al., 2002), a meta-analysis by Johnson and Curtis (2001) suggested that N fertilization caused an 18% increase in soil carbon content.

There is also evidence of a relationship between N deposition and root production Nadelhoffer (2000) argued that it is likely that N deposition functions to decrease forest fine-root biomass but to stimulate fine-root turnover and production. However, very high levels of N (> 100 kg N/ha/yr) decreased root life span of *Pinus ponderosa* (Johnson et al., 2000).

Litter fall is usually the dominant source of soil organic C and a substantial source of organic N. Decomposition of litter fall is often facilitated by heterotrophic bacteria and mycorrhizae. The quantity of litter has been shown to increase with elevated N deposition (Schulze et al., 2000), with the result of increased microbial metabolism in soil. It is also well demonstrated that increased N availability reduces the ratio of C:N in leaf tissue. In turn, lower C:N in leaf litter has been shown to cause faster initial rates of decomposition (Melillo et al., 1982), however the biochemistry of the leaf tissue is also important and higher N litter can actually decompose more slowly in the long-term (Berg 2000). Under higher decomposition rates, N bound by leaf organic matter is released over a shorter period and lead to lower N retention by the soil (De vries 2006). A 10–year experiment that investigated decomposition in 21 sites from 7 biomes found net N release from leaf litter is predominantly driven by the initial N concentration and mass remaining regardless of climate, edaphic conditions, or biota (Parton et al., 2007). A recent meta-analysis by Knorr et al. (2005) indicated that, as expected, litter decomposition was stimulated by additional N deposition, however only at sites with low ambient N deposition (< 5 kg N/ha/yr).

Additional N deposition reduced decomposition at sites with moderate levels of N deposition (5 to 10 kg N/ha/yr).

Soil respiration is the dominant source by which plant-assimilated C is returned to the atmosphere via CO_2. Changes in the magnitude of soil CO_2 efflux due to changes in environmental conditions will likely influence the global atmospheric CO_2 budget (Schlesinger and Andrews, 2000). The effects of N addition on soil respiration are mixed; reductions at high levels of N (Lu, 1998, Bowden et al., 2004), no effect (Vose et al., 1995), and increases (Griffin et al., 1997; Mikan et al., 2000) all have been observed. At the Harvard Forest LTER Site Chronic Nitrogen Amendment Study, N additions increased soil respiration for hardwood stand, but not for pine stand during the first year of fertilization. However, continued N additions over a decade caused a 40% decrease in soil respiration for both stands and that was attributed mostly to a decrease in microbial respiration (Bowden et al., 2004).

Regional Trends in NEP and NEE

An analysis of > 100 young and mature forest stands from around the world indicated that annual values of CO_2 exchange varied from approximately −100 to 250 g C/m^2/yr for boreal forests and 250 to 700 g C/m^2/yr for temperate forests (Malhi et al., 1999). Net ecosystem exchange (NEE), defined as the difference between NPP and heterotrophic respiration, was positive when the forest was a sink that took up CO_2. Townsend et al. (1996) and Holland et al. (1997) modeled the impact of NO_Y and NH_X deposition on ecosystem C budgets by combining estimates of emissions with three dimensional transport models. They used spatially explicit estimates of N inputs and climate data as drivers for a process-based biogeochemical model to simulate ecosystem C dynamics globally. Their simulations predicted that CO_{2}–C uptake due to NO_Y deposition on land surfaces ranged from 0.3 to 1.4 Pg C uptake/yr (Townsend et al., 1996; Holland et al., 1997; Holland and Lamarque, 1997). The model allowed for variations in the degree of ecosystem N retention. The highest C uptake was calculated when trees were assumed to uptake 80% of N inputs, which is a likely overestimation because field studies suggested trees only took up a small portion (7–16%) of N deposition.

Analyses of satellite observations of canopy greenness over the last 20 years across North America suggests enhancement of NEP in some regions, corresponding to observed changes in climate and forest management. Few such changes were observed in the northeastern U.S., where rates of N deposition are relatively high (Hicke et al., 2002). In another study, evaluation of tree growth rates in five states (Minnesota, Michigan, Virginia, North Carolina, and Florida) found little evidence for growth enhancement due to any factor examined, including N deposition, carbon dioxide (CO_2) fertilization, or climate change (Caspersen et al., 2000). Potential effects of N deposition on boreal forests of North America are of concern in part due to the large size of this terrestrial biome. Climate warming and N deposition may increase NPP and C sequestration in the boreal forest, but may also stimulate decomposition of soil organic matter, potentially leading to a net loss of C from the ecosystem (Kirschbaum, 1994; Mäkipää et al., 1999).

A recent European study suggested that N deposition increased forest growth (Magnani, 2007), but these findings have been disputed. Magnani et al. (Magnani, 2007) reported a strong correlation between estimated average long-term NEP and estimated 1990 wet N deposition (Holland et al. 2005) for 20 forest stands mostly in western Europe and the conterminous U.S. The authors reported that when confounding effects of disturbance were factored out, carbon sequestration was found to be increased by moderate N deposition (estimated up to 9.8 kg N/ha/yr). However, this study did not evaluate forest stands that receive higher levels of N deposition that may be showing negative symptoms of N saturation. Several responses to this study have been critical of the methods and conclusions have been published (De Schrijver et al 2008, De Vries et al. 2008, Sutton et al. 2008). For example, Sutton et al. (2008) re-analyzed the data from Magnani et al. (Magnani, 2007) and concluded the NEP response to N response reported by Magnani et al. (2008) was implausibly high (725 kg C/wet-deposited N). After considering the uncertainties in wet and dry N deposition and climate variability, Sutton et al. (2008) reported the estimated NEP response to N deposition was 68 kg C/ deposited N. Sutton et al (2008) concluded that N deposition remains an important driver of NEP, but did not find support that the NEP was overwhelmingly driven by N deposition.

EPA conducted a meta-analysis of 17 observations from 9 studies in U.S. forests to examine the impact of N fertilization on forest ecosystem C content (EC). Here EC was defined as the sum of C content of vegetation, forest floor and soil (Johnson et al. 2006). To avoid possible confounded variability caused by site conditions, this meta-analysis only included studies of which control and treatment sites experienced same climatic, soil and vegetation conditions. Studies on N nutrient effects along a deposition gradient, such as Magnani et al. (Magnani, 2007), were not included. EPA's meta-analysis revealed that while there was a great deal of variation in response, overall N addition increased EC by 6% for U.S. forest ecosystems (see Figure 3-37). Different from Magnani et al. (Magnani, 2007), this study did not find any correlation between the amount of N addition and the response magnitudes of EC.

However, it is uncertain if short term C accumulation may lead to long term C sequestration. N fertilization could reduce the capacity of ecosystem to sequester decay resistant soil C. Giardina et al. (Giardina, 2004) found that although N fertilization significantly increased plant production, the C flux moving to mineral soil was reduced by 22% in a humid tropical forest in Hawaii. Mycorrhizal biomass comprises a substantial carbon pool – represent up to 15% of soil organic matter in some ecosystems (Vogt et al. 1982). A meta-analysis by (Treseder, 2004) suggested that mycorrhizal abundance decreased 15% under N fertilization.

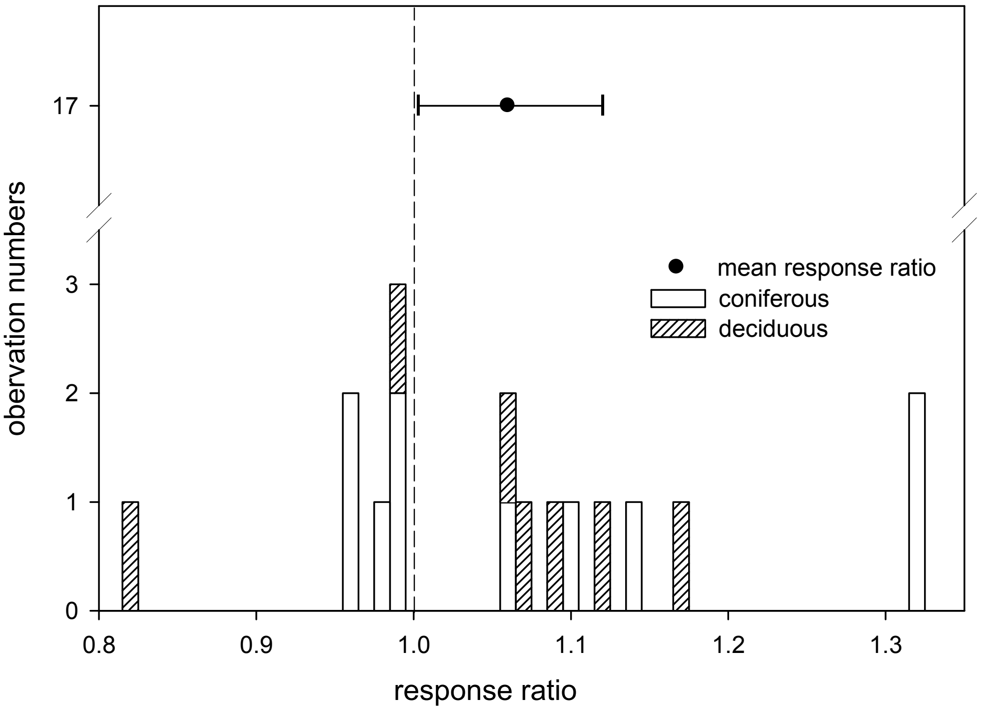


Figure 3-37. Effects of N addition on forest ecosystem C content. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.

Arctic Tundra

Arctic tundra is adapted to cold temperature, short growing season, high soil moisture, and periodically low soil O_2 level. In general, arctic tundra plants respond to reduced N availability by changing the allocation of biomass to favor root growth (Bloom, 1985) or changing the efficiency with which N is used or stored (Chapin, 1980).

Mack et al. (2004) examined C and N pools in a long-term fertilization experiment at the arctic Long-Term Ecological Research site near Toolik Lake, AK. Fertilized plots in moist acidic tundra received 10 g N and 5 g N/m^2/yr from 1981 to 2000. This is approximately 5 to 8 times the annual soil N uptake requirement for above-ground production in the ecosystem. Two decades of fertilization shifted community composition from graminoid tundra dominated by the tussock-forming sedge, *Eriophorum vaginatum*, to shrub tundra dominated by *Betula nana* (Shaver et al., 2001). Consequently, this greatly increased above-ground NPP, but had a larger effect on decomposition than on plant production, resulting in a net loss of almost 2,000 g C/m^2 from this ecosystem over 20 yr ($p < 0.04$). Carbon storage increased above ground because of the accumulation of woody shrub biomass and litter, but this was offset by a larger decrease of C in below-ground pools due to a pronounced decrease in the C contained in deep organic (> 5 cm depth) and upper mineral soil layers. This study clearly showed that increased nutrient availability enhanced decomposition of below-ground C pools in deep soil layers more than it increased primary production, leading to a substantial net loss of C from this ecosystem.

The key process responsible for the C loss was identified as increased deep soil C decomposition in response to increased nutrient availability. The authors noted that increasing temperatures may amplify these effects and further stimulate C losses from high-latitude systems. As temperature rises, the amount of N released due to a 3 to 7 EC increase in mean annual temperature (MAT) is likely to range in magnitude from 7 to 9.4 g N/m^2/yr, respectively (Mack et al., 2004). This will cause species shifts in the vegetation community from tussock to increased shrub abundance and lead to decreased ecosystem C storage. Finally, the decreased soil moisture and increased depth of thaw with temperatures rise are predicted to have a positive effect on decomposition (Shaver, 2001), releasing more CO_2.

Grasslands

Below-ground Factors

An investigation by Neff et al. (2002) of long-term effects (10 years) of N deposition (10 kg N/ha/yr) in a dry meadow ecosystem indicated that N additions significantly accelerated decomposition of soil C fractions with decadal turnover times while further stabilizing soil C compounds in mineral-associated fractions with multi-decadal to century lifetimes. Despite these changes in the dynamics of different soil pools, no significant changes in bulk soil C were observed, highlighting a limitation of the single-pool approach for investigating soil C responses to changing environmental conditions (Neff et al., 2002). The authors noted that it remains to be seen if the effects that were caused by relatively high, decadal-term fertilizer additions are similar to those which would arise from lower, longer-term additions of N to natural ecosystems from atmospheric deposition.

Interactions with Fire

Several lines of evidence suggest that N_r deposition may be contributing to greater fuel loads and thus altering the fire cycle in a variety of ecosystem types (Fenn et al., 2003a). Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations (D’Antonio and Vitousek, 1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of CSS to grassland in California (Minnich and Dezzani, 1998).

High grass biomass has also been associated with increased fire frequency in the Mohave Desert (Brooks, 1999; Brooks and Esque, 2002; Brooks et al., 2004). This effect is most pronounced at higher elevation, probably because the increased precipitation at higher elevation contributes to greater grass productivity. Increased N supply at lower elevation in arid lands can only increase productivity to the point at which moisture limitation prevents additional growth. Fire was relatively rare in the Mojave Desert until the past two decades, but now fire occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

3.3.3.2. Wetlands

Above-ground processes

The 1993 NOx AQCD showed that N applications, ranging from 7 to 3120 kg N/ha/yr, stimulated standing biomass production by 6–413% (U.S. EPA, 1993). However, the magnitude of the changes in primary production depended on soil N availability and limitation of other nutrients. The degree of N limitation to growth is varied among wetlands across the U.S. (Bedford, 1999).

The genus *Sphagnum* dominates ombrotrophic bogs and some nutrient poor fens in the Northern US and Canada. These mosses efficiently capture atmospheric deposition with retention rates between 50–90%, much of the variation due to the depth of the water Table (Aldous 2002a). Studies conducted on 4 species of Sphagnum in Maine (2 to 4 kg N/ha/yr ambient deposition) and New York (10 to 13 kg N/ha/yr ambient deposition) document that higher N deposition resulted in higher tissue N concentrations (Aldous 2001) and greater NPP (Aldous 2002a), but lower bulk density (Aldous 2002a). A study of *Sphagnum fuscum* in six Canadian peatlands showed a weak, although significant, negative correlation between NPP and N deposition when deposition levels were greater than 3 kg N/ha/yr ($y = 150 – 3.4x$, $p=0.04$, $R^2=0.01$) (Vitt et al. 2003). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition ($y = 2.84x +0.67$, $r^2 =0.32$, $P < 0.001$), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al. 2004).

Primary production of plant species from intertidal wetlands typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Mendelssohn 1979, Wigand et al. 2003, Tyler et al. 2007, Darby and Turner 2008). In comparison, N loads brought by tidal water and ground water (565–668 kg N/ha/yr) are much larger than N depositing directly to the surface of coastal marshes, which suggested that direct N deposition may have limited impacts on this ecosystem (Morris 1991). On the other hand, indirect atmospheric deposition that is N deposited to the watershed and transported via surface or ground water, could be the major sources of the total N load to coastal marshes. For example, model calculation suggested that the contribution from the atmosphere (36 million kg N/yr) was about 21–30% of the total N loading (170 million kg N/yr) in Chesapeake Bay waters (EPA 2000). Therefore 30% of the N delivered to wetlands via estuarine tides would originate from atmospheric deposition. Future studies are needed to determine the role of indirect atmospheric N deposition on the nutrient budget of intertidal wetlands.

Below-ground Processes

Bragazza et al. (2006) investigated the decomposition rates of recently formed litter peat samples collected in nine European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher carbon dioxide (CO_2) emissions and dissolved organic carbon release. The increased N availability favored microbial decomposition (i) by removing N constraints on microbial metabolism and (ii) through a chemical amelioration of litter peat quality with a positive feedback on microbial enzymatic activity. Although some uncertainty remains about whether decay-resistant Sphagnum will continue to dominate litter peat, the data indicated that, even without such changes, increased N deposition poses a serious risk to the valuable peatland C sinks.

Reduced vs. Oxidized N

The form of added N may regulate wetland response to N deposition. Experimental applications of NO_3^- appear to have been less effective at stimulating wetland plant productivity than applications of NH_4^+ (EPA, 1993). This may reflect higher rates of denitrification in response to the added NO_3^-, suggesting the importance of competition between plants and microbes for bioavailable N. Plants appear to compete more successfully for NH_4^+ and microbes to compete more successfully for NO_3^-. An important caveat expressed by U.S. EPA (1993), however, was that the results of relatively short-term N fertilization experiments are not necessarily good predictors of long-term wetland community responses to increased N inputs.

NEE of grassland, tundra and wetlands

In the meta-analysis of 16 observations from 9 publications on the relationship between N addition and C sequestration of non-forest ecosystems, N addition had no significant effect on NEE of non-forest ecosystems (Figure 3-38). N limitation to NPP is globally distributed and therefore plant productivity is normally enhanced by N addition. A meta-analysis by Lebauer and Treseder (LeBauer, 2008) indicated that N fertilization increased aboveground NPP (ANPP) in all non-forest ecosystems except for desert. However, N addition also has been observed to stimulate ecosystem C loss. For example, N fertilization stimulated soil organic carbon decomposition in arctic tundra. Increasing N deposition led to higher C loss in temperate peatlands (See Section 3.3.3.2). In an agricultural experiment site, Khan et al. (Khan, 2007) observed that 40 to 50 years N fertilization resulted in a net decline in soil C despite massive residue C incorporation. This meta-analysis indicated that N addition had no significant impact on C sequestration in non forest ecosystems, which may be due to C gain via NPP was exceeded by C loss via heterotrophic respiration.

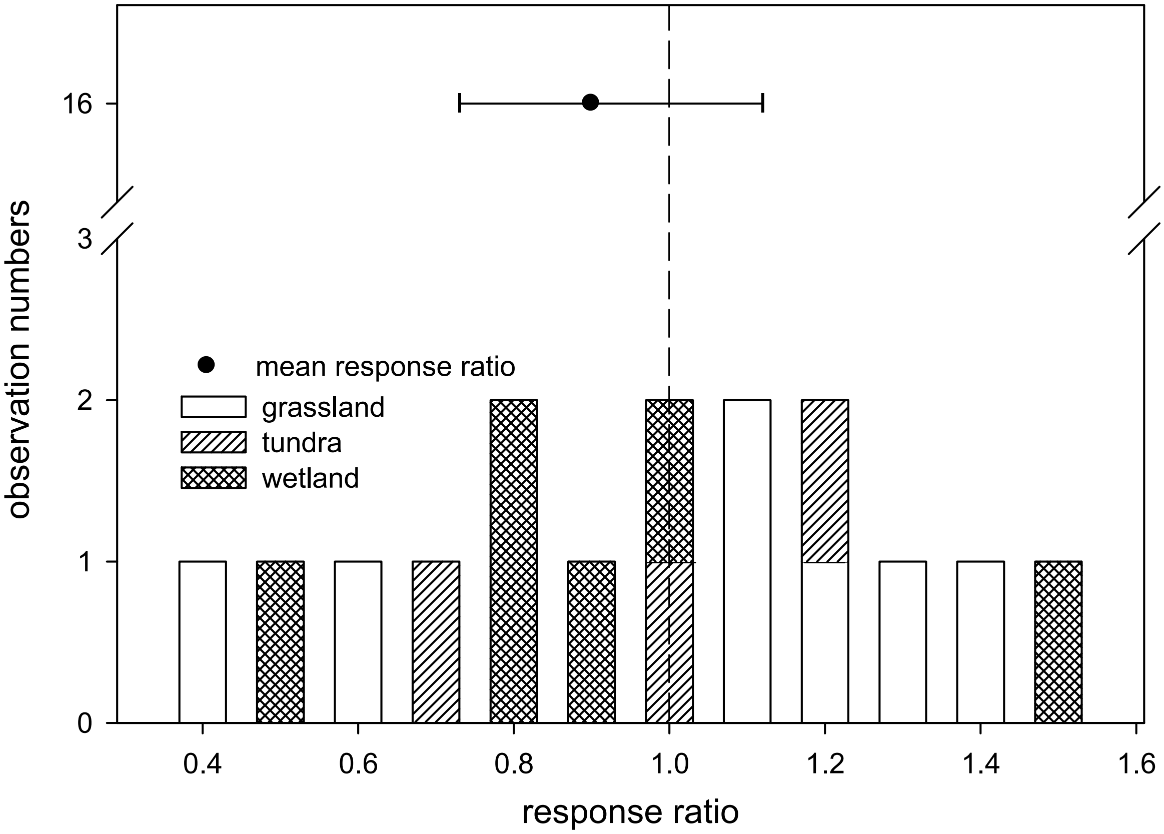


Figure 3-38. Effects of N addition on NEE of non-forest ecosystems. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.

3.3.3.3. Freshwater Aquatic

N deposition effects on productivity are discussed here. The biogeochemical cycles of N, P and C are linked in freshwater ecosystems (Figure 3-39), therefore N additions alter the balance of all three cycles. In N-limited aquatic systems, atmospheric inputs of N increase productivity and alter biological communities, especially phytoplankton. The results of numerous publications addressing the experimental additions of N are tabulated in Annex C. Evidence that altered productivity leads to altered community structure is discussed in Section 3.3.5.

Generally, the dose-response data for aquatic organisms such as those cited below are expressed in concentration units, as mg/L or µmol/L of N, for example. Such concentration data cannot be directly related to ecosystem exposure, which is generally expressed in such units as kg N/ha. This is because N deposition can result in widely varying concentrations of N compounds (especially NO_3^-) in water. For convenience, a concentration of 1 mg/L of N (as, for example, in the case of NO_3^--N or NH_4^+-N) is equal to 71.4 µmol/L or 71.4 µeq/L of NO_3^- or NH_4^+.

N-limitation

A freshwater lake or stream must be N-limited in order to be sensitive to N-mediated eutrophication. There are many examples of fresh waters that are N-limited or N and P co-limited (e.g., (Elser, 1990; Fenn et al., 2003a; Tank and Dodds, 2003; Bergström et al., 2005; Baron, 2006; Bergström and Jansson, 2006). Recently, a comprehensive study of available data from the northern hemisphere surveys of lake along gradients of N deposition show increased inorganic N concentration and productivity to be correlated with atmospheric N deposition (Bergström and Jansson, 2006). The results are unequivocal evidence of N limitation in lakes with low ambient inputs of N, and increased N concentrations in lakes receiving N solely from atmospheric N deposition (Bergström and Jansson, 2006). These authors suggested that the majority of lakes in the northern hemisphere may have originally been N-limited, and that atmospheric N deposition has changed the balance of N and P in lakes so that P-limitation is generally observed today. If this is correct, the role of atmospheric N deposition as an influence on aquatic primary production may have been underestimated throughout the entire history of limnology.

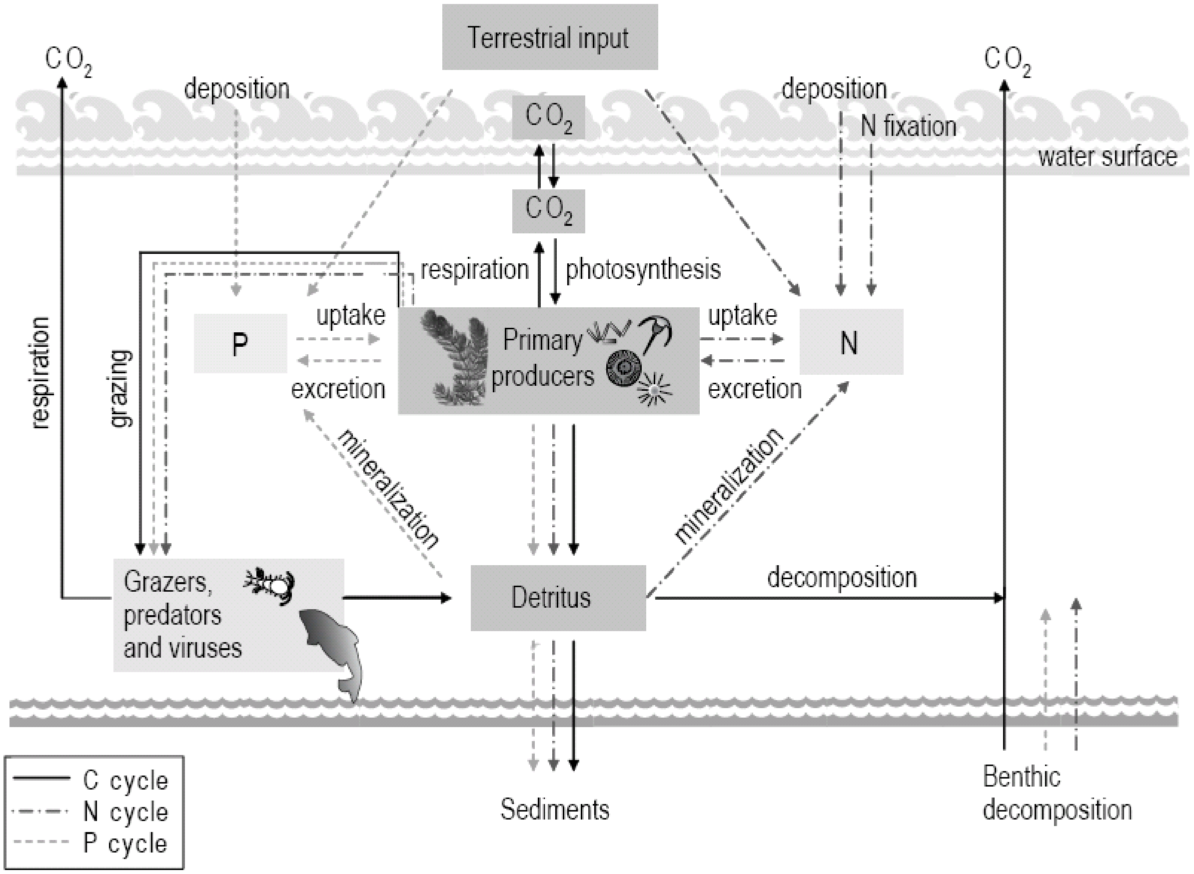


Figure 3-39. N cycle in freshwater ecosystem.

Recent research (e.g., Wolfe et al., 2001, 2003, 2006; Lafrancois(Lafrancois, 2003; Das, 2005) (Saros, 2005) has provided additional evidence indicating that N deposition has played an important role in influencing the productivity of oligotrophic, high-elevation lakes in the western U.S. and Canada, and the Canadian arctic. There is evidence suggesting historical N-limitation of some lakes based on paleolimnological studies conducted in mountainous regions of the western U.S. that have been the recipient of elevated levels of N, but not S, deposition over background values (see Section 3.3.4). Interactions between N and P loading are discussed in Annex C.

Productivity investigations have included gradient studies in which the relationship between lake N concentration and primary productivity (reported as chlorophyll *a*, NPP, or an index such as the lake chemistry ratio of dissolved inorganic N [DIN] to total P, DIN:TP) was surveyed and correlated with atmospheric N deposition. Productivity studies have also included lake and stream bioassays in which N was added to waters in field or laboratory in order to measure the response. The most common, and easiest to document, indicators of change in algal productivity are measures of the concentration of chlorophyll *a* and water clarity. However, clarity is also strongly influenced by erosional inputs of fine sediment to the lake or stream system. Chlorophyll *a* concentration is generally more directly tied to algal productivity than is water clarity.

Phytoplankton Biomass

Studies have shown an increase in lake phytoplankton biomass with increasing N deposition in several regions, including the Snowy Range in Wyoming (Lafrancois, 2003), the Sierra Nevada Mountains in California (Sickman et al., 2003), and across Europe (Bergström and Jansson, 2006). Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Fenn et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006).

Bergström and Jansson (2006) concluded the eutrophication caused by inorganic N deposition indicates that phytoplankton biomass in a majority of lakes in the northern hemisphere is limited by N in their natural state. Chemical data from 3,907 lakes and phytoplankton biomass data from 225 lakes from Swedish monitoring programs showed a clear north-south gradient of increasing lake concentrations and algal productivity related to the pattern of increasing N deposition input (Bergström et al., 2005). The lowest productivity was found at sites where wet N deposition was about 1.3 kg N/ha/yr; increasing productivity occurred at greater than 2.2 kg N/ha/yr (Bergström et al., 2005). Although these lakes are all in Sweden, the study size and the strong correlation between productivity and atmospheric N deposition makes the results likely relevant to North American audiences.

Experiments conducted with mesocosms in lakes where NO_3^- was below the detection level found a strong response in phytoplankton biomass with additions of N (bringing concentrations to ~1.0 mg N/L) and even stronger responses to additions of N plus P, but not P alone (Lafrancois, 2004). The reverse was also found in Colorado Front Range lakes with ambient NO_3^- concentrations of ~1.0 mg/L: productivity increased with additions of N plus P or P only, but not NO_3^- alone (Lafrancois, 2004).

A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America, including many of the studies described above, found algal growth enhancement from N amendments to be common in slightly less than half the studies (Elser, 1990). There was a mean increase in phytoplankton biomass of 79% in response to N enrichment (average of 46.3 μeq/L N) (Elser, 1990). This meta-analysis was recently repeated with a much large data set and similar results (Elser, 2007). Freshwater enrichment bioassay studies from 990 separate studies worldwide were gleaned from the literature. The *ln*-transformed response ratio (RRX), a frequently used effect metric in ecological meta-analysis, was equal at about 0.3 for N and P experiments with stream benthos (periphyton) bioassays, and approximately equal at about 0.2 for lake phytoplankton. There was a stronger response to P than N in lake benthos studies, but the RRX for N was still about 0.3, showing that many sites increased productivity when fertilized with N alone (Elser, 2007).

Table 3-16. Summary of additional evidence of N effects on productivity of freshwater ecosystems.

Region	Endpoint	Observation	Ecosystem Type	Reference
Lake Tahoe, CA	productivity water clarity	Long-term (28 years) measurements showed that primary productivity has doubled, while water clarity has declined, mostly as a result of atmospheric N deposition	lake	Goldman (Goldman, 1988) ; Jassby et al. (Jassby, 1994)
Alaska	primary production fungal biomass decomposition rates benthic macroinvertebrate	N amendment experiments with 6.4 µM N to elicited responses throughout the ecosystem, including enhanced primary production, enhanced fungal biomass and elevated leaf litter decomposition rates, and a fourfold to sevenfold greater benthic macroinvertebrate abundance	small arctic streams	(Benstead et al., 2005).

Chlorophyll *a*

The most widely used index of biological change in response to nutrient addition is measurement of chlorophyll *a* concentration in water. Surveys and fertilization experiments show increased inorganic N concentration and aquatic ecosystem productivity (as indicated by chlorophyll *a* concentration) to be strongly related. For example, a series of in situ meso- and microcosm N amendment experiments more than 30 years ago showed increases in lake algal productivity. Lake 226S in Ontario's Experimental Lake District (ELD) showed doubling of average epilimnetic chlorophyll *a* over five years of fertilization. However, because the response to P fertilization was much greater, the effects of N received less attention

(Schindler, 1980). Other ELD lakes that had relatively low N to P concentration ratios experienced 3 to 10 times greater increases in chlorophyll *a* than Lake 226S (Schindler, 1980) f

Similar experiments at Castle Lake, California, the Snowy Range of southern Wyoming, and Alaskan arctic foothill lakes yielded measurable increases in chlorophyll *a* and primary productivity with N amendments (Axler and Reuter, 1996; Levine and Whalen, 2001; Nydick et al., 2003, 2004a; Lafrancois, 2004).

Periphyton Biomass

N effects have been observed in periphyton which grows on rocks or sediment in lakes and streams where there is sufficient light for photosynthesis. We found no studies that documented resource requirements for periphyton, although several papers described stimulated growth with N amendments from ecosystems throughout the U.S. (Annex C), including streams in Alaska, Arizona, Iowa, Texas, Minnesota, Missouri, and lakes in California, Colorado, and Massachusetts. Growth stimulation occurred with N additions ranging from 8 to 50 µM/L, or with exposure to 0.5 M N concentrations on agar substrate (e.g., Bushong and Bachmann, 1989; Allen and Hershey, 1996; Wold and Hershey, 1999; Smith and Lee, 2006). Additional lake bioassay experiments that enriched the water column down into the sediments found enhancement of periphyton growth on bioassay container walls in experiments in California, Wyoming, and Massachusetts (Axler and Reuter, 1996; Nydick et al., 2004b; Smith and Lee, 2006). Strong N limitation of benthic algae has also been inferred in streams of Arizona (Grimm and Fisher, 1986), California (Hill and Knight, 1988), Missouri (Lohman et al., 1991), and Montana (Lohman and Priscu, 1992; Smith and Nicholas, 1999).

Trophic Status Indices

Nutritional responses of aquatic ecosystems to atmospheric N deposition are heavily dependent on surface water P concentrations. Thus, chemical ratios of N to P can be very useful in evaluating eutrophication potential. A series of papers, described below, has been published exploring nutrient limitations and offering indices that describe the trophic state of freshwaters. Valuable insights have been gained from several indices, including total N to total P (TN:TP), dissolved inorganic N to total P (DIN:TP), dissolved inorganic N to total dissolved P (DIN:TDP), dissolved inorganic N to soluble reactive P (DIN:SRP), and dissolved inorganic N to the ratio of chlorophyll *a* to total P (DIN:[chl *a*:TP]). While there are publications that compare the effectiveness of some of these indices, it appears that different indices are useful for different purposes; we make no attempt to favor one over another.

Algal growth was reported to be limited at DIN:TP values between 5 and 20 (Schindler, 1980) Grimm and Fisher, 1986; Morris and Lewis, 1988; Downing and McCauley, 1992; Bergström and Jansson, 2006). When DIN:TP ratios are greater than reference values, growth stimulation, N and P colimitation, or P limitation commonly occurs (Sickman et al., 2003b). In a Swedish lake survey, N-limitation occurred in lakes where the DIN:TP ratio was less than 7 (concentrations < 33 µM N/L). Co-limitation of both N and P were found in lakes with DIN:TP ratio between 8 and 10, and P-limitation at DIN:TP values greater than 10. This corresponds roughly to N concentrations of 45 to 80 µM N/L for co-limited lakes, and concentrations > 80 µM N/L for P-limited lakes (Bergström et al., 2005). Other thresholds for N-limitation were reported in the literature to occur at DIN:SRP ratios < 4 (Lohman and Priscu, 1992) and < 10 (Wold and Hershey, 1999).

Bergström et al. (2005) reported a new index, (DIN:[chl *a*:TP]) to indicate the eutrophication of lakes from N deposition. The choice of DIN/[chl *a*:TP] was based on whole lake experiments in Sweden (Jansson et al., 2001) and permits the assessment of a possible eutrophication effect of N deposition independent of differences in P input between lakes in different regions. These researchers found that the mean chl *a*:TP ratios increased more than three times from low N to high N deposition areas, indicating that N deposition contributed to eutrophication.

Freshwater summary

The productivity of many freshwater ecosystems is currently limited by the availability of N. European and North American lakes may have been N-limited before human-caused disturbance, and remote lakes may have remained N-limited until slight increases in atmospheric N deposition brought about an increase in phytoplankton and periphyton biomass and induced P limitation. Increases in algal biomass are associated with changes in algal assemblages that favor certain species over others. These effects are described below in the discussion of biodiversity.

3.3.3.4. Estuarine and Marine

In coastal marine ecosystems, the nutrients most commonly associated with phytoplankton growth are N, P, and Si (see Annex C for interactions between hydrology and nutrient cycling). Interactions among the supplies of these nutrients can affect phytoplankton species composition in ways that might impact ecosystem function (Riegman, 1992; Paerl, 2001). The relative proportions of these nutrients are important determinants of primary production, food web structure, and energy flow through the ecosystem (Dortch, 1992; Justic, 1995; Justic, 1995; Turner, 1998). There is a strong scientific consensus that N is the principal cause of coastal eutrophication in the U.S. (NRC, 2000). On average, human activity has likely contributed to a sixfold increase in the N flux to the coastal waters of the U.S., and N now represents the most significant coastal pollution problem (Howarth et al., 2002; Howarth and Marino, 2006). Atmospheric deposition is responsible for a portion of the N input.

Ecological effects of accelerated estuarine eutrophication and climatic perturbations such as droughts, floods, and hurricanes are often expressed most closely at the level of the primary producers.

Phytoplankton can be divided into functional groups that reflect ecological change, for example: chlorophytes, cryptophytes, cyanobacteria, diatoms, and dinoflagellates (Pinckney et al., 2001).

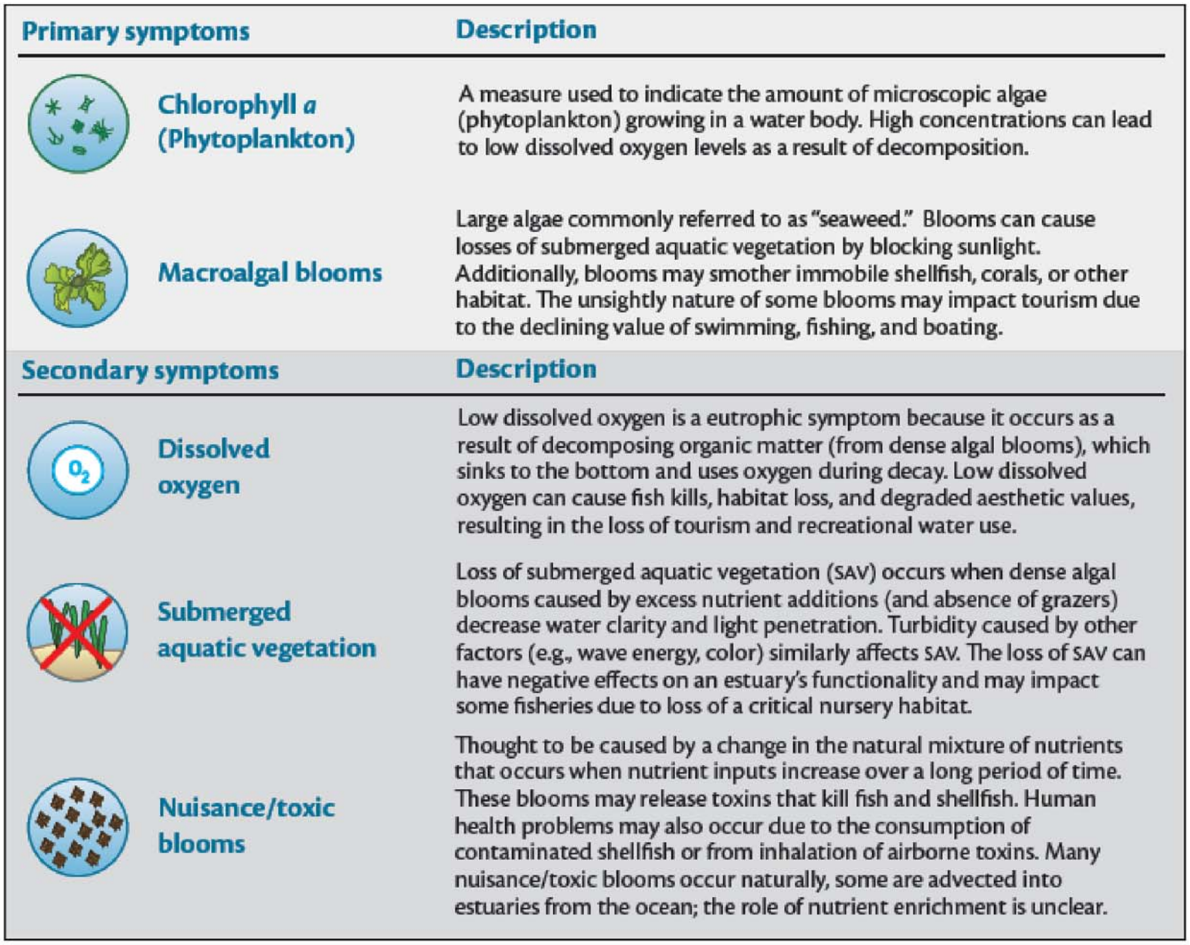
These groups have the added benefit that their relative abundances are reflected in photopigment indicators which can be easily measured in the laboratory (Paerl, 2003). Changes in phytoplankton community composition, which may affect food web interactions, can have important effects on nutrient cycling. For example, if the growth of phytoplankton species that are more readily grazed by zooplankton (i.e., diatoms) is favored, trophic transfer will occur in the water column from diatoms to fish and nutrient export will take place as fish move to the ocean. However, if the phytoplankton that are favored by nutrient addition and disturbance are not readily grazed (i.e., cyanobacteria and dinoflagellates), trophic transfer will be poor. In that case, more unconsumed algal biomass will settle to the bottom where it can contribute to O_2 consumption and associated hypoxia (Paerl, 2003).

In order to evaluate the impacts of eutrophication, five biological indicators were used in the recent national assessment of estuary trophic condition: chlorophyll *a*, macroalgae, dissolved O_2, nuisance/toxic algal blooms, and submerged aquatic vegetation (SAV) (Bricker, 2007) (Figure 3-40). Each of these indicators is discussed below and/or within the biodiversity section of this document (see Section 3.3.5.4).

N limitation

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased N loading (D'Elia et al., 1986; Howarth, 2006). There is a scientific consensus that N-driven eutrophication of shallow estuaries has increased over the past several decades and that environmental degradation of coastal ecosystems is now a widespread occurrence (Paerl, 2001). For example, the frequency of phytoplankton blooms and the extent and severity of hypoxia have increased in the Chesapeake Bay (Officer, 1984) and Pamlico estuaries in North Carolina (Paerl et al., 1998) and along the continental shelf adjacent to the Mississippi and Atchafalaya rivers discharges to the Gulf of Mexico (Eadie et al., 1994). It is partly because many estuaries and near-coastal marine waters are degraded by N enrichment that they are highly sensitive to potential adverse impacts from N addition from atmospheric deposition.

N enrichment of marine and estuarine waters can alter the ratios among nutrients and affect overall nutrient limitation. The sensitivity of estuarine and coastal marine waters to eutrophication from atmospheric N deposition depends on the supply of, and relative availability of, N and P. At upstream freshwater locations in Chesapeake Bay, P is often the limiting nutrient (Larson et al., 1985). At the transition between fresh water and salt water, N and P may be co-limiting, whereas the saltwater environments of the outer bay are usually N-limited (Fisher, 1998) Rudek et al., 1991). Nutrient limitation varies in space and over time, in response to changes in discharge and temperature that interact with estuarine morphology and hydrology (Paerl et al., 2006).



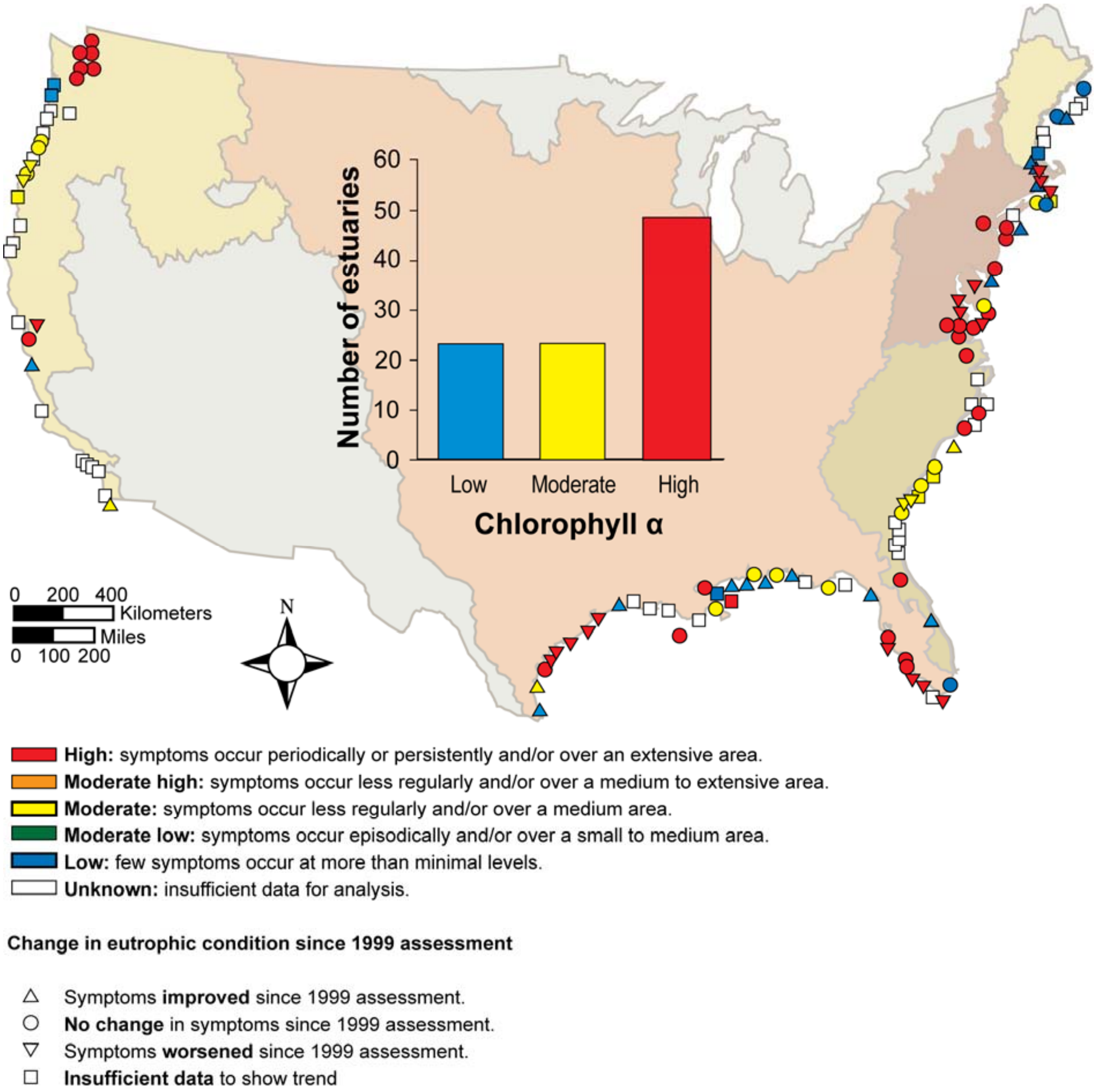
Primary symptoms	Description
Chlorophyll *a* (Phytoplankton)	A measure used to indicate the amount of microscopic algae (phytoplankton) growing in a water body. High concentrations can lead to low dissolved oxygen levels as a result of decomposition.
Macroalgal blooms	Large algae commonly referred to as "seaweed." Blooms can cause losses of submerged aquatic vegetation by blocking sunlight. Additionally, blooms may smother immobile shellfish, corals, or other habitat. The unsightly nature of some blooms may impact tourism due to the declining value of swimming, fishing, and boating.
Secondary symptoms	**Description**
Dissolved oxygen	Low dissolved oxygen is a eutrophic symptom because it occurs as a result of decomposing organic matter (from dense algal blooms), which sinks to the bottom and uses oxygen during decay. Low dissolved oxygen can cause fish kills, habitat loss, and degraded aesthetic values, resulting in the loss of tourism and recreational water use.
Submerged aquatic vegetation	Loss of submerged aquatic vegetation (SAV) occurs when dense algal blooms caused by excess nutrient additions (and absence of grazers) decrease water clarity and light penetration. Turbidity caused by other factors (e.g., wave energy, color) similarly affects SAV. The loss of SAV can have negative effects on an estuary's functionality and may impact some fisheries due to loss of a critical nursery habitat.
Nuisance/toxic blooms	Thought to be caused by a change in the natural mixture of nutrients that occurs when nutrient inputs increase over a long period of time. These blooms may release toxins that kill fish and shellfish. Human health problems may also occur due to the consumption of contaminated shellfish or from inhalation of airborne toxins. Many nuisance/toxic blooms occur naturally, some are advected into estuaries from the ocean; the role of nutrient enrichment is unclear.

Source: Bricker et al. (2007)

Figure 3-40. Description of the eutrophic symptoms included in the national estuary condition assessment.

The data for 92 worldwide coastal marine sites analyzed by Smith (2006), for which measurements of both total N and total P were available, illustrated that about half of the sites had total nitrogen (TN):total phosphorus (TP) above the Redfield ratio, which is commonly used to evaluate nutrient limitation in freshwater (TN:TP = 16). As was emphasized in earlier work on nutrient limitation in fresh waters by Redfield (1958) and Reiners (1986), elemental stoichiometry is a fundamental property of life that probably stems from the shared phylogenetic histories of marine and freshwater autotrophs (Sterner and Elser, 2002; Smith, 2006).

In general, the scientific community is at an early stage in development of an understanding of the effects of anthropogenic activities on the stoichiometry of nutrient loading to estuaries and marine waters (Turner, 2002) Dodds, 2006). Changes in nutrient stoichiometry in estuarine and marine ecosystems could alter algal assemblages and cascade to higher trophic levels (Frost et al., 2002).



Source: Bricker et al. (2007)

Figure 3-41. A high chlorophyll a rating was observed in a large number of the nation's estuaries. White squares indicate that data were not available for a particular estuary.

Chlorophyll *a*

Chlorophyll *a* concentration in estuarine or marine water is an indicator of total phytoplankton biomass. It can signal an early stage of water quality degradation related to nutrient loading. High concentration of chlorophyll *a* suggests that algal biomass is sufficiently high that it might contribute to low dissolved O_2 concentration due to increased decomposition of dead algae. In the national estuary condition assessment, high chlorophyll *a* concentration was the most widespread documented symptom of eutrophication (Bricker, 2007) (see Figure 3-41). Half of the estuaries for which there were available data exhibited high chlorophyll *a* concentration (Bricker, 2007).

San Francisco Bay, California is an example of an estuary that has experienced considerable increases in chlorophyll *a* concentrations in recent years. Phytoplankton biomass in much of the bay has increased by more than 5% per year from 1993 to 2004. During this time, modeled primary production has doubled and nutrient loading is identified as one of eight possible causes (Cloern et al., 2006).

Macroalgal Abundance

Macroalgae are generally referred to collectively as seaweed. Macroalgal blooms can contribute to loss of important SAV by blocking the penetration of sunlight into the water column. Although macroalgal data for estuaries in the U.S. were generally sparse, the national estuary condition assessment reported that conditions were moderate or high for 33 of the estuaries evaluated (Bricker, 2007).

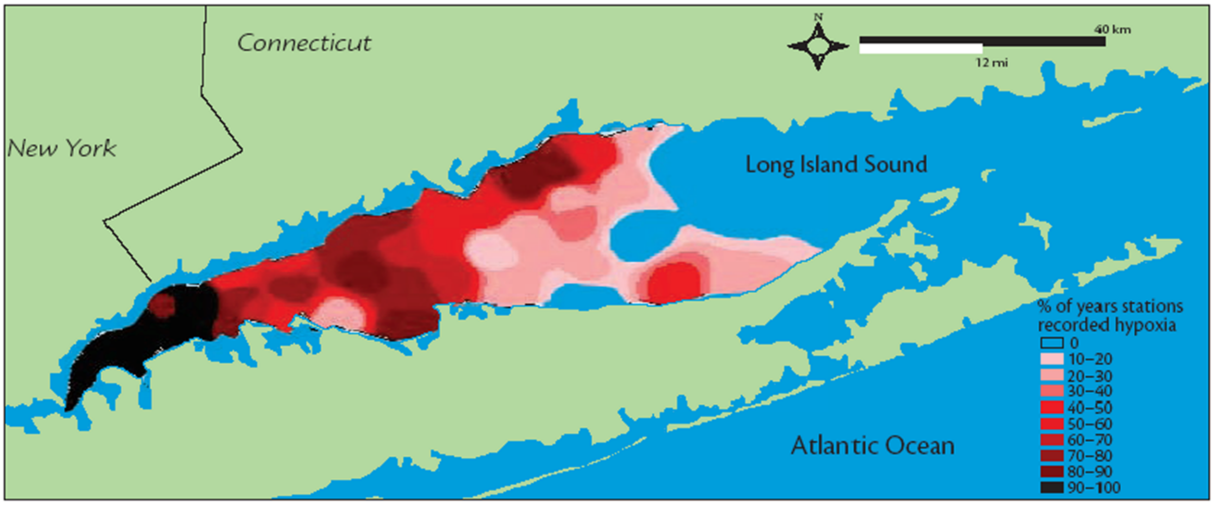
Dissolved O_2

The decomposition of organic matter associated with increased algal abundance consumes dissolved O_2 and can reduce dissolved O_2 concentrations in eutrophic waters to levels that cannot support aquatic life. Decreased dissolved O_2 can lead to development of hypoxic or anoxic zones that are inhospitable to fish and other life forms. Perhaps the most important environmental effect of N input to coastal waters is the development of hypoxia. The largest zone of hypoxic coastal water in the U.S. has been documented in the northern Gulf of Mexico on the Louisiana-Texas continental shelf. During midsummer, this hypoxic zone has regularly been larger than 16,000 km^2 (Rabalais, 1998). The timing, duration, and spatial extent of hypoxia in this case are related mostly to the nutrient flux from the Mississippi River (Justic, 1997; Justic, 1993; Rabalais, 1996; Lohrenz, 1997; Paerl, 2001).

Although impacts on dissolved O_2 can be quite severe in the areas where they are manifested, the national assessment reports that the severity of dissolved O_2 impacts related to eutrophication are relatively limited in many of the systems assessed (Bricker, 2007). In the shallow estuary of Long Island Sound, the existence of extended periods of low dissolved O_2 is a notable problem, and atmospheric deposition is considered to comprise a significant fraction of the total N loading. Dissolved O_2 levels below 3 mg/L are common, and levels below 2 mg/L also occur. During some years, portions of the Long Island Sound bottom waters become anoxic (< 1 mg/L) (Bricker, 2007) (Figure 3-42).

Nuisance/Toxic Algal Blooms

Nuisance or toxic algal blooms reflect the proliferation of a toxic or nuisance algal species that negatively affects natural resources or humans. Such blooms can release toxins that kill fish and shellfish and pose a risk to human health. Unlike the other indicators of estuarine eutrophication, the role of nutrients in stimulating toxic algal blooms is less clear. Of the 81 estuary systems for which data were available, 26 exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker, 2007).



Source: Bricker et al. (2007)

Figure 3-42. Frequency of hypoxia in Long Island Sound, 1994 to 2002.

3.3.3.5. Summary

N_r deposition causes alteration to the C cycle in forest ecosystems. Experimental N addition studies show a range of responses in terms of mortality and productivity. In general, moderate to high additions of N lead to either no significant change in growth rates or transient growth increases followed by increased mortality, especially at higher rates of fertilization (See Table 3-15). Although there remains considerable uncertainty in the potential response of soil C to increases in reactive N additions (Neff et al., 2002), a meta-analysis by Johnson and Curtis (2001) suggested that N fertilization caused an 18% increase in soil carbon content. The effects of N addition on soil respiration are mixed; reductions at high levels of N (Lu, 1998), no effect (Vose et al., 1995), and increases (Griffin et al., 1997; Mikan et al., 2000) all have been observed.

Region trends in NEP have been documented through models based on observational gradient studies. Magnani et al. (Magnani, 2007) recently reported a strong correlation between estimated average long-term NEP (NEP_{av}) and estimated 1990 wet N deposition (up to 9.8 kg/ha/yr) for 20 forest stands mostly in Western Europe and the conterminous U.S. Sutton et al. (2008) critiqued the methods of Magnani et al. (2007). After considering the uncertainties in N deposition and climate variability, Sutton et al. (2008) reported the estimated NEP response to N deposition was 68 kg C/wet-deposited N. The authors did agree N deposition remains an important driver of NEP_{av}, but did not support the NEP_{av} was overwhelmingly driven by N deposition. NCEA conducted a meta-analysis to examine the impact of N fertilization on forest ecosystem C content, defined as the sum of C content of vegetation, forest floor and soil (Johnson et al. 2006) and found that N addition increased ecosystem C by 6%.

N_r addition causes alterations to the C cycle of Tundra, however there is no evidence linking deposition to Tundra ecosystem C dynamics. Mack et al. (2004) examined C and N pools in a long-term fertilization experiment at the arctic Long-Term Ecological Research site near Toolik Lake, AK. This study clearly showed that increased nutrient availability enhanced decomposition of below-ground C pools in deep soil layers more than it increased primary production, leading to a substantial net loss of C from this ecosystem.

N_r deposition causes alteration to the C cycle in freshwater wetlands. In *Sphagnum*-dominated ombrotrophic bogs, higher N deposition resulted in higher tissue N concentrations (Aldous 2001) and greater NPP (Aldous 2002a), but lower bulk density (Aldous 2002a). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition ($y = 2.84x + 0.67$, $r^2 = 0.32$, $P < 0.001$), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al. 2004). Soil respiration has been studied in European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher CO_2 emissions from soil. Primary production of plant species from intertidal wetlands typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Mendelssohn 1979, Wigand et al. 2003, Tyler et al. 2007, Darby and Turner 2008).

N_r deposition causes alteration to the C cycle in freshwater aquatic ecosystems. Numerous studies investigate the relationship between lake N concentration and primary productivity (reported as chlorophyll *a*, NPP, or an index such as the lake chemistry ratio of dissolved inorganic N [DIN] to total P, DIN:TP) and atmospheric N_r deposition. N addition experiments of lake and stream bioassays in which N was added to waters in field or laboratory in order to measure the response. Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Fenn et al., 2003a; Bergström et al., 2005; Bergström and Jansson, 2006).

The evidence is sufficient to infer a casual relationship between N_r deposition and alteration to the biogeochemical cycling of C. Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia et al., 1986; Howarth, 2006). This is at least partly because denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek, 1997). However, other limiting factors occur in some locations and during some seasons. Levels of N limitations are affected by seasonal patterns. N-limited conditions are likely to be found during the peak of annual productivity in the summer.

3.3.4. Biogenic Nitrous Oxide and Methane Flux

Methane (CH_4) and nitrous oxide (N_2O) are greenhouse gases (GHGs) contributing to global warming. Although atmospheric concentrations of CH_4 (1774 ppb) and N_2O (319 ppb) are much lower than CO_2 (379 ppm), their global warming potential is 23 and 296 times that of $CO_{2,}$ respectively. Human activities have dramatically increased atmospheric concentration of CH_4 by 48% and N_2O by 18% since pre-industrial times (IPCC 2007). The continuing increase of those GHGs concentrations have been shown to threaten human and ecosystem health.

Anthropogenic N deposition to natural ecosystem is a primary component of global changes (UNEP 2007). Additional N input not only changes global N cycle, but also has profound impacts on biogeochemical processes associated with GHGs emission (Vitousek, 1997; Dalal, 2003; Bodelier, 2004). In the following section, the impacts of N addition on CH_4 and N_2O emissions were reviewed and quantitatively synthesized by meta-analysis. Further details on this meta-analysis including study site, exosystem type, N addition level, form of N fertilizer, experimental conditions, relationship between N addition and CH_4 flux, are in included Annex C.

3.3.4.1. Methane

Atmospheric CH_4 originates mainly (70–80%) from biogenic sources (Le Mer, 2001). Methane is produced in anaerobic environment by methanogenic bacteria during decomposition of organic matter. Once produced in soil, CH_4 can be then released to the atmosphere or oxidized by methanotrophical bacteria in aerobic zone (Le mer and Roger 2001). Methane production and oxidation processes occur simultaneously in most ecosystems. Wetland soils are generally CH_4 sources, accounting for about 20% of global CH_4 emission (see Annex C for a more detailed discussion of methane in wetlands). Non-flooded upland soils are the most important biological sink for CH_4, consuming about 6% of the atmospheric CH_4 (Le mer and Roger 2001). Numerous researches have demonstrated that N is an important regulatory factor for both CH_4 production and oxidation (Bodelier, 2004).

EPA conducted a meta-analysis, including 61 observations from 27 publications, to evaluate the relationship between N addition and CH_4 flux. Details on those publications, including study site, ecosystem type, N addition level, form of N fertilizer, experimental condition, are given in Annex C. The impact of N addition on CH_4 source and sink strength were estimated by CH_4 emission and CH_4 uptake respectively. The result suggested that N addition significantly increased CH_4 emission by 115% for grasslands and wetlands (Figure 3-43). This response ratio did not differ among vegetation type, N addition level, form of N fertilizer and experiment condition.

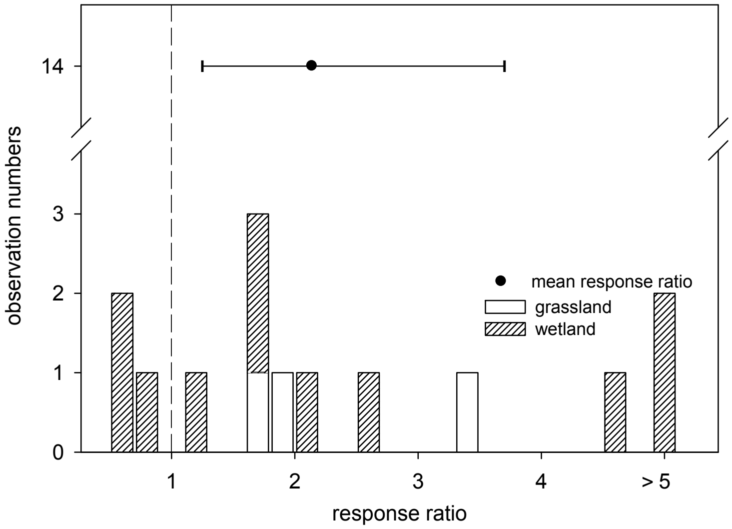


Figure 3-43. Effects of N addition on biogenic CH_4 emission. The bars show the distribution of the number of studies categorized by ecosystem type. The dot with error bars shows the overall mean response ratio with 95% CI.

Overall, N addition significantly reduced CH_4 uptake by 38% (Figure 3-44). Ecosystem type, N form and experiment condition influenced the degree of CH_4 uptake response to N addition (Figure 3-45). Methane uptake was reduced for all ecosystems, but this inhibition was significant only for coniferous and deciduous forest, with a reduction of 28% and 45%, respectively (Figure 3-45).

All forms of N fertilizer except urea were shown to reduce CH_4 uptake (Figure 3-45). Several possible mechanisms have been proposed to explain the inhibition in CH_4 oxidation by N addition. Besides the oxidation of CH_4, methane monooxygenase (MMO) can convert NH_4^+ to NO_3^-, and NH_4^+ therefore usually inhibits CH_4 oxidation by competing for MMO (Bodelier, 2004). Methanotrophic bacteria are sensitive to osmotic stress induced by salts. Inhibition of CH_4 uptake by nitrogenous salts (e.g. KNO_3, NH_4Cl, NH_4NO_3) and non-nitrogenous salts (e.g. K_2SO_4, KCl and NaCl) has been observed in field and laboratory studies (King and Schnell 1998; Bodelier, 2004). Other mechanisms, such as toxicity of nitrite (NO_2^-) produced by nitrification or denitrification processes, may also involve in the inhibition of CH_4 oxidation (Schnell and King 1994).

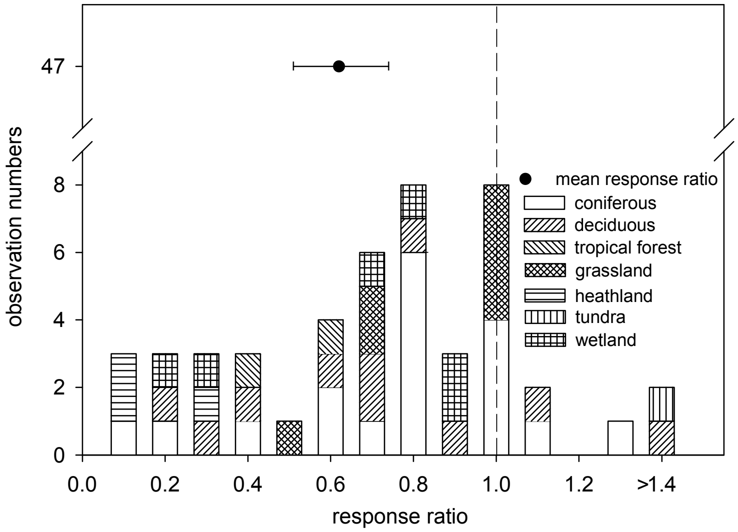


Figure 3-44. Effects of N addition on biological CH_4 uptake. The bars show the distribution of the number of studies categorized by ecosystem type. The dot with error bars shows the overall mean response ratio with 95% CI.

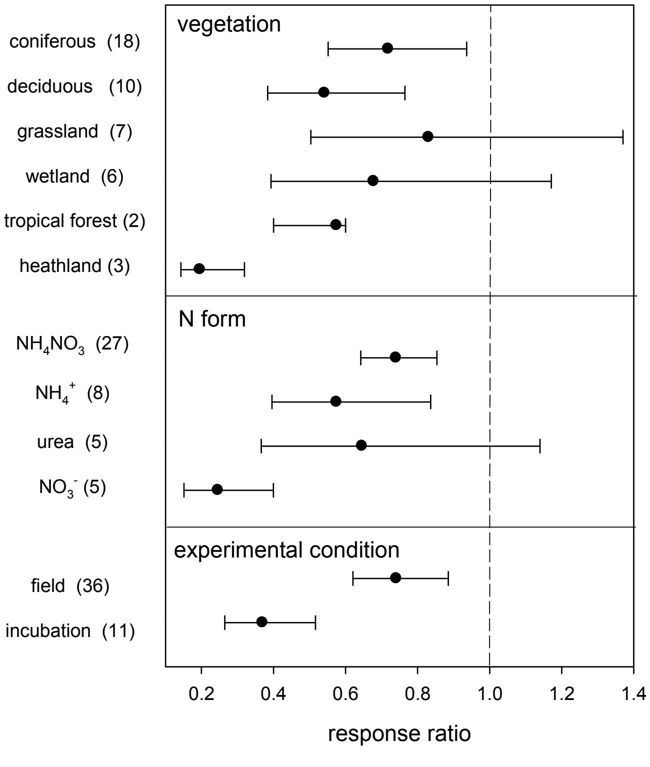


Figure 3-45. Effects of N addition on biological CH_4 uptake. The data are expressed as the mean response ratio with 95% confident intervals. The numbers of studies included are indicated in parentheses.

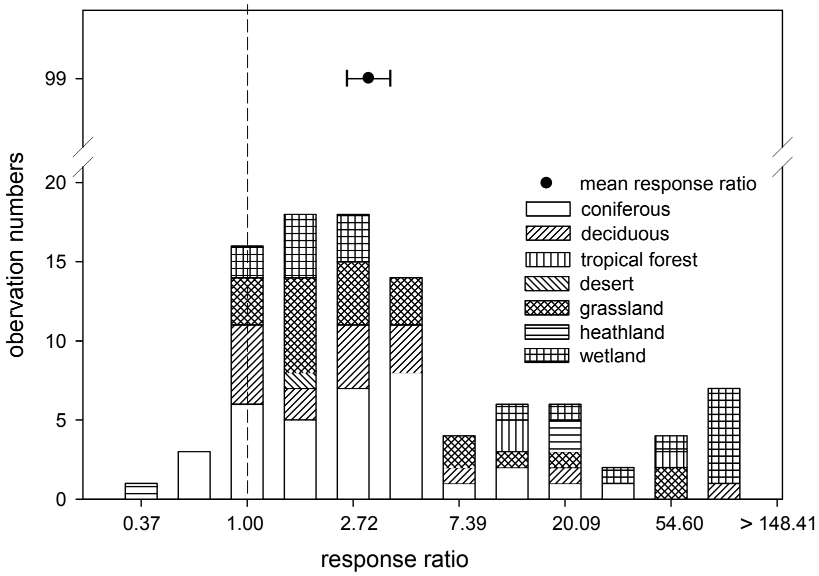
The mean response ratio of CH_4 uptake from laboratory incubation studies was significantly lower than that from field studies (Figure 3-45). This difference could be due to that the spatially and chemically heterogeneous field conditions resulted in large experimental errors (Crill, 1994; Weitz, 1999) Gulledge and Schimel 2000). Also laboratory microcosms were characterized by a closed and incomplete N cycle, where N loss by leaching was very small and no plant competed for N with soil microbes. Therefore, N addition may result in stronger impacts on microbial processes under laboratory condition than under field condition

Several laboratory incubation studies found that CH_4 uptake rates decreased with increasing N input (Schnell and King 1994; King and Schnell 1998). This meta-analysis did not find significant correlation between the amount of N addition and the response ratio of CH_4 production/consumption (Figure 3-45). The lack of dose response relationship is probably because CH_4 production is influenced by multiple interactions of soil N content, soil moisture, pH and temperature et al (Le Mer and Roger 2001), and varies greatly over small spatial and temporal scales (IPCC 2001).

3.3.4.2. Nitrous oxide

Biogenic sources are the dominating contributors (> 90%) to atmospheric N_2O. Terrestrial soil is the largest source of atmospheric N_2O, accounting for 60% of global emissions (IPCC 2001). Nitrous oxide production in soil is mainly governed by microbial nitrification and denitrification (Dalal, 2003). The contribution of each process to the total N_2O production varies with environmental conditions. Denitrifying bacteria reduce NO_3^- or NO_2^- into N_2O or N_2 under anaerobic condition. In submerged soils such as wetland soil, denitrification should be the dominant contributing process to N_2O emission (Conrad 1996). Increasing NO_3^- input generally increases denitrification rate under suitable condition of temperature and organic C supply. High soil NO_3^- concentrations also inhibit N_2O reducing to N_2 and result in high N_2O/N_2 ratio (Dalal, 2003). Under aerobic environment, autotrophic nitrifying bacteria obtain energy by reducing NH_4^+. Nitrous oxide is an intermediate product of the oxidation of NH_4^+ to NO_2^- or decomposition of NO_2^-. The increase in N_2O emission following NH_4^+ addition has been observed in many lab and field experiments (Aerts and Toet 1997; Aerts and Caluwe 1999; Keller et al 2005).

EPA conducted a meta-analysis on the effects of N addition on N_2O emission from non-agricultural ecosystems, including 99 observations from 30 publications. N addition normally enhanced N_2O emission, but some studies also observed N_2O emission was decreased by N addition (Skiba et al. 1999; Borken et al. 2002; Ambus et al. 2006; Ambus and Robertson 2006; Curtis et al 2006). Although some natural ecosystem can be a N_2O sink (Chapuis-Lardy et al. 2007), very limited publications assessed the impact of N addition on N_2O uptake. Thus, only changes in N_2O production were estimated in this meta-analysis. Overall, the results of the meta-analysis indicated that N addition increased N_2O emission by 215%



(Figure 3-46). The response of N_2O emission was influenced by ecosystem type, the form and the amount of the N addition (Figure 3-47).

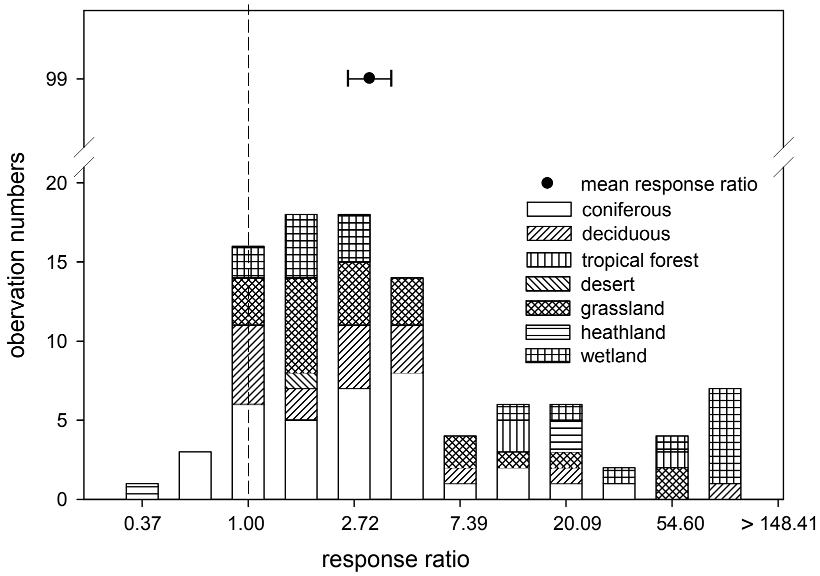


Figure 3-46. Effects of N addition on biogenic N_2O emission. The bars show the distribution of the number of studies categorized by vegetation type. The dot with error bars shows the overall mean response ratio with 95% CI.

Compared to other ecosystems, tropical forest emitted more N_2O under N enrichment condition (+735%) (Figure 3-47). This greater response may be because tropical forests are often P limited rather than N limited (IPCC 2001). Hall and Matson (1999) measured N_2O emission after adding N fertilizer in two tropical rainforests in Hawaii. They found that N_2O emission from P-limited sites was 54 times greater in the short term N addition experiment and 8 times greater in the chronic N addition experiment compared to that from N-limited sites. The P-limited soil had higher inorganic N concentration than the N-limited soil (Hall and Matson 1999), which increased N availability to the nitrifying and denitrificating bacteria. However, climatic conditions, especially temperature and precipitation, could also be the key factors to drive N_2O emission from tropical forest ecosystem.

NO_3 caused a higher stimulation (+494%) on N_2O emission than NH_4^+ did (+95%) (Figure 3-47), which was consistent with the previous field studies (Keller, 1988; Wolf and Russow 2000; Russow et al. 2008). By adding ^{15}N labeled NO_3^- and NH_4^+ to soil, Russow et al. 2008 found that N_2O was mainly emitted by denitrification and the contribution of denitrification to the total N_2O production increased from 54% in soil with normal SOM content to 76% in soil with high SOM.

The Intergovernmental Panel on Climate Change (IPCC) issued a guideline for national GHGs inventories of biogenic N_20 (IPCC 2000). In this guideline, the default N_2O emission factor is 1.25% for N fertilizer applied to agricultural fields (i.e. 1.25% of the amount of N applied to a field will be emitted to the atmosphere as N_2O). Several studies have questioned the validity of this emission factor. Some studies suggested a much lower emission factor, such as 0.25% for rice paddy field (Yan et al. 2003) and 0.02% for semi-arid regions (Barton et al. 2008), while others found the amount of N_2O emission was not clearly related to the amount of N addition (FAO/IFA 2001; Akiyama et al. 2005; Barnard et al. 2005). EPA compiled ambient N_2O emission data from 36 studies and did not find any correlation between N_2O emission and the level of N deposition (Figure 3-48). In this meta-analysis, although the mean response ratio increased with the amount of N addition, the difference among the three levels (< 75, 75–150 and > 150 kg N/ha/yr) were not significant (Figure 3-47). The weak correlation is probably due to that the effect of N addition on N_2O emission is affected by many other biotic and abiotic factors such as fertilizer type, vegetation, temperature, soil drainage et al. (Dalal, 2003).

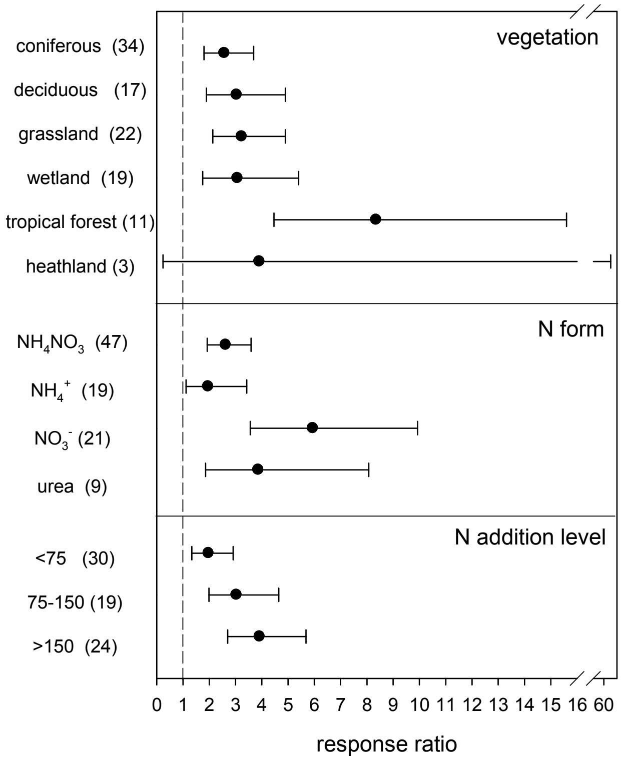


Figure 3-47. Effects of N addition on biogenic N_2O emission. The data are expressed as the mean response ratio with 95% confident intervals. The numbers of studies included are indicated in parentheses.

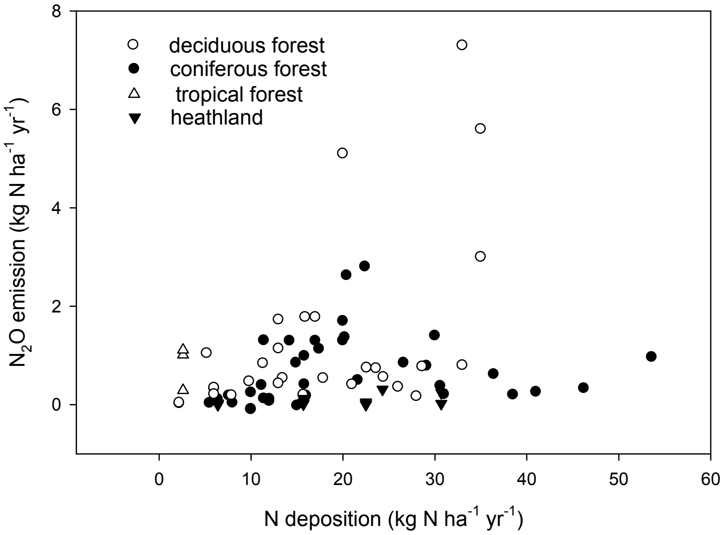


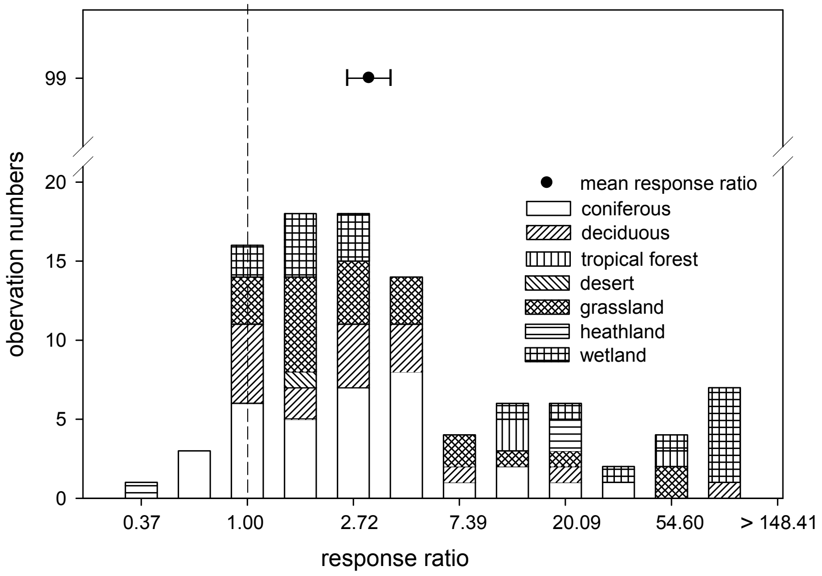
Figure 3-48. The relationship between N_2O emission and N deposition. The data were compiled from 36 independent studies.

3.3.4.3. Summary

Integrating 160 observations across 57 independent studies, this meta-analysis suggested that N addition tended to increase CH_4 emission, reduce CH_4 uptake and increase N_2O emission. Overall, N deposition may result in higher CH_4 and N_2O concentrations in atmosphere and exacerbate global warming, but the response magnitudes were influenced by many environmental factors, such as vegetation type, N form, and climate.

The evidence is sufficient to infer a casual relationship between N_r deposition and the alteration of biogeochemical flux of CH_4 in terrestrial ecosystems. N addition ranging from 10 to 560 kg N/ha/yr reduced CH_4 uptake by 38% across all ecosystems (Figure 3-44), but this inhibition was significant only for coniferous and deciduous forest, with a reduction of 28% and 45%, respectively (Figure 3-45).

The evidence is sufficient to infer a casual relationship between N_r deposition and the alteration of biogeochemical flux of N_2O in terrestrial ecosystems. **Overall, the results of the meta-analysis discussed in section 3.3.4 indicated that N addition ranging from 10 to 560 kg N/ha/yrd. increased N_2O emission by 215%** (Figure 3-46). The response of N_2O emission to N for coniferous forest, deciduous forest and grasslands was significant (Figure 3-47).



The evidence is sufficient to infer a casual relationship between N_r deposition and the alteration of N_2O flux in wetland ecosystems. In the meta-analysis of 19 observations from studies that evaluated the effects of N additions ranging from 15.4 to 300 N kg N/ha/yr N addition was shown to increase the production of N_2O by 207% (Figure 3-47).

The evidence is sufficient to infer a casual relationship between N_r deposition and the alteration of CH_4 flux in wetland ecosystems. Wetlands are generally net sources of CH_4, but some wetlands can be net sinks depending on environmental conditions such as drainage and vegetation (Crill, 1994) Saarnio et al. 2003). The meta-analysis indicated that N addition, ranging from 30 to 240 N kg N/ha/yr, increased CH_4 production by 115% from the source wetlands (Figure 3-43, but had no significant impact on CH_4 uptake of the sink wetlands (Figure 3-45).

3.3.5. Species Composition, Species Richness and Biodiversity

A common response to environmental stress is the tendency for the more sensitive species to decrease in abundance, or to be eliminated, while the more tolerant species increase in abundance (Woodwell, 1970). Species composition and species richness, as well as impacts on rare or threatened species, indicate changes to biodiversity. The ecological consequences of changing species composition, richness and/or biodiversity can be profound. Selective removal of certain species can result in an impairment of ecosystem function, change in community structure and food web dynamics, and decrease in species richness and diversity. Such changes in species composition can occur in response to N addition to terrestrial, aquatic, and transitional ecosystems.

Weis et al. (2006) presented an overview of potential biodiversity loss from N enrichment. A survey by Stohlgren et al. (1999) of variables that contribute to species richness and invasibility of sites found positive relationships of soil N with species richness and numbers of nonnative plant species. The implication of this work is that N fertilization alters competitive interactions that may cause native species to be lost, with subsequent decrease in species richness.

Alteration of plant productivity and growth by N deposition (see Section 3.3.3) causes a cascading effect on the competitive interactions among species. Atmospheric deposition of N is expected to benefit those species that are best able to take advantage of the increased nutrient availability. Other species may experience decreased growth, reproduction and population size, because they are out-competed by species that are more successful under conditions of enhanced N availability. Numerous studies evaluate ecosystem response to levels of N addition that far exceed the range of N deposition levels in the U.S. This assessment focuses on the information most relevant to the review of the NAAQS, therefore research conducted at N loading levels that greatly exceed current conditions (> 150 kg N/ha/yr) are excluded from the discussion.

3.3.5.1. Terrestrial Ecosystem Biodiversity

Atmospheric inputs of N can alleviate deficiencies and increase growth of some plants at the expense of others. Thus, N deposition can alter competitive relationships among terrestrial plant species and therefore alter species composition and diversity (Ellenberg, 1987; Kenk, 1988) EPA, 1993b). Wholesale shifts in species composition are easier to detect in short-lived ecosystems such as annual grasslands, in the forest understory, or mycorrhizal associations than for long-lived forest trees where changes are evident on a decadal, or longer, time scale. Note species shifts and ecosystem changes can occur even if the ecosystem does not exhibit signs of N saturation.

Forests

Trees

There is very little information on the effect of N deposition on the biodiversity of overstory trees in the U.S. However, the altered growth rates caused by N enrichment have the potential to affect forest structure and biodiversity. The life span of many trees is 100yrs or more, therefore observation of how growth rates effect biodiversity within established forests are difficult to observe on a decadal time scale.

N deposition has been observed to cause tree invasion into grasslands, also called forest encroachment. A study of the northern edge of the Great Plains (southern Canada), showed that increasing N deposition over a range of 8 to 22 kg N/ha/yr to aspen-dominated forest and boreal forest caused an increase forest expansion into the grasslands (Kötchy and Wilson 2001). The following mechanisms have been document to facilitate forest encroachment. Due to their height, trees and shrubs can intercept more airborne particulate N than grasses and they should therefore benefit most from N deposition (Kellman & Carty 1986; Binkley 1995). Fertilization also increases the water-use efficiency of woody invaders (Bert et al 1997) and this may enable them colonize temperate grasslands on dry, coarsely textured soils. Accelerated N cycling following deposition (Högbom & Högberg 1991; Berendse 1994; Carreiro et al. 2000) decreases competition for N and increases competition for light (Wilson & Tilman 1991), and may give further advantage to tall or fast growing trees (Aerts 1999). Overall, therefore, increased deposition rates may result in a self-maintaining positive feedback that allows trees to establish in grasslands (Wilson 1998).

Understory Herbaceous Plants and Shrubs

Studies in Europe have generally been based on natural gradients, whereas findings in the U.S. have mostly been based on experimental N addition. The negative effects of increasing N deposition on herbaceous plants were reviewed by Gilliam (Gilliam, 2006). Reported effects include (a) species shifts towards nitrophilous and more acid-tolerant plant species along a deposition gradient from 6 to 20 kg

N/ha/yr in Swedish oak forests; b) a decline in abundance and cover of ericaceous shrubs along a deposition gradient from < 3 to > 12 kg N/ha/yr in the boreal forest in Sweden; and (c) a decline in herbaceous cover under hardwoods following 3 years of N additions applied as $(NH_4)_2SO_4$ at rates ranging from 14 to 28 kg N/ha/yr. The decline in herbaceous cover in the latter study was attributed to increased shading by ferns, and the effect was more pronounced at sites that experienced lower ambient atmospheric N inputs.

Van Breemen and Van Dijk (1988) noted that over the previous several decades of N deposition the composition of plants in forest herb layers in The Netherlands had shifted toward species commonly found in N-rich areas. Brunet et al. (1998) and Falkengren-Grerup (1998) reported the effects of excessive N deposition on mixed-oak forest vegetation along a depositional gradient. Results of this study suggest that N deposition had affected non-woody vegetation directly by increased N availability and, indirectly, by accelerating soil acidity. Time series studies indicated that 20 of the 30 non-woody plant species that were associated most closely with high N deposition had increased in abundance in those areas in Europe that received high N deposition.

Mixed results have been reported in other studies. Research at Fernow Experimental Forest, West Virginia, indicated that application of 35 kg N/ha/yr applied as $(NH_4)_2SO_4$ for 6 years had no significant impact on the herbaceous layer in an Appalachian hardwood forest (Gilliam et al., 2006). Fernow has been the recipient of high levels of N deposition for decades, raising the possibility that the herbaceous layer responded long ago to changes in N availability.

Mycorrhizal and Microbial Diversity

Mycorrhizal and microbial biodiversity can also be affected by N enrichment. Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. Mycorrhizal fungal diversity has been shown to be associated with above-ground plant biodiversity and ecosystem productivity (Wall, 1999) and to be adversely affected by increased N availability (Egerton-Warburton, 2000). The loss of mycorrhizal function has been hypothesized as a key process contributing to reduced N uptake by vegetation and increased NO_3^- mobility from soil into drainage water under conditions of high N supply (EPA, 2004).

Progressive decline in ectomycorrhizal fungal species richness in Alaskan coniferous forest (white spruce [*Picea glauca*] dominant) occurred along a local N deposition gradient, from 1 to 20 kg N/ha/yr, downwind from an industrial complex (Lilleskov et al., 2002). Ectomycorrhizal fungal communities are important in tree nutrition, and ectomycorrhizal fungal trees tend to be dominant in N-limited forest ecosystems.

N fertilization at rates of 54 and 170 kg N/ha/yr (as NH_4NO_3) led to a decline in ectomycorrhizal fungal diversity and species composition in an oak savanna at Cedar Creek Natural History Area in

Minnesota (Avis et al., 2003). In the reference plots, five species collectively accounted for more than 40% cover versus four plant species in the lower N addition plots. In the higher N addition plots, a single plant species accounted for more than 40% cover.

Compton et al. (2004) investigated the effects of 11 years of experimental N addition on forest soil microbial ecology. Experimental N addition decreased the C content of microbial biomass in the O horizon of both experimental forest stands, based on chloroform fumigation-extraction. In addition, the use of N-containing substrates by microbes appeared to be reduced by N addition in the pine stand, but not in the hardwood stand. In addition, the use of N-containing substrates by microbes appeared to be reduced by N addition in the pine stand, but not in the hardwood stand. The mechanisms responsible for such changes are not clear (Arnebrandt et al., 1990; Compton et al., 2004). It is possible that added N has both direct (nutrient) and indirect (soil chemistry, organic matter quality, and quantity) effects on microbial ecology. Effects can be manifested on mycorrhizal fruiting body abundance, hyphal networks, and community composition (Lilleskov et al., 2002; Frey et al., 2004).

Grasslands

Reduced biodiversity in response to N deposition is reported for grasslands in the U.S. and Europe. Clark and Tilman (2008) recently evaluated the effects of chronic N deposition over 23 years in Minnesota prairie-like successional grasslands and in a native savanna grassland, each originally dominated by a species-rich mixture of native C_4 grasses and forbs.(Cedar Creek Long Term Ecological Research Site, Minnesota). Experimental N addition ranged from 10 to 95 kg N/ha/yr above ambient atmospheric N deposition (6 kg N/ha/yr). The N addition rate reduced plant species numbers by 17% relative to controls receiving ambient N deposition. Moreover, species numbers were reduced more per unit of added N at lower addition rates and relative species number was reduced at all addition levels. This suggests that chronic but low-level N deposition may decrease diversity below the lowest addition levels tested (the critical load was calculated as 5.3 kg N/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr). A second experiment showed that a decade after cessation of N addition, relative plant species number, although not species abundances, had recovered, demonstrating that some effects of N addition are reversible.

Change in species composition in response to N deposition has been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Stevens et al., 2004; Bobbink, 1992; Bobbink, 1998; Bobbink, 1998). A transect of 68 acid grasslands across Great Britain, covering the lower range of ambient annual N deposition (5 to 35 kg N/ha/yr), indicates that long-term, chronic N deposition significantly reduced plant species richness. Species richness declined as a linear function of the rate of inorganic N deposition, with a reduction of one species per 4–m^2 quadrant for every 2.5 kg N/ha/yr of chronic N deposition.

Grasslands are well known to respond to increased N availability through changes in growth rates of both native and exotic species. Under high N supply, exotic grasses often out-compete other species, and cause changes in plant community composition (Lowe, 2002). A summary of studies which have show altered plant community composition or growth rates of plant species that have implications for community composition is in Table 3-17. Increased availability of N to grasses can also affect herbivores that feed on grasses by altering food quality, quantity, and phenology, and also perhaps by changing the relationships between herbivores and their predators (Throop and Lerdau, 2004).

Table 3-17. Summary of N effects on grassland biodiversity.

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
San Francisco Bay Area, CA	Bay Checkerspot Populations	Observation: Serpentinitic soils sustain support native grasses that support populations of the endangered Bay Checkerspot butterfly. Several lines of evidence indicate that dry N deposition is responsible for grass invasion and subsequent decline of the butterfly population, however this relationship is uncertain.	Serpentine Grasslands Bay Checkerspot Butterfly (*Euphydryas Editha Bayensis*)	Weiss (1999)
Colorado	Growth	Greenhouse experiment: they tested the response of grassland species to increased N availability (0, 10, 40, 70, or 100 kg N/ha/yr) over 75 days. All of the grass species exhibited increased growth with increased N availability. Native species did not consistently grow better at low N levels than the exotic species. Two of the exotic grasses exhibited the greatest increase in growth, while another of the exotics exhibited the smallest increase in growth.	Two North American Native Species (Blue Grama And Western Wheatgrass) and Four Exotic Species (Cheatgrass, Leafy Spurge, Canada Thistle, and Russian Knapweed)	Lowe et al. (2002)
Plant Research Laboratory, University of Illinois at Chicago	Growth and Tissue Quality	Field Addition: N additions in (0.1, 1, 3 mmol N addition for 80 days), caused species-specific growth and plant tissue quality changes. C_3 grasses (*Elymus virginicus L., E. Canadensis L.*) showed a greater positive growth response to N additions than C_4 grasses (*Andropogon geradii Vitmanm, Schizachyrium scoparium Michx*.) and forbs (*Solidago nemoralis Ait., S. rigida L.*). Species with smaller initial biomass exhibited the greatest increase in biomass, with a sevenfold to eightfold increase in *S. nemoralis* and *E. canadensis* and only a threefold increase in *S. rigida*.	Tallgrass Prairie	Lane and BassiriRad (2002)
Jasper Ridge Biological Preserve in California	Species Richness and Diversity	Field addition: 70 kg N/ha/yr over three years led to decreased to a decline in total species richness, species diversity decreased by 5% and all three N-fixing forbs disappeared.	Nine Annual Species: *Avena Barbata, Bromus Hordeaceus, Lolium Multiflorum, Avena Fatua, Bromus Diandrus, Anagallis Arvensis, Geranium Dissectum Erodium Botrys, Vicia Sativa,* and one Biennial Species*, Crepis Vesicaria*	(Zavaleta et al., 2003)
Lund University, Lund, Southern Sweden	Growth	Greenhouse experiment: Sand-solution experiments studying how growth was effected by N concentrations of 50, 250 and 1250 μM in a simulated acid forest soil solution, similar to naturally occurring soil solutions is Southern Sweden. 46% of grasses displayed a significantly greater biomass at 250 than at 50 μM N as compared with only 7% for the herbs. Some species attained their highest biomass at 1250 μM N and others at 50 μM N. Grasses grew better than herbs in response to experimental addition of N. At the highest experimental N deposition rates, growth was limited for most species by the supply of nutrients other than N.	15 Herb and 13 Grass Species	Falkengren-Grerup (1998)
Minnesota, Cedar Creek Natural History Area	Species Composition	Field addition: N enrichment over a 12-year period on 162 plots using a N addition gradient from 0 to 30 g m-2 year-1. Plots initially dominated by native warm-season grasses shifted to low-diversity mixes of species dominated by cool-season grasses at all but the lowest rates of N addition. Grasslands with high N retention and C storage rates were the most vulnerable to loss of species and major shifts in N cycling in response to experimental N enrichment.	Three N-Limited Minnesota Grasslands with Varying Successional Age, Species Composition, and Total Soil C	Wedin and Tilman (1996)

Region/Country	Endpoint	Observations	Grassland Type/ Species	Reference
San Francisco Bay Area, CA	Species Composition	Observational: N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have been reported to have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system	Grasslands	Fenn et al. (2003a)
Jasper Ridge Biological Preserve in California	Npp	Field addition: 70 kg N/ha/yr applied as $(CaNO_3)_2$ increased NPP by 30%	Grasslands	Shaw et al. (2003)
Jasper Ridge Biological Preserve in California	Herbivory, Leaf Tissue N And Growth Rates	Field addition: 70 kg N/ha/yr applied as $(CaNO_3)_2$ caused altered herbivory by gastropod which differed by species (↓, ↑ and no change), 5 out of 6 species had increased leaf tissue, 5 out of 6 species had increased growth rates	Grasslands	Cleland et al. (2006)
Michigan old field	Biomass	Field addition: 120 kg N/ha/yr applied as NH_4NO_3 pellets had a significant positive growth effect on annual dicot biomass but no significant growth effect on annual grass biomass.	Grasslands	Huberty et al. (1998)
Brookhaven Nat. Lab., Long Island, New York and the Sciences greenhouse facility, SUNY, Stony Brook, NY	Vegetative and Seed Biomass and Decreased Root: Shoot Ratios	Field additions and Greenhouse experiment: N addition to common ragweed (*Ambrosia artemisifolia*) led to increased vegetative and seed biomass and decreased root: shoot ratios. N deposition may indirectly affect biomass production and allocation through affecting insect herbivory. The particularly strong influence of both herbivory and N deposition on *A. artemisiifolia* reproduction suggests potential population and community-level consequences.	*Ambrosia Artemisiifolia* (Common Ragweed) and two of its Insect Herbivores; a Leaf Beetle, *Ophraella Communa Lesage* (*Coleoptera: Chrysomelidae*), and an Aphid, Uroleucon Tuataiae Olive (*Hemiptera: Aphididae*)	Throop (2005)

Region / Country	Endpoint	Observations	Forest type / species	Reference
Europe	forest Biomass	Modeling: using growing stock of large forest regions over an entire country as empirical data, the authors determine forest biomass is accumulating, largely in response to increases in forest area and improved management, but other possible mechanisms of growth enhancement (including N) cannot be ruled out	Forests from Austria, Finland, Sweden, France, Germany , and Switzerland	Kauppi et al., 1992; Spiecker et al., 1996
Norway	growth (tree ring increments)	Deposition gradient: A comprehensive analyses of regional forest growth trends analyzed tree increment cores from more than 31,000 plots. In this study, growth increased during the 1960s and 1970s and then declined in the 1990s, especially in southern regions exposed to the highest rates of N deposition (Figure 4.3−7)	boreal forest (Picea abies and Pinus sylvestris)	Nellemann and Thomsen, 2001
Sweden	growth (stem volume)	Field addition: chronic fertilization at 30 kg N/ha/year continued to stimulate stemwood production even after 30 years, whereas a higher application (90 kg N/ha/year) decreased stem volume growth, and an intermediate application (60 kg N/ha/year) had little positive or negative effect relative to the control plots	Boreal forest Scots pine forest	Högberg et al., 2006
Bear Brook, ME, U.S.	growth (basal area)	Field Addition: basal area increment of sugar maple was enhanced 13 to 104% by addition of 25 kg N/ha/year as ammonium SO_4^{2-} ($(NH_4)_2SO_4$), whereas red spruce was not significantly affected.	sugar maple and red spruce	Elvir et al., 2003
Fernow Experimental Forest, WV, U.S.	growth	Field addition: The application of 35 kg N/ha/year as $(NH_4)_2SO_4$ enhanced growth of (Prunus serotina) and yellow poplar (Liriodendron tulipifera) during the first 7 years, but led to reduced growth of these species relative to control trees in years 9 through 12, with no change in red maple or weet birch (Betula lenta)	black cherry, yellow poplar, red maple, sweet birch	DeWalle et al., 2006
Harvard Forest, MA, U.S.	mortality	Field addition: chronic N addition levels of 50 and 150 kg N/ha/year for 15 years caused a 31% and 54% decrease, respectively, in red pine growth. As red pine has died, striped maple (Acer pensylvanicum), black cherry, and black birch (Betula lenta) have increased their contributions to annual litterfall production.	red pine, striped maple, black cherry, black birch	Magill et al., 2004
northeastern U.S.	live basal area	Field addition: In a high-elevation red spruce-balsam fir (Abies balsamea) forest in the, N fertilization over 14 years led to a decrease in live basal area (LBA) with increasing N additions. In control plots, LBA increased by 9% over the course of the study, while LBA decreased by 18% and 40% in plots treated, respectively, with 15.7 kg N/ha/year and 31.4 kg N/ha/year.	red spruce-balsam fir	(McNulty et al., 2005)
Harvard Forest, MA, U.S.	growth mortality root production	Field addition: N fertilization of a 50–year-old red-oak/red maple stand largely stimulated productivity, although the drought in 1995 induced significant mortality in small red maple trees. Fine root biomass was slightly, but not significantly, lower in highly fertilized stands relative to controls in both red pine and oak/maple ecosystems	old red-oak, red maple	Magill et al., 2004
Ysselsteyn, The Netherlands	growth root production	Field addition and deposition exclusion: improvements in wood accumulation rate, root production, and mycorrhizal associations occurred when a "clean roof" was installed at the site receiving the highest rate of N deposition (>40 kg N/ha/year). Decreased production of fine roots may predispose N-fertilized plants to be more sensitive to intermittent drought, as well as to nutrient depletion exacerbated by acid deposition.	Coniferous- Picea abies, Picea sitchesis, Pseudotsuga menziesii, Pinus sylvestris	Boxman et al., 1998b Emmett et al. Emmett

Region / Country	Endpoint	Observations	Forest type / species	Reference
Southern CA, U.S.	N- saturation- reduced soil base saturation, and lack of a growth response	Observational: Areas of chaparral and mixed conifer forests that receive very high levels of dry N deposition in southern California have experienced significant environmental change over the past several decades	chaparral and mixed conifer	Fenn et al., 1996, 2003a
CA, U.S.	Growth	Observational: Some southern California forests experience N deposition up to 45 kg N/ha/year, and that increased N deposition caused increased growth of Jeffrey and ponderosa pine stands.	mixed conifers; jeffrey and ponderosa pine	Takemoto et al., 2001
CA, U.S.	growth (productivity) and mortality	Observational: high inputs of reactive N appear to exhibit decreases in productivity and increases in mortality (Fenn, 1998).	Conifer forests	Fenn et al. (Fenn, 1998)
California	litter accumulation, above-ground woody biomass, fire susceptibility	Field addition: N fertilization has been shown to cause increased litter accumulation and C storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires.	Ponderosa pine	Fenn et al., 2003a
California	growth	increased N deposition caused increased growth for Jeffrey (Pinus jeffreyi) and ponderosa pine (Pinus ponderosa) stands,	mixed conifers	Takemoto et al. (2001)
North Carolina and Virginia	growth (basal area), foliar chemistry, nitrification and mineralization	Deposition gradient: Results from a study of 46 forest plots on six sites in North Carolina and Virginia dominated by American beech, sugar maple, and yellow birch suggested that N deposition is associated with changes in basal area, foliar chemistry, and nitrification and mineralization rates. Growth rates for the three tree species were similar at the lowest rates of N deposition, and then diverged as N deposition increased, with growth of yellow birch and American beech decreasing at the high N deposition loads. These differential growth rates have the potential to affect forest structure and biodiversity	American beech, sugar maple, and yellow birch	Boggs et al., (2005)
California, Sequoia National Park	growth	Field addition: Aspen (Populus tremuloides) have been reported to show positive growth effects from fertilization at N deposition rates as low as 10 kg N/ha/year	Aspen	Bytnerowicz, (2002)
Michigan	ANPP and surface soil organic matter	Field addition: Chronic N fertilization (30 kg N/ha/year) for 20 years caused significant increases in ANPP by 10% and surface soil organic matter (0–10 cm) by 26%	Sugar maple	Pregitzer et al. (2008)

Not all studies have shown an effect of N addition on species richness or diversity. In old agricultural fields in Michigan, increased N deposition changed neither the successional timing nor the gain or loss of species numbers (Huberty et al., 1998). A lack of response in species richness may have been due to application of mid-growing season fertilization in the experimental design. Huberty and colleagues (1998) suggested that N additions may change the dominance structure instead of the species composition, of these successional old-field communities. Other studies in Michigan on successional grasslands showed no response to N application of 10 kg N/m^2/yr, equivalent to about 2.5 times ambient deposition rates (Ambus and Robertson, 2006).

Arid and Semi-Arid Land Ecosystems

Some arid, and semi-arid ecosystems in the southwestern U.S. are considered sensitive to N enrichment effects and receive high levels of atmospheric N deposition. However, water is generally more limiting than N in these systems. Nevertheless, enhanced N may play a role in the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate.

In semi-arid ecosystems, results from several N fertilization experiments showed (1) increased biomass of nonnative plant species over native species, (2) decreased soil moisture under some conditions, and (3) increased fire risk where dense mats of grasses replaced shrub cover (See Table 3-18).

Much of the arid land data are from the coastal sage scrub (CSS) communities of southern California, down-wind of the Los Angeles Basin, where dry N deposition is very high. The CSS community in California has been declining in land area and in shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Padgett and Allen, 1999; Padgett et al., 1999). N deposition is considered a possible cause or contributor to this ecosystem alteration. More than 30 kg N/ha/yr of atmospheric N is deposited to portions of the Los Angeles Air Basin (Bytnerowicz and Fenn, 1996). The CSS community is of particular interest because about 200 sensitive plant species and several federally listed threatened or endangered animal species are found in the area.

Native shrub and forb seedlings in the CSS community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Eliason and Allen, 1997; Yoshida, 2001; Cione et al., 2002). Biodiversity impacts have also been documented for microbial communities in coastal sage scrub ecosystems. It has been hypothesized that the decline in coastal sage shrub species could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton, 2000).

Table 3-18. Summary of N effects on arid and semi-arid ecosystems.

Region/Country	Endpoint	Observations	Ecosystem Type/ species	Reference
Southeast Idaho	species composition and cover	Field addition: 6 or 12 kg N/ha/yr applied as NH_4NO_3 for 6 years (in addition to ambient inputs of 1.3 to 1.4 kg N/ha/yr) resulted in a decrease in soil moisture caused by shifts in plants species composition and cover. However, there were no effects on perennial grass cover in response to experimental N additions	sagebrush (Artemisia tridentata) steppe ecosystem	(Inouye, 2006).
southern California	Plant community	Observational: Dry N deposition is above 30 kg N/ha/yr in some places. Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire	coastal sage scrub	Eliason and Allen, 1997; Yoshida and Allen (Yoshida, 2001); Cione et al., 2002).
southern California	Plant community	Greenhouse and deposition gradient experiments: N deposition is considered a possible cause or contributor to declining shrub density over about the past 60 years and is being replaced in many areas by Mediterranean annual grasses	coastal sage scrub	Allen et al., 1998; Padgett and Allen, 1999; Padgett et al., 1999).
southern California	response of native and nonnative plants.	Greenhouse experiment: N (as 5.4 g/L NH_4Cl or 10g/L KNO_3) was added to obtain soil N concentrations of 2, 20, 40, and 80 µg/g. The grasses demonstrated a 1.5– to 2.5–fold growth increase when soil N levels increased from 20 to 40 µg/g. To achieve a comparable growth increase, shrubs required higher soil N levels (between 20 and 80 µg/g). These lab experiments agree with observations in the field, where exotic grasses, especially once established, have replaced native shrubs under elevated N deposition.	coastal sage scrub	Padgett and Allen, 1999
southern California	plant root-to-shoot growth ratios	Greenhouse experiment: Changes in plant root-to-shoot growth ratios were observed in the plant community, which is composed largely of the drought-resistant deciduous shrubs Artemisia californica, Encelia farinosa, and Eriogonum fasciculatum.	coastal sage scrub	(Padgett and Allen, 1999; Padgett et al., 1999).
southern California	response of native and nonnative plants.	Observational: more than 30 kg N/ha/yr of atmospheric N is deposited to this ecosystem in portions of the Los Angeles Air Basin). Decreases in the diversity of native plants paralleled increases in exotic grass biomass.	coastal sage scrub	(Bytnerowicz and Fenn, 1996

Region/Country	Endpoint	Observations	Ecosystem Type/ species	Reference
Colorado Plateau	response of native and nonnative plants.	Field addition: For 2 years, plots were treated with 0, 10, 20, or 40 kg N/ha/yr as a KNO_3 solution. Galleta (Hilaria jamesii) and Indian ricegrass (Oryzopis hymenoides) showed no increase in leaf photosynthesis or tiller size, but ricegrass showed a 50% increase in tiller density in the second year at the 20 and 40 kg N/ha/yr application levels. For both species, the increased N application hastened the onset of water stress. Unexpectedly, a non-native species, Russian thistle (Salsola iberica) showed a rapid growth response to the highest fertilization rate in the first summer, when rainfall was above average. The authors suggested that the timing and amount of N deposition could facilitate noxious weed invasion and thus change community composition in	arid grassland	(Schwinning et al., 2005)
Joshua Tree National Park, California	response of native and nonnative plants.	Deposition gradient: 18 locations, chosen to cover the dominant vegetation types (Creosote Bush Scrub, Joshua Tree Woodland, Pinyon Juniper Woodland), were sampled for atmospheric concentrations of NO, NO_2, NH_3, and soil [N]. The relationship between reactive atmospheric N concentrations and soil N were consistent in most sites. Observations along the N gradient did not reveal a clear relationship between non-native grass cover and soil N concentration up to 20 µg/g.	arid grassland	(Allen et al., 2007).
Joshua Tree National Park, California	response of native and nonnative plants.	Field addition: was applied at levels of 5 and 30 kg N/ha/yr at four sites over a 2–year period. Low-elevation sites were dominated by creosote bush scrub and higher-elevation sites by pinyon-juniper woodland. Non-native grass biomass increased significantly at three of four treatment sites that received 30 kg N/ha/yr, but not at the sites that received 5 kg N/ha/yr. A soil N concentration of 23 µg/g was conservatively considered the low threshold for significant plant N response based on this fertilization study.	arid grassland	Allen et al. (2007)
Western U.S.	Fire cycle	Observational: Vegetative changes stimulated by nutrient enrichment from N deposition may affect the frequency and severity of subsequent disturbance. Several lines of evidence suggest that N deposition may be contributing to greater fuel loads, thus altering the fire cycle in a variety of ecosystem types. Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations	arid grassland	(Fenn et al., 2003a)
San Francisco Bay area	response of native and nonnative plants	Observational: N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system. Since this change in species composition, populations of the rare and threatened bay checkerspot butterfly (Euphydryas editha bayensis) have declined greatly. It has been hypothesized that the response of the butterfly has been due to the vegetative changes.	grasslands dominated by exotic annuals such as wild oat (Avena fatua), brome (Bromus mollis), and ryegrass (Lolium multiflorum).	(Fenn et al., 2003a).

Mycorrhizal and Microbial Diversity

It has been hypothesized that the decline in coastal sage shrub species in California could be linked to the decline of the arbuscular mycorrhizal community (Egerton-Warburton, 2000). They discerned a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along a deposition gradient (2 to 57 µg N/g as soil NO_3^-). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by Mediterranean annual grasslands. Larger-spored fungal species (*Scutellospora* and *Gigaspora*) have decreased in number due to a failure to sporulate, with a concomitant proliferation of small-spored species. This pattern suggests selective pressure favoring the smaller spored species of fungi (Egerton-Warburton, 2000), and that N enrichment of the soil might alter the arbuscular mycorrhizal species composition and diversity.

Desert Ecosystems

Some desert ecosystems in the southwestern U.S. are considered sensitive to N enrichment effects and receive high levels of atmospheric N deposition. However, water is generally more limiting than N in these systems. Nevertheless, N deposition can stimulate plant growth and cause the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate. The majority of evidence is from field additions of N, levels ranging from 10–100 kg N/ha/yr (Table 3-19).

Fertilization experiments in the Mojave Desert showed that increased levels of N deposition could favor the establishment of nonnative species where the non-natives are already prevalent (Brooks, 2003). There is also evidence that N deposition decreases the growth of desert legumes (Baez et al., 2007). A link between N deposition and decrease in legumes has been found across other North American sites (Suding et al., 2005). The effect on legumes may be attributable to the fact that legumes, which are N fixers, often compete better under low N supply.

There is evidence from the desert ecosystems that N accumulates during periods of drought, and that more N is immobilized during periods of high precipitation (Stursova et al., 2006). Thus, where water and N appear to be co-limiting factors, the observed pattern of higher rates of N deposition during months with higher precipitation may result in a stronger fertilization effect than if N deposition were independent of precipitation (Hooper and Johnson, 1999; Asner et al., 2001; Knapp and Smith, 2001; McLain and Martens, 2006).

Table 3-19. Summary of N effects on desert ecosystems.

Region/Country	Endpoint	Observations	Grassland type/ species	Reference
Chihuahuan Desert	Growth response of native species	Field addition: 20 kg N/ha/yr addition in one season showed blue gramma (Bouteloua gracilis) was favored over black gramma (Bouteloua eriopoda), the current dominant species	blue gramma and black gramma	(Baez et al., 2007).
Jornada basin, New Mexico	Growth response of native species	Field addition: black grama and another dominate species, creosote bush (Larrea tridentate) did not significantly increase biomass after experimental additions of 25 kg N/ha/yr, but did after additions of 100 kg N/ha/yr	black grama and creosote bush	(Ettershank et al., 1978; Fisher et al., (1998)
Chihuahuan Desert,	Growth response of native species	Field addition: Additions of 100 kg N/ha/yr over about a decade, resulted in percent soil N that was 15–61% higher, extractable NO_3– that was 25–175% higher, and extractable NH_4 that was 247–1721% higher compared to control plots (Stursova et al., 2006). The resultant biologic effects were a 30% increase in cover of warm season grasses and a 52% reduction in cover of legumes (Baez et al., 2007).	Grasses and legumes	Stursova et al., 2006; Baez et al., 2007
Mojave Desert	Native vs. non-native	Field addition: At application rates of 32 kg N/ha/yrr over 2 years, both density and biomass of non-native plants increased (54% increased biomass), while native species biomass declined by about 39%. Plant responses were influenced by rainfall events rather than by average annual rainfall, with the annual plants thriving in a year when high rainfall events triggered germination.	grasses	(Brooks, 2003)
Great Basin Desert, sites near Mono Lake, CA	Growth and seed viability	Field addition: Sarcobatus vermiculatus, a desert shrub found demonstrated a twofold to threefold increase in stem growth, a 2.5 to 4 fold increase in viable seed production, and a 17% to 35% increase in leaf N with N additions. N was applied in March and November as NH_4NO_3, at a cumulative addition rate of 233.6 g N per plant.	Sarcobatus vermiculatu	Drenovsky and Richards, 2005
Mojave desert	growth response	Field addition: The shrub Larrea tridentata showed no increased growth response to N additions (at 10 and 40 kg N/ha/yras $CaNO_3$) but did respond to increased water	Larrea tridentata	(Barker et al., 2006).
Mojave and Sonoran deserts.	Navtive vs. non-native	Observational: Invasive annuals showed a greater response to elevated N than native species, and have recently invaded. Though their invasion is correlated with greater N deposition, no causation has been established.		Fenn et al., 2003a).

Lichens

Lichens are frequently used as indicators of air pollution and atmospheric deposition levels (see Annexes A and C for an additional discussion). In addition to being good subjects for biomonitoring, they constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune and Geiser, 1997).

Little is known about the mechanisms that control growth and resource partitioning in lichens, which are complex symbiotic systems comprised of a fungus (mycobiont) and a green alga and/or cyanobacterium (photobionts) (Palmqvist, 2000); Sundberg et al., 2001). Organic compounds required for growth are produced via photobiont photosynthesis. Production is strongly coupled with N utilization. The non-photosynthetic fungus comprises much of the lichen biomass and requires N for protein synthesis, nucleic acids and fungal cell wall (chitin) synthesis (Palmqvist et al., 1998). Carbon and N uptake must be balanced for coordinated development of lichen thalli (Sundberg et al., 2001).

Lichens can be classified on the basis of their response to atmospheric pollution. Nitrophytic lichens occur in areas that receive high atmospheric N deposition; acidophytic lichens are prevalent in areas that receive low N input (Rouss 1999, Van Herk 2001, Gaio-Oliveira et al. 2005). Lichens differ with respect to N requirements. Many lichens that have a cyanobacterial photobiont are N-fixing, whereas those with a green algal photobiont are dependent on atmospheric deposition for their N supply.

N-fixing lichen species are particularly affected by N deposition (Dahlman et al., 2002). Cyanobacteria have been shown to grow on either NO_3^- or NH_4^+ sources when administered at non-toxic concentrations. More rapid growth was observed with NH_4^+ fertilization as compared with NO_3^- fertilization (von Rückert and Giani, 2004). Amonium is more easily assimilated; both NO_3 and nitrite must first be reduced to NH_4^+ prior to assimilation (von Rückert and Giani, 2004).

Lichens with a green algal photobiont are solely dependent on atmospheric deposition as a source of N. However, a buildup of N within the thallus can lead to toxicity. Lichens exhibit varying degrees of sensitivity to increasing N deposition, owing to diverse mechanisms of responding to high N supply by reducing N uptake or assimilating N into non-toxic forms such as arginine (Gaio-Oliverira et al., 2001; Gaio-Oliverira et al., 2005; Dahlman et al., 2003).

Lichens that contain a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens (Hallingbäck, 1991; Hallingbäck and Kellner, 1992). In Sweden, the proportion of cyanobacterial lichens that has disappeared or is threatened is three times as large as the corresponding proportion of lichens having green algal photobionts (Hallingbäck, 1991). Low pH may be the most important effect of air pollution on *Peltigera aphthosa* in Sweden. Nevertheless, there is some indication that NH_4^+ in combination with SO_4^{2-} is more detrimental than low pH *per se* (Hallingbäck and Kellner, 1992). The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr (Bobbink et al., 1998). In fact, epiphytic cyanobacteria-containing lichens may be among the most sensitive species in humid forested ecosystems to atmospheric N deposition (Hallingbäck, 1991; Bobbink et al., 1998).

Epiphytic macro lichens (those that grow attached to trees or other plants) exhibit different sensitivities to atmospheric pollutants, with some species being adversely impacted at air pollution levels that may not be considered high relative to other sensitive receptors. Particularly sensitive genera include A*lectoria, Bryoria, Ramalina, Lobaria, Pseudocyphellaria, Nephroma,* and *Usnea* (McCune and Geiser, 1997; Blett et al., 2003).

Community composition of epiphytic lichens in the U.S. can be altered by relatively small increases in N deposition (Fenn et al., 2003a). Most epiphytic lichens meet their nutritional requirements from atmospheric deposition and can store N in excess of their nutritional needs (van Herk, 1999). Early work in the San Bernardino Mountains, California, lichen cover was inversely related to estimated oxidant doses (Sigal, 1983). In recent analysis it has been determined that up to 50% of lichen species that occurred in the region in the early 1900s have disappeared, with a disproportionate number of locally extinct species being epiphytic cyanolichens (Nash, 1999 ; Fenn et al., 2003a). The calculated critical load for lichen communities in mixed conifer forests in California is 3.1 kg/ha/yr (Fenn et al. 2008).

The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn et al., 2003a). However, in urban areas, intensive agricultural zones, and downwind of major urban and industrial centers in the Pacific Northwest, there are few air pollution-sensitive lichen species, such as epiphytic cyanolichens, and high N concentrations have been measured in lichen tissue (Fenn et al., 2003a). With N enrichment, especially around urban and agricultural areas, there is a shift towards weedy, nitrophilous lichen species (Fenn et al., 2003a). Replacement of sensitive lichens by nitrophilous species has undesirable ecological consequences. In late-successional, naturally N-limited forests of the Coast Range and western Cascade Mountains, for example, epiphytic cyanolichens make important contributions to mineral cycling and soil fertility (Pike, 1978; Sollins et al., 1980; Antoine, 2001), and together with other large, pollution-sensitive macrolichens, are an integral part of the food web for mammals, insects, and birds (McCune and Geiser, 1997). Sensitive lichen species appear to be negatively affected by N inputs as low as 3 to 8 kg N/ha/yr (Fenn et al., 2003a). (A summary of additional experiments on lichens is given by Table 3-20.)

Table 3-20. Summary of N effects on lichens.

Region/Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Netherlands	Species richness	Deposition gradient: Van Dobben, et al. (2001) recorded epiphytic lichen presence, tree bark chemical composition, and atmospheric concentrations of SO_2, NO_2 and NH_3 at 123 sites along depositional gradients. Relationships between atmospheric and bark chemistry and the composition of the lichen vegetation were evaluated (ter Braak and Wiertz, 1994). Results showed neearly all lichen species investigated were negatively effected by exposures to SO_2 and NO_2, collectively decreasing lichen species richness. Of somewhat less importance were the ecological factors such as bark pH, host tree species and tree diameter.	Epiphytic lichens	Van Dobben, et al. (van Dobben, 2001) ter Braak and Wiertz (1994)
Scotland and northern England	Community composition	Deposition gradient: The authors suggested that the empirical critical load of N deposition for protection of community composition of lichens and bryophytes was in the range of 11 to 18 kg N/ha/yr	Atlantic oak woods	Mitchell et al., 2005
Umea, Vasterbotten, Sweden	NH_4+ vs. NO_3 uptake rate	Isotopic tracer: In a study of ^{15}N uptake in 14 lichen associations (for simplicity, designated as "species"), found that NH_4^+ uptake was significantly greater, and to a higher extent passive, relative to amino acid or NO_3^- sources of N. Differences were also observed in NO_3^- uptake, depending on photobiont group; cyanobacterial lichens had a lower NO_3^- uptake rate than green algal lichens. Morphology and microhabitat were not found to be associated with N uptake	Cyanobacterial lichens and green algal lichens	Dahlman et al (2004)
Sweden	NH_4^+ vs. NO_3 uptake	The assimilation and allocation of externally added N was investigated for two N-fixing tripartite (possessing both green algal and cyanobacterial phytobionts) lichen species, Peltigera aphthosa and Nephroma articum. N uptake ranged from 2 to 27 percent of the 5 kg N/ha/yr that was applied during the experiment over a 3 month period. Atmospheric deposition in this part of Sweden (~5 kg N/ha/yr was about one-fourth the total experimental N application rate. NH_4^+ was absorbed to a greater extent than was NO_3^-. In general, ^{15}N levels of NH_4^+ treated thalli were about four times higher than for NO_3^- treated thalli. To some extent, this may reflect the increased energy requirements of NO_3^- reduction as compared with NH_4^+ assimilation (Raven et al., 1992) and/or the adsorption of positively charged NH_4^+ on the negatively charged functional groups present on hyphal cell walls.	*Peltigera aphthosa* and *Nephroma articum*	Dahlman et al., 2002
Sweden	NH_4^+ vs. NO_3 uptake	$NH_4^+$to be the preferred N source for the green algal foliose lichen *Plathismatia glauca*, followed by glutamine and then NO_3^-. This species responded to increased N availability by increasing growth rate and C assimilation capacity through increased investment in the photobiont cells	*Plathismatia glauca*, a foliose lichen	Palmqvist and Dahlman (2006)
Pampulha reservoir (Belo Horizonte, Brazil)	NH_4^+ vs. NO_3 growth	Cyanobacteria have been shown to grow on either NO_3^- or NH_4^+ sources when administered at non-toxic concentrations. More rapid growth was observed with NH_4^+ fertilization as compared with NO_3^- fertilization. Ammonium is more easily assimilated; both NO_3 and nitrite must first be reduced to NH_4^+ prior to assimilation	Cyanobacteria	von Rückert and Giani, 2004
Sweden	NH_4^+ in combination with SO_4^{2-}	Low pH may be the most important effect of air pollution on *Peltigera aphthosa* in Sweden. Nevertheless, there is some indication that NH_4^+ in combination with SO_4^{2-} is more detrimental than low pH per se (Hallingbäck and Kellner, 1992).	*Peltigera aphthosa*	Hallingbäck and Kellner, 1992
Santo Antonio, near Serra de Aire Candeeiros Natural Park, central Portugal	NH_4^+ uptake Physiological responses	Comparison of the physiological responses of two lichens to increased N supply. Uptake was quantified using ^{15}N labeled NH_4^+. Cholorophyll a and ergonsterol were used as indirect markers of algal and fugal activity, respectively. The acidophytic lichen *Evernia prunastri* showed greater N uptake from NH_4^+ than the nitrophytic lichen Xanthoria parietina. In the acidophytic lichen, but not the nitrophytic lichen, ergosterol concentrations decreased with increasing N uptake, and an increase in the NH_4^+ pool was also observed at the highest N doses (216 kg N/ha/yr, applied as nine applications over a 2-month period). These differences can partially explain the higher tolerance of *X. parietina* to high N deposition.	*Evernia prunastri* and *Xanthoria parietina*	Gaio-Oliveira et al. 2005

Alpine

Herbaceous plants in alpine communities are considered very sensitive to changes in N deposition. A combination of short growing season, strong seasonal variation in moisture and temperature, shallow and poorly developed soils, steep terrain, sparse vegetation, and low rates of primary productivity generally limit the N uptake and retention capacity of herbaceous plant species in alpine ecosystems (Fisk, 1998) Burns, 2004). Alpine herbaceous plants are generally considered N-limited and changes in alpine plant productivity and species composition have been noted in response to increased N inputs (Vitousek, 1997; Bowman et al., 2006). See Table 3-21.

Research on N enrichment effects on alpine and subalpine ecosystems in the Western U.S. has mainly been limited to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge LTER site, both located east of the Continental Divide in Colorado (see review by Burns, 2004). Changes in alpine plant species composition on Niwot Ridge have included increased cover of the plant species that tend to be most responsive to N fertilization in some of the long-term monitoring plots (Korb and Ranker, 2001; Fenn et al., 2003a). These changes are likely due to response to changes in N deposition. However, the influences of climatic change, particularly changes in precipitation (Williams et al., 1996), and pocket gopher disturbance (Sherrod and Seastedt, 2001) could not be ruled out as contributors to vegetation change (Fenn et al., 2003a). Other environmental factors also affect the species make-up of alpine ecosystems, but long-term experimental fertilization plots demonstrate a clear response of alpine flora to N, including shifts toward graminoid plants that shade smaller flowering species, and accompanying changes in soil N cycling (Bowman et al., 2006).

Table 3-21. Summary of N effects on alpine ecosystems.

Region/Country	Endpoint	Observations	Ecosystem Type / Species	Reference
Niwot Ridge, CO and Southern Wyoming	Community shift	Field addition: 25 kg N/ha/yr added during summer caused a community shift towards greater dominance of hairgrass (*Deschampsia sp.*) in wet alpine meadows, but the increase in plant biomass (+67%) and plant N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows than in forb-dominated wet meadows (+53% plant biomass, +64% standing N crop, respectively)	Wet and dry alpine meadow,alpine tundra, talus, alpine and subalpine forest—Englemann spruce, Bristlecone pine, surface waters, algae, amphibians	Bowman et al. (1995); Burns (2004).
Niwot Ridge, CO	Plant foliage productivity species richness.	Field addition: Showed that 4 years of N addition to alpine vegetation at rates ranging between 100 and 200 kg N/ha/yr (depending on the year) caused marginal increases in alpine plant foliage productivity but reduced species richness.	Wet and dry alpine tundra- sedge *Kobresia myosuroides*. *Acomastylis rossii*, *Polygonum viviparurn Trifolium*. A.rossii and *Deschumnpsia caespitosa. D. caespitosa*, *Caltha leptosepala*, *Sibbaldia procurnbens* and *Trifolium parryi.*	Seastedt and Vaccaro (Seastedt, 2001)
Niwot Ridge, CO	Species composition species diversity plant biomass tissue [N]	Field addition: Additions of 20, 40, and 60 kg N/ha/yr (on top of ambient N deposition near 5 kg N/ha/yr) over an 8–year period to a dry alpine meadow led to a change in plant species composition, an increase in species diversity and plant biomass, and an increase in tissue N concentration at all treatment levels within 3 years of application. Much of the response was due to increased cover and total biomass of sedges (*Carex spp*.). There was a significant decrease in Kobresia biomass with increasing N input. Vegetation composition appeared to respond at lower N input levels than those that caused measurable changes in soil inorganic N content. Changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr. Changes in the plant community, based on the first axis of a detrended correspondence analysis, were estimated to occur at deposition levels near 10 kg N/ha/yr. In contrast, increases in NO_3^- leaching, soil solution NO_3^- concentration, and net nitrification occurred at levels above 20 kg N/ha/yr. The authors concluded that changes in vegetation composition preceded detectable changes in soil indicators of ecosystem response to N deposition.	Dry alpine meadow	Bowman et al. (2006)

Mycorrhizae across ecosystems

Microbial biodiversity can also be affected by N enrichment. Interactions between atmospherically deposited N and terrestrial vegetation frequently occur in the rhizosphere. The rhizosphere includes the soil that surrounds and is influenced by plant roots (Wall, 1999). Relationships among plant roots, mycorrhizal fungi, and microbes are critical for N cycling and for the growth and health of plants. The plant provides shelter and C; the fungi and bacteria provide access to potentially limiting nutrients, particularly N and P.

A meta-analysis of the effect of N and P fertilization on mycorrhize observed a 15% decrease in mycorrhizal abundance due to N fertilization across 16 studies at 31 sites, covering a range of grassland, shrubland, temperate and boreal forest ecosystems (Treseder, 2004). Declines in mycorrhizal abundance were slightly higher at higher rates of N fertilization, but there was significant variation across all studies. The loss of mycorrhizal function has been hypothesized as a key process contributing to reduced N uptake by vegetation and increased NO_3^- mobility from soil into drainage water (EPA, 2004).

NO_3^- versus NH_4^+ deposition

Plants also exhibit different degrees of response to NO_3^- versus NH_4^+ deposition. In general, fast-growing annual species, including many agricultural crops, and fast growing pioneer trees such as birch (*Betula* spp.) prefer NO_3^- (Pearson and Stewart, 1993). Slow-growing perennial plant species generally prefer NH_4^+. There are also many plant species which readily utilize both NO_3^- and NH_4^+ (Krupa, 2003). These include members of the family Ericaceae (e.g., *Calluna, Erica, Vaccinium*), conifer trees, and climax species such as *Quercus* and *Fagus* (Krupa, 2003).

3.3.5.2. Transitional Ecosystems

Wetlands in the U.S. support over 4200 native plant species, of which 121 are federally threatened or endangered (http://plants.usda.gov/). Wetlands can be divided into three general categories based on hydrology. Hydrologic pathways are often the same pathways of N input; therefore they are useful for discussing the N sources and sensitivity to atmospheric N deposition. Nearly all new N comes from atmospheric deposition in ombrotrophic bogs because they only receive water inputs via precipitation and they develop where precipitation exceeds evapotranspiration and where there is some impediment to drainage of the surplus water (Mitsch and Gosselink, 1986). Fens, marshes and swamps are characterized by ground and surface water inputs that are often on the same order of magnitude as precipitation (Koerselman 1989). Lastly, intertidal wetlands receive water from precipitation, ground/surface water and marine/estuarine sources.

The balance of competition among plant species in some sensitive wetland ecosystems can be altered by N addition, with resulting displacement of some species by others that can utilize the excess N more efficiently (EPA, 1993). The sensitivity of wetlands is particularly important given that they contain a disproportionately high number of rare plant species that have evolved under N-limited condition (Moore et al., 1989) (See Annex D). In general these include the genus *Isoetes sp.,* of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila;*

and the genus *Sphagnum*, of which there are 15 species are listed as endangered by Eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York (http://plants.usda.gov/).

Freshwater wetlands

Peatlands and bogs are among the most vulnerable transitional ecosystems to adverse nutrient-enrichment effects of N deposition (Krupa, 2003). The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker, 1994). The genus *Sphagnum* dominates ombrotrophic bogs and some nutrient poor fens in the Northern US and Canada. These mosses efficiently capture atmospheric deposition with retention rates between 50–90%, much of the variation due to the depth of the water Table (Aldous 2002a). Studies conducted on 4 species of Sphagnum in Maine (2 to 4 kg N/ha/yr ambient deposition) and New York (10 to 13 kg N/ha/yr ambient deposition) document that higher N deposition resulted in higher tissue N concentrations (Aldous 2001) and greater NPP (Aldous 2002a), but lower bulk density (Aldous 2002a). A study of *Sphagnum fuscum* in six Canadian peatlands showed a weak, although significant, negative correlation between NPP and N deposition when deposition levels were greater than 3 kg N/ha/yr ($y = 150 – 3.4x$, $p=0.04$, $r^2=0.01$) (Vitt et al. 2003). A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition ($y = 2.84x +0.67$, $r^2 =0.32$, $P < 0.001$), however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore et al. 2004).

The sensitivity of peatland *Sphagnum* species to elevated atmospheric N deposition is well documented in Europe (Berendse et al., 2001; Tomassen et al., 2004). *Sphagnum squarrosum* and *S. fallax* have been observed to be negatively affected by experimentally elevated atmospheric N and S inputs in Europe (Kooijman and Bakker, 1994). Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York.

Sarracenia purpurea is a long lived (30–50 years) northern pitcher plant and widely distributed in bogs, fens and swamps across Canada and the eastern U.S. (Ellison, 2002). *S. purpurea* has adapted to nutrient poor environments and very sensitive to increasing N input. In a study of *S. purpurea* in Vermont and Massachusetts, Ellison and Gotelli (Ellison, 2002) conducted a series of N enrichment experiments by augmenting N availability to leaves with 0, 0.1 and 1 mg N/L NH_4^+ solution for one growing season. Population growth rates, estimated by demographic survey, were positive for 0 and 0.1 mg N/L additions (equal to atmospheric deposition of 0–1.4 kg N/ha/yr)[1] and negative for 1 mg N/ L additions (equivalent to 10–14 kg N/ha/yr)* (Gotelli and Ellison 2006). Based on the annual demographic rates, a non stationary matrix model forecasted that the extinction risk within the next 100 years increased substantially if N deposition rate increase (1–4.7%) from the rate of 4.5–6.8 kg N/ha/yr (Gotelli and Ellison 2002).

Increasing N availability not only reduced population growth of *S. purpurea*, also dramatically altered plant morphology. *S. purpurea* produces carnivorous leaves (pitcher) and photosynthesis efficient leaves (phyllodia). N enrichment was shown to stimulate the photosynthesis rate and increase the production of phyllodia relative to pitcher (Ellison, 2002). The field N deposition simulation experiment (ranged from 0–35 kg N/ha/yr)* revealed a positive linear relationship between N deposition level and relative keel size (keel width/total width). This correlation was supported by the field surveys of 26 sites across Massachusetts and Vermont (Ellison, 2002), and 39 sites across Canada and eastern U.S. (Ellison et al. 2004). The relative kneel size of northern pitcher plant increased with increasing NH_4^+ concentration in soil water, and may be used as bio indicator (log $[NH_4^+]$ = -1.57 + 1.78x relative keel size).

In wet heathlands in Europe, changes in plant species composition have been attributed to elevated atmospheric N deposition (Roem and Berendse, 2000). Diverse plant communities have been replaced by monospecific stands Dutch wet heathlands (Aerts and Berendse, 1988; Houdijk et al., 1993). In other studies, wetland species such as *Calluna vulgaris* can successfully compete with grasses even at relatively high rates of N deposition, as long as the vegetative canopies are closed (Aerts et al., 1990). However, N deposition causes nutrient imbalances, and increased plant shoot-to-root ratio, and therefore increases in the sensitivity of shrubs to drought stress, frost stress, and attack by insect pests (Heil and Diemont, 1983). These can result in gaps in the canopy of the shrub layer, which can then be readily invaded by grasses that are more efficient in using the additional N and therefore gain a competitive advantage (Krupa, 2003).

Riparian wetlands

Marler et al. (2001) evaluated the potential impacts of experimentally elevated stream water nutrient concentrations on three riparian wetland tree species: Fremont cottonwood (*Populus fremontii*),

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[1] N treatments were selected to represent annual N deposition measured at the nearest monitoring sites of National Atmospheric Deposition Program (NADP). The unit of N treatments reported in the publication was precipitation-weighted mean concentrations (mg N/ L), from which we calculated the level of deposition (kg N/ha/yr) using the equation: *Deposition= Precipitation-Weighted Mean Concentrations* × A*nnual Precipitation*. More detailed information on nitrogen deposition is available on the NADP website: http://nadp.sws.uiuc.edu/sites/ntnmap.asp?

Goodding willow (*Salix gooddingii*), and exotic saltcedar (*Tamarix ramosissima*) in the riparian zone of the Salt River near Phoenix, Arizona. The results from this 43−day experiment showed that growth of all three riparian plant species responded positively to increased nutrient supply (treatment 3 and 4) (Marler et al., 2001). The exotic and invasive salt cedar showed the greatest increases in biomass at high nutrient supply. Other studies have also found that exotic plant species often respond more rapidly than native vegetation to increased nutrient supply (Milberg et al., 1999; Paschke et al., 2000). This experiment was conducted to simulate impacts of wastewater effluent on riparian zones, and N additions were therefore very large nutrient supply to riparian systems via atmospheric N deposition in the U.S. is more typically in the range of treatments in this experiment that showed minimal response to N addition.

Intertidal wetlands

Wetland eutrophication could significantly damage the structure and function of coastal marshes. N enrichments were shown to facilitate the invasion of nonnative species (Tyler et al. 2007); shift the competition between native species (Mendelssohn. 1979; Wigand et al. 2003; Crain 2007); increase herbivore damage on plants (Bertness et al. 2008); stimulate evapotranspiration (Howes et al. 1986); change microbial community and pore water chemistry (Caffrey et al. 2007); and alter carbon allocation between root and shoot (Darby and Turner 2008). The majority of N fertilization experiments add levels of N orders of magnitude above that expected by atmospheric deposition. A summary of experiments at addition levels below 400 kg N/ha/yr is given in Table 3-22.

Table 3-22. Summarized responses of coastal marshes ecosystem to N fertilization. The Table includes studies in which the lowest fertilization treatment is below 400 kg N/ha/yr, a value at the higher end of the range that includes direct and indirect N deposition.

Site	Species	Responses	N enrichment	Reference
Walden Creek (NC)	Spartina alterniflora	Field addition: 1) increased the growth of short Spartina, but had no effect on tall Spartina; 3) biomass production of short Spartina increased linearly with N addition; 2) ammonium showed higher growth stimulation on short Spartina than NO_3 does	0, 280, 560, 1120 kg N/ha/yr	Mendelssohn et al. 1979
Narragansett Bay (RI)	Spartina patens; Spartina alterniflora	Field addition: 1) decreased the density and extent of S patens; 2) decreased the extent of tall S. alterniflora increased with	N gradient from 9 to 3282 kg N/ha/yr	Wigand et al. 2003
Great Sippewissett Marsh (MA)	Spartina alterniflora	Field addition: increased live above ground biomass, leaf area coverage, evapotranspiration	396 kg N/ha/yr	Howes et al. 1986

3.3.5.3. Freshwater Aquatic Ecosystems

Paleolimnological studies

The paleolimnological method of taxonomic identification of fossil diatoms in lake sediments has been augmented in recent years with cell counts and pigment concentrations of chlorophyll and chlorophyll derivatives, rendering inferences about trophic state from proxies preserved in sediments more robust than before (Das, 2005). Paleolimnological studies of mountain lakes that have only been disturbed by atmospheric deposition and climate change have reported changes in diatom species assemblages, increases in cell numbers, and pigment-inferred increases in whole lake primary production. These inferred changes have been coincident with regional surrogates for increased N deposition. Such changes have included increases in human population, industrial animal production, and fossil fuel combustion emissions (Wolfe et al., 2001, 2003; Saros, 2003; Das, 2005). In most, but not all, of these studies, the observed changes in ecology were inconsistent with changes in climate and more concordant with effects from increased atmospheric N deposition.

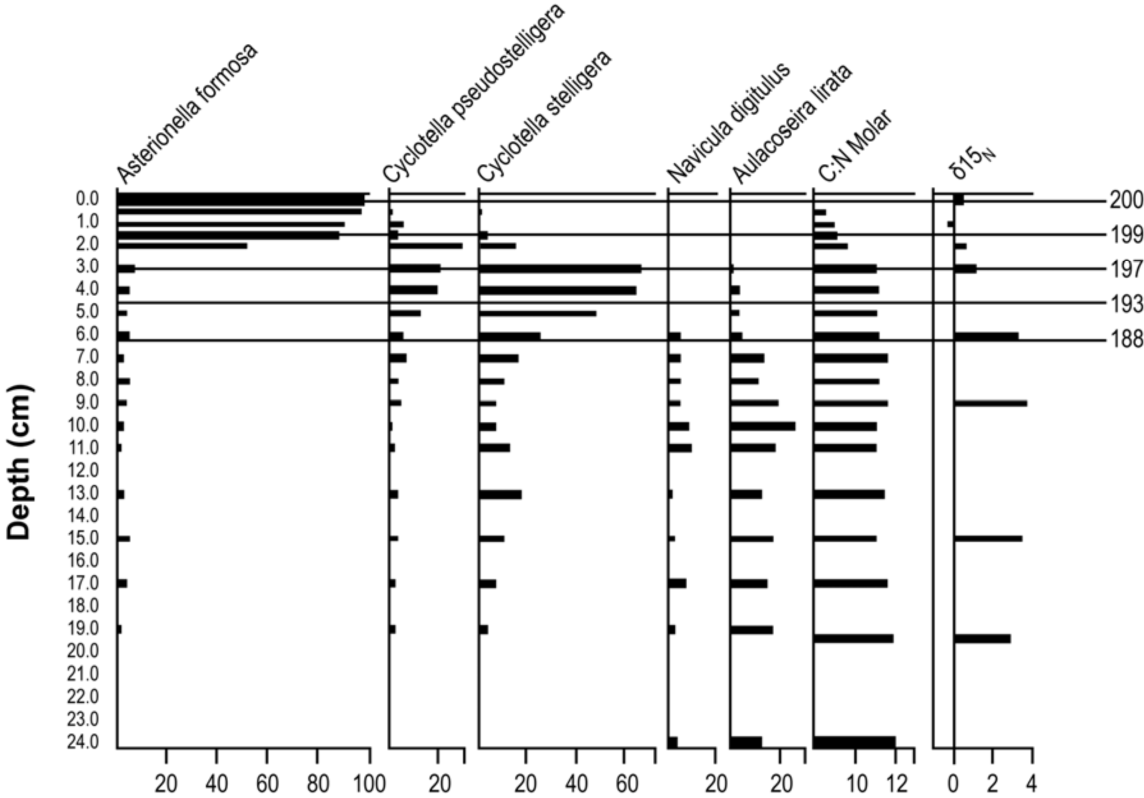
Available data suggest that the increases in total N deposition do not have to be large in order to elicit an ecological effect. For example, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros, 2003). Pre-industrial inorganic N deposition is estimated to have been only 0.1 to 0.7 kg N/ha based on measurements from remote parts of the world (Galloway, 1995) Holland et al., 1999). In the western U.S., pre-industrial, or background, inorganic N deposition was estimated by Holland et al. (1999) to range from 0.4 to 0.7 kg N/ha/yr.

Bioassay, mesocosm, and laboratory experiment

Bioassay, mesocosm, and laboratory experiments have been conducted on algae (both phytoplankton and periphyton), invertebrates, amphibians, and fish, in order to determine effects of N on sensitive aquatic organisms (see Annex C). Some freshwater algae are particularly sensitive to the effects of added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Interlandi and Kilham, 1998; Baron, 2000; Wolfe et al., 2001, 2003; Saros, 2003; Saros, 2005). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains (Figure 3-49). These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world (See Annex D for additional discussion).

Further evidence for the relationship between N enrichment and algal changes has been provided by N addition studies that include in situ mesocosm studies (McKnight et al., 1990; Lafrancois, 2004; Saros, 2005) and in situ incubations in large lakes (Interlandi and Kilham, 1998). Differences in resource requirements allow some species to gain competitive advantage over others upon nutrient addition, causing changes in species composition (Wolfe et al., 2001, 2003; Lafrancois, 2004; Saros, 2005). A summary of these experiments is given in Table 3-23. This is in keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species diversity was maintained when N levels were low (< 3 µM) in lakes in the Yellowstone National Park region.

The implication of this research is that species diversity declines with increasing availability of N. In studies of lake sediment diatom remains, typical oligotrophic species such as *Aulacoseria perglabra*, *Cyclotella steligera*, and *Achnanthes spp*. declined coincident with the rise in dominance of *A. formosa* and *F. crotonensis* (Wolfe et al., 2001, 2003).



Source: Saros et al. (Saros, 2003)

Figure 3-49. Diatom assemblage sediment patterns in Emerald Lake, WY.

Community shifts in phytoplankton other than diatoms have also been observed under conditions of elevated N availability (Lafrancois, 2004). For example, a positive correlation between the proportion of the phytoplankton comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of 15 Snowy Range lakes (Lafrancois, 2003). Chlorophytes, like the two diatom species identified above, generally have a preference for high concentrations of N and are able to rapidly dominate the flora when N concentrations increase (Findlay et al., 1999). This occurs in both circumneutral and acidified waters (Wilcox and Decosta, 1982; Findlay et al., 1999).

In summary, survey data and fertilization experiments demonstrate that increase in algal productivity, as well as species changes and reductions in biodiversity, have occurred at sensitive high elevation lakes in the western U.S. in response to increased availability of N.

Table 3-23. N effects on species composition and biodiversity

Region	Endpoint	Observation	Ecosystem type	Reference
Snowy Range, Wyoming	Community shifts in phytoplankton	Mesocosm experiment: correlation between the proportion of the phytoplankton comprised of chrysophytes and the concentration of NO_3^- in lake water was found in a survey of 15 lakes. Chrysophytes were favored in lakes having lower N and cyanophytes and chlorophytes favored in lakes having higher N	lakes	Lafrancois et al. (Lafrancois, 2003)
Beartooth Mountains of Montana-Wyoming	Diatom community	Paleo and observational: evaluation of resource requirements for dominant diatom species with paleolimnological reconstructions and contemporary surveys of the flora of seven lakes. Results reinforced the likelihood that recent increases in dominant diatom numbers have been the result of N enrichment rather than climatic change	lakes	Saros et al. (Saros, 2005)
Colorado Front Range	Community shifts in phytoplankton	Paleo: Sediment cores showed increasing representation of mesotrophic diatoms in recent times, as compared with pre-development conditions	lakes	Wolfe et al., 2001
Lake Tahoe, CA	Community shifts in phytoplankton	Paleo: there has been a sharp increase in the ratio of araphidinate pennate to centric diatoms since about 1950 (largely due increases in *Fragilaria crotenensis*), associated with increased N loading to the lake. Jassby et al. (Jassby, 1994) showed that atmospheric deposition supplies most of the N to Lake Tahoe.	lake	Goldman (Goldman, 1988)
Rocky Mountain Lakes, Colorado	growth	In situ mesocosm: incubations the growth of the diatom A. formosa has been stimulated with N amendments during from 6.4 to 1616 μM N	Diatoms	McKnight et al., 1990;
Yellowstone National Park, Wyoming	growth	In situ incubations in large lakes: stimulated F. crotonensi. This publication did not reveal how much N was added to the incubations	lakes	Interlandi and Kilham, 1998
		The N requirements for A. formosa and F. crotonensis were determined to be 0.041 μM and 0.006 μM, respectively, and higher concentrations stimulated growth	Alpine lakes	Michel et al., 2006

3.3.5.4. Estuarine and Marine Ecosystems

In coastal ecosystems, eutrophication can cause changes in marine biodiversity and species composition. Phytoplankton production and community composition in estuarine and marine environments also respond to differences in the form of atmospheric N input. Major algal functional groups, including diatoms, dinoflagellates, cyanobacteria, and chlorophytes, may show different responses to changing mixtures of added N (Paerl et al., 2002). Differential phytoplankton responses, in turn, may cause changes in the species composition of zooplankton, herbivous fish, and higher trophic levels of aquatic biota.

Phytoplankton

In addition to causing increased phytoplankton biomass, as indicated by chlorophyll a measurements (see Section 3.3.3.4), excess N can contribute to changes in phytoplankton species composition. High loadings of N and P can also increase the potential for Si limitation, with associated changes in diatoms. Such changes to the phytoplankton community can also affect higher trophic levels. For example, Officer and Ryther (1980) and Turner et al. (Turner, 1998) suggested that a shift in the Si-to-N atomic ratio to less than 1 would alter the marine food web. Specifically, the diatom-to-zooplankton-to-higher tropic level ratios would decrease, whereas flagellated algae (including those that often contribute to hypoxia) would increase (Paerl, 2001).

Changes in phytoplankton species abundances and diversity have been further documented through in situ bioassay experiments such as the results reported by Paerl et al. (Paerl, 2003) for the Neuse River Estuary in North Carolina. Effects were species-specific and varied dramatically depending on whether, and in what form, N was added. The findings illustrate the potential impacts of N additions on phytoplankton community structure (see Figure 3-50).

Changing phytoplankton community composition has numerous potential ecological ramifications, including modifications to the ecosystem food web and nutrient dynamics. For example, if the nutrient mix favors species that are not readily grazed (e.g., cyanobacteria , dinoflagellates), trophic transfer will be poor and relatively large amounts of unconsumed algal biomass will settle to the bottom, which could stimulate decomposition, O_2 consumption, and the potential for hypoxia (Paerl, 2003).

Reduced vs. Oxidized N

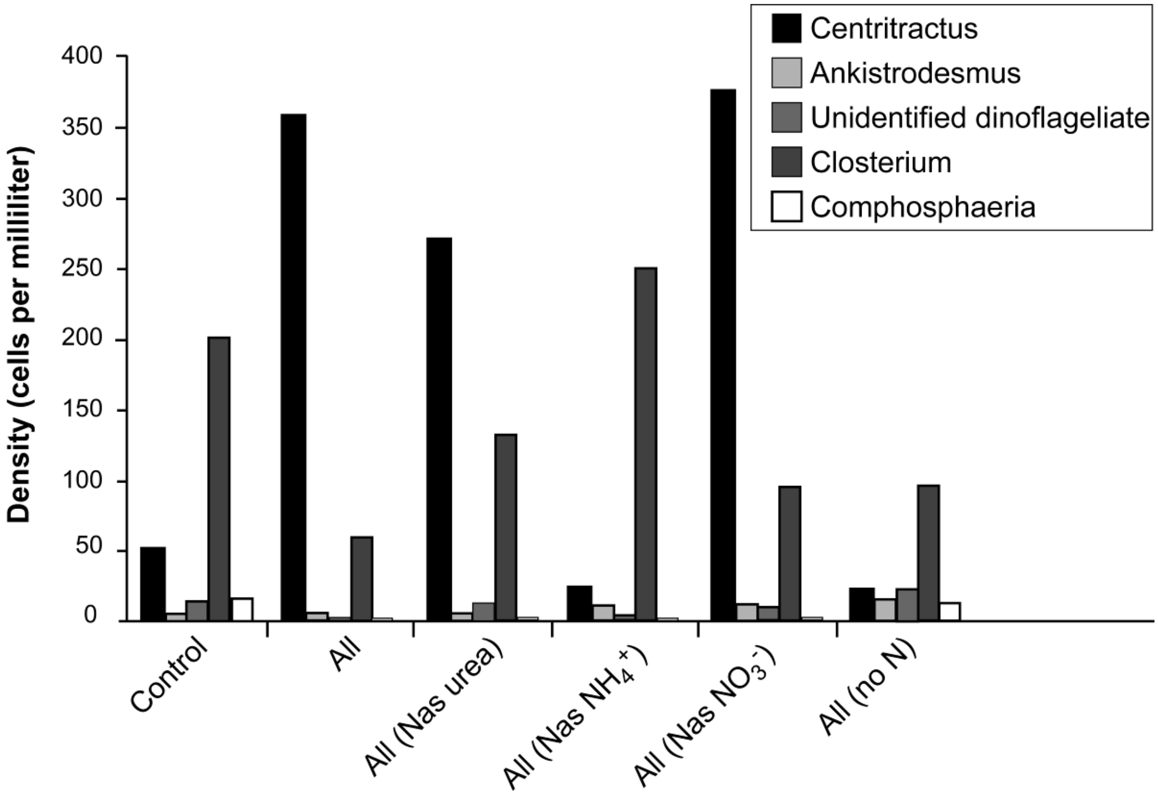
The form of N input to coastal aquatic ecosystems has an important influence on its effects. Atmospheric deposition of reduced N has increased relative to oxidized N in the eastern U.S., and this trend is expected to continue in the future under existing emissions controls. Such patterns can influence marine eutrophication responses. Some studies suggest that large diatoms tend to dominate coastal waters when NO_3^- is supplied (Stolte, 1994; Paerl, 2001), whereas smaller diatom species have a greater preference for NH_4^+ uptake. Thus, ongoing trends of decreasing NO_3^- deposition and increasing NH_4^+ deposition might lead to changes in species distributions and size distributions of phytoplankton, with cascading effects on trophic structure and biogeochemical cycling (Paerl, 2001).

Not all studies have found different levels of algal response depending on the form of N applied. For example, Richardson et al. (2001) examined the effects of different forms of N application (NO_3^-, NH_4^+, urea) on the structure and function of estuarine phytoplankton communities in mesocosm experiments in the Neuse River Estuary, NC. Even though NH_4^+ is more readily taken up by phytoplankton in this estuary than is NO_3^- (Twomey, 2005), results of the Richardson et al (2001) study suggested that phytoplankton community structure was determined more by the hydrodynamics of the system than by the form of N available for growth.

Twomey et al. (2005) measured Neuse River Estuary phytoplankton uptake rates of NH_4^+, NO_3^-, and urea. Ammonium was the dominant form of N taken up, contributing about half of the total N uptake throughout the estuary. Uptake varied spatially; in particular NO_3^- uptake declined from 33% of the total uptake in the upper estuary to 11% and 16%, respectively in the middle and lower estuary. Urea uptake contributed least to the total in the upper estuary (16%) but comprised 45 and 37% of the total N uptake in the middle and lower estuary. Therefore, N budgets based only on inorganic forms may seriously underestimate the total phytoplankton uptake (Twomey, 2005).

Submerged Aquatic Vegetation (SAV)

SAV provides important nursery grounds to many estuarine fish. There are few data documenting the long-term response of SAV in coastal ecosystems to N loading. The national assessment (Bricker, 2007) suggested that only a small fraction of the estuary systems evaluated reported high severity of SAV loss. Most of those that did report moderate or high loss were located in the Mid-Atlantic region. However, where SAV loss is a problem, the results can be severe, and there is evidence suggesting a correlation with increases in N loading. For example, at Waquoit Bay, Massachusetts, Valiela et al. (1990) reported a strong negative relationship between modeled N loading and measured eelgrass area based on measurements of eelgrass coverage from 1951 to 1992.



Source: Paerl et al. (Paerl, 2003)

Figure 3-50. Microscopic counts of phytoplankton species composition in the Neuse River Estuary, NC following 36–h in situ bioassays to manipulate available forms of N. Treatments included a control (unamended estuarine water sample), all nutrients (N, P, vitamins, trace metals, and Si), all with urea as the N form, all with ammonium (NH_4^+) as the N form, all with NO_3^- as the N form, and all with no N. Bars represent the mean density of cells present (three replicate counts for each treatment).

3.3.5.5. Summary

Terrestrial

The evidence is sufficient to infer a causal relationship between N deposition on the alteration of species richness, species composition and biodiversity in terrestrial ecosystems. The ecological effects of N deposition were described for a variety of taxa and ecosystem types including: forests, grasslands, arid and semi-arid, deserts, lichens, alpine, and mycorrhizae. The most sensitive terrestrial taxa are lichens. Empirical evidence indicates that lichens in the U.S. are adversely affected by deposition levels as low as 3/ha/yr. Among the most sensitive ecosystems are Alpine ecosystems; alteration of plant cover of an individual species (*Carex rupestris*) in Alpine communities were estimated to occur at deposition levels near 4 kg N/ha/yr and modeling indicates that deposition levels near 10 kg N/ha/yr alter plant community assemblages.

Wetland

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in wetland ecosystems. The effect of N deposition on wetland ecosystems depends on the fraction of rainfall in its total water budget and the sensitivity to N deposition was suggested as: bogs > fens > intertidal wetlands (Morris, 1991).

Excess N deposition can cause shifts in wetland community composition by altering competitive relationships among species, which potentially leads to effects such as decreasing biodiversity, increasing non-native species establishment and increasing the risk of extinction for sensitive and rare species. Wetlands contain a high number of rare plant species (Moore et al., 1989; EPA, 1993; Bedford and Godwin, 2003). High levels of atmospheric N deposition increase the risk of decline and extinction of these species that are adapted to low N conditions. In general these include the genus *Isoetes sp*., of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila*; and the genus Sphagnum, of which there are 15 species are listed as endangered by Eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York (http://plants.usda.gov/). In the U.S., *Sarracenia purpurea* can be used as a biological indicator of local N deposition in some locations (Ellison, 2002).

Freshwater Aquatic

The evidence is sufficient to infer a causal relationship between Nr deposition and the alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems. Evidence from multiple lines of research and experimental approaches support this observation, including paleolimnological reconstructions, bioassays, mesocosm and laboratory experiments. Increased N deposition can cause a shift in community composition and reduce algal biodiversity. Elevated N deposition results in changes in algal species composition, especially in sensitive oligotrophic lakes.

In the west, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros, 2003).

Some freshwater algae are particularly sensitive to added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom (a group of algae), Asterionella formosa and Fragilaria crotonensis, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Interlandi and Kilham, 1998; Baron, 2000)Wolfe et al., 2001, 2003; Saros, 2003; Saros, 2005). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains. These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

Estuarine Aquatic

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in estuarine ecosystems. Increased N deposition can cause shifts in community composition, reduced hypolimnetic DO, reduced biodiversity, and mortality of submerged aquatic vegetation. The form of deposited N can significantly affect phytoplankton community composition in estuarine and marine environments. Small diatoms are more efficient in using NO_3^- than $NH4^+$. Increasing $NH4^+$ deposition relative to NO_3^- in the eastern U.S. favors small diatoms at the expense of large diatoms. This alters the foundation of the food web. Submerged aquatic vegetation is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor contributing to declines in submerged aquatic vegetation coverage. The Mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of submerged aquatic vegetation due to eutrophication. Indicators to assess the eutrophic condition of estuarine and coastal waters are given in the following table:

3.3.6. N_r Deposition Effects on NO_3^- Toxicity

NO_3^- in freshwater at extremely high concentrations can have direct adverse effects on many life stages of fish, as well as on invertebrates and amphibians. These effects occur at levels that are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition, and therefore NO_3^- concentration has not been defined as a primary biological indicator. These effects are described in Annex C.

3.3.7. Critical Loads and Other Quantified Relationships between Deposition Levels and Ecological Effects

This section highlights a variety of sensitive chemical and biological receptors that have been used in developing critical loads for nutrient effects of N deposition on natural ecosystems. Sensitive receptors for effects of excess nutrient N deposition on surface water could include water chemistry, productivity, and the response of important taxa. Key sensitive receptors for assessing impacts on soil include soil chemistry and soil solution chemistry. Sensitive receptors for flora include macro-lichens and vascular plant species that are adapted to nutrient-poor environments. In some cases, the chemical receptors may be easier to characterize, although they likely also reflect important biological changes that may be more difficult to document. Background information on critical loads is presented in Annex C`.

The ecological indicators that are used for critical loads are considered important aspects of the ecosystem. Perturbation of these endpoints is ecologically adverse. Empirical models of critical loads for nutrient-N have been in use in Europe for some time (e.g., UNECE, 2004). Efforts have begun to develop empirical relationships in the U.S.

3.3.7.1. Empirical Critical Loads for Europe

Within the United Nations Economic Commission for Europe (UNECE) Long Range Transboundary Air Pollution (LRTAP) convention, empirical procedures have been developed to set critical loads for atmospheric N deposition to protect against effects caused by nutrient enrichment. Empirical critical loads of N deposition for natural and semi-natural terrestrial and wetland ecosystems were first presented in a background document for the 1992 LRTAP workshop on critical loads held at Lökeberg, Sweden (Bobbink, 1992). A number of European expert workshops have taken place in order to reach agreement among specialists regarding the impacts of N deposition on various ecosystems and related critical loads (Nilsson, 1988; Bobbink, 1992; Hornung, 1995; Bobbink et al., 1996; Achermann, 2003).

Information from the period 1996–2002 on the effects of increased N deposition on the structure and function of natural and semi-natural ecosystems in Europe was evaluated in Bobbink et al. 2003. The updated N critical loads were discussed and approved by full consensus at the November 2002 expert meeting held under the LRTAP Convention in Berne (Switzerland, (Achermann, 2003). Values for areas with low N deposition were updated by a CLRTAP workshop on critical loads of N in low-deposition areas (Stockholm, Sweden, March 2007) and adopted by ICP M&M and WGE in 2007. The resulting values are given in Table 3-24.

Table 3-24. Biological indicators for the effects of elevated N deposition and related empirical critical loads for major ecosystem types (according to the eunis classification) occurring in Europe.

Ecosystem Type	Biological Effect Indicators	Empirical Critical Load (kg N/ha/yr)
Grasslands and tall forb habitats (E)		
Sub-atlantic semi-dry calcareous grassland	Increased mineralization, nitrification and N leaching; increased tall grasses; decreased diversity	15–25
Non-mediterranean dry acid and neutral closed grassland	Increase in nitrophilous graminoids, decline of typical species	10–20
Inland dune grasslands	Decrease in lichens, increase in biomass, accelerated succession	10–20
Low and medium elevation hay meadows	Increased tall grasses, decreased diversity	20–30
Mountain hay meadows	Increase in nitrophilous graminoids, changes in diversity	10–20
Moist and wet oligotrophic grasslands	Increase in tall graminoids, decreased diversity, decrease in bryophytes	10–25
Alpine and subalpine meadows	Increase in nitrophilous graminoids, changes in diversity	10–15
Moss and lichen dominated mountain summits	Effects on bryophytes and lichens	5–10
Heathland habitats (F)		
Northern wet heaths	Decreased heather dominance, transition heather to grass, decline in lichens and mosses	10–20
Dry heaths	Transition heather to grass, decline in lichens	10–20
Arctic, alpine, and subalpine scrub habitats	Decline in lichens, mosses, and evergreen shrubs	5–15
Coastal habitat (B)		
Shifting coastal dunes	Increased biomass, increased N leaching	10–20
Coastal stable dune grasslands	Increase in tall grasses, decreased prostrate plants, increased N leaching	10–20
Coastal dune heaths	Increase in plant production, increased N leaching, accelerated succession	10–20
Moist to wet dune slacks	Increase in biomasss and tall graminoids	10–25
Mire, bog, and fen habitats (D)		
Raised and blanket bogs	Changed species composition, N saturation of Spagnum	5–10
Poor fens	Increased sedges and vascular plant, negative effects on mosses	10–20
Rich fens	Increase in tall graminoids, decreased diversity, decrease of characteristic mosses	15–35
Mountain rich fens	Increase in vascular plants, decrease in bryophytes	15–25
Forest habitats (G)		
Mycorrhizae	Reduced sporocarp production, reduced below ground species composition	10–20
Ground vegetation	Changed species composition, increased nitrophilous species; increased susceptibility to parasites (insects, fungi, virus)	10–15
Lichens and algae	Increase in algae; decrease in lichens	10–15

Source: Adapted from Achermann and Bobbink (2003).

3.3.7.2. U.S.

Efforts have begun to develop empirical relationships in the U.S., particularly for western ecosystems, however there is currently no published national assessment of empirical critical loads for N in the U.S., nor is there an assessment for the continent of North America. Table 4-4 summarizes publications of deposition levels and related ecological effects, presenting critical load levels when reported in the original publication. Table 4-4 includes N levels at which effects are manifested in terrestrial and freshwater ecosystems that have been documented through N addition and deposition gradient studies. Several important studies from Europe published after the assessment by Bobbink et al. are included in addition to some publications from Asia. Dose-response relationships between N and environmental indicators are given in Table 3-25.

In terrestrial ecosystems, the reported effect levels range from 4 to 5 kg N/ha/yr for changes in the abundance of individual sensitive alpine plant species, to 20 kg N/ha/yr for community level changes in alpine plant communities. Clark and Tilman (2008) calculate the CL for the onset of reduced relative species number in grasslands to be 5.3 kg N/ha/yr with a 95% inverse prediction interval of 1.3–9.8 kg N/ha/yr. A critical load of 3.1 kg N/ha/yr is considered protective of lichen communities in the West (Fenn et al. 2008).

Differences in the levels at which increased nitrification and NO_3^- leaching have been observed in eastern and western watersheds. For example, Rueth (2002) observed increased rates of nitrification in old-growth forests in Colorado at approximately 5 kg N/ha/yr, whereas Aber et al. (2003) associated the onset of NO_3^- leaching in eastern forests with deposition levels of 7 to 10 kg N/ha/yr. The critical load for NO_3^- leaching in Western chapparal ecosystems is 17 kg N/ha/yr (Fenn et al. 2008).

There is evidence that freshwater wetlands in the U.S. and Canada that are dominated by Sphagnum sp. are affected by N deposition. Most evidence documents N retention, peat accumulation and changes in NPP, and is not sufficient to quantify a critical load. The suggested critical load for protecting the population health of northern pitcher plant is 10–14 kg N/ha/yr (Ellison, 2002)Gotelli and Ellison 2006). There are no publications suggesting critical loads for coastal marsh ecosystems.

Table 3-25. Summary of dose-response curves for N deposition and ecological indicators.

Ecosystems	Deposition range (kg $N/ha^2/yr$)	Effect	Indicator	Study region	Response curve	Reference
N deposition						
Forest	1–75	Nutrient enrichment	N leaching	65 forest sites across Europe	$Y = 0.48 \times X - 2.17$ (r2=0.69; $P<0.001$) Y: N leaching(kg $N/ha^2/yr$) X: total inorganic N deposition (kg $N/ha^2/yr$)	Dise and Wright (Lawrence, 2007) (1995)
Forest	2–8* *wet deposition only	Acidification/ Nutrient enrichment	%N in the Oa horizon	12 red spruce stands across the northeastern US	$Y=0.097 \times X+1.03$ ($r^2=0.63$) Y: N content in the Oa horizon (%) X: wet inorganic N deposition (kg $N/ha^2/yr$)	Driscoll et al. (Driscoll, 2001)
Forest	0–50 *throughfall N	Acidification/ Nutrient enrichment	Soil solution NO_3-N	104 European monitoring site	Conifers: Y=0.06e0.132x ($r^2=0.59$ P=0.0001) Deciduous: Y=0.018e0.266x ($r^2=0.65$ P=0.0001) Y : NO_3– concentration in soil water (avages Jan 1996 to Jan. 1998) (mg N /L) X: throughfall N deposition (averages 1993–1997) (kg $N/ha^2/yr$)	Gundersen et al. (Gundersen, 2006)

Ecosystems	Deposition range (kg N/ha^2/yr)	Effect	Indicator	Study region	Response curve	Reference
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	Soil solution NO_3-N	104 European monitoring site	Conifers: log(Y)=0.06X-1.2 (r^2=0.59 P=0.0001) Broadleaves: log (Y)=0.12X-1.8 (r^2=0.65 P=0.0001) Y : NO_3– concentration in soil water (averages Dec 1995 to Feb. 1998) (mg N/L) X: Throughfall N deposition (averages 1993–1997) (kg N/ha^2/yr)	Kristensen et al. (Kristensen, 2006)
Forest	0–25 *Bulk precipitation N	Acidification/ Nutrient enrichment	Soil solution NO_3-N	104 European monitoring site	Conifers: log(Y)=0.09X-1.3 (r^2=0.32 P<0.0001) Broadleaves: log (Y)=0.09X-1.18 (r^2=0.16 P=0.02) Y : NO_3– concentration in soil water (avages Dec 1995 to Feb. 1998) (mg N/L) X: Bulk precipitation N deposition (averages 1993–1997) (kg N/ha^2/yr)	Kristensen et al. 2006
Forest	Relation between throughfall and bulk precipitation N input			104 European monitoring site	Conifers: Y=1.8X-2.3 (r^2=0.65 P<0.0001) Broadleaves: Y=0.86X-4.9 (r^2=0.32 P=0.0008) Y : Throughfall N deposition (averages 1993–1997) (kg N/ha^2/yr) X: Bulk precipitation N deposition (averages 1993–1997) (kg N/ha^2/yr)	Kristensen et al. 2006
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	Foliage N	104 European monitoring site	Conifers: Y=0.14X+12.7 (r^2=0.40 P<0.0001) Y: Foliage N concentration (mg/g) X: Throughfall N deposition (averages 1993–1997) (kg N/ha^2/yr)	Kristensen et al. 2006
Forest	0–40 *throughfall N	Acidification/ Nutrient enrichment	C:N organic layer	104 European monitoring site	Conifers: Y= -0.21X+31.5 (r^2=0.19 P=0.0002) Broadleaves : Y= -0.48X+32.3 (r^2=0.14 P=0.036) Y: C:N organic layer X: Throughfall N deposition (averages 1993–1997) (kg N/ha^2/yr)	Kristensen et al. 2006
Grassland	5–35	Acidification/ Nutrient enrichment	Species richness	68 acid grasslands across UK	Y=23.3 – 0.408 ×X (r^2=0.70; P<0.0001) Y: plant species richness X: total inorganic N deposition (kg N/ha^2/yr)	Stevens et al. 2004
Lakes	1–16* *wet deposition only	Nutrient enrichment	water [DIN]	4296 lakes across USA, Canada and Europe	logY = 1.34×logX-1.55 (r^2=0.70; P<0.001) Y: water DIN (µg/L) X: wet deposition (kg N km-2yr-1)	Bergstrom and Jansson 2006
Lakes	1–16* *wet deposition only	Nutrient enrichment	Chl a: Tot-P	515 lakes across USA, Canada and Europe	Log Y = 1.03 ×ln(logX)-1.43 (r^2=0.52; P<0.001) Y: Chl a : Tot-P X: wet deposition (kg N km-2yr-1)	Bergstrom and Jansson 2006
Surface water	3.1 to 17.6 * * Net anthropogenic nitrogen inputs (NANI)	Nutrient enrichment	Riverine exports of anthropogenic N	16 watersheds from Maine to Virginia	Y=(0.00087×Q-0.096) × NANI – 101 Y: Riverine N flux (kg N km-2/yr) Q: rivine discharge NANI: Net anthropogenic N inputs (N km-2/yr)	Howarth et al. 2006
Surface water	4–12	Acidification/ Nutrient enrichment	Surface water [NO_3–]	220 lakes and streams across the northeastern US	Summer: Y=2.5×X-14.4 (r^2=0.30, P<0.001) Spring: Y=6.7×X-40.7 (r^2=0.38, P<0.001) Y: NO_3– concentration in water (µmol/L) X: N deposition (kg N/ha^2/yr)	Aber et al. (2003)
Stream water	5–13	Acidification/ Nutrient enrichment	N export	83 lakes and streams across the northeastern US	Y=0.85×X-5.8 (r^2=0.56, P=0.01) Y: NO_3– export (kg N/ha^2/yr) X: N deposition (kg N/ha^2/yr)	Aber et al. (2003)
Stream water	5–13	Acidification/ Nutrient enrichment	Inorganic N retention	83 lakes and streams across the northeastern US	Y=-0.07×X+1.44 (r^2=0.50, P=0.01) Y: inorganic N retentions (kg N/ha^2/yr) X: N deposition (kg N/ha^2/yr)	Aber et al. (2003)

Ecosystems	Deposition range (kg N/ha^2/yr)	Effect	Indicator	Study region	Response curve	Reference
Estuary	8–24* *N loads from atmospheric deposition, human waster water and fertilization application	Nutrient enrichment	Eelgrass area (ha)	Waquoit Bay	Y=-1.9×X + 50.7 (r^2=0.89) Y: Eelgrass area (ha) X: modeled N load (kg N/ha^2/yr)	Driscoll et al. 2003
Peatland	0–160	Acidification/ Nutrient enrichment	NPP of Sphagnum fuscum	8 bogs in North America and Europe	Y=831*e-0.185x – 48 (r^2=0.73, P<0.01) Y: difference between NPP of Sphagnum fuscum under augmented N and control treatment (g m-2yr-1); X: N deposition (kg N/ha^2/yr)	Vitt et al. 2003
Peatland	2–20	Nutrient enrichment	Decomposition of litter collected from the field and incubated and constant temperature	12 bogs from 9 European countries	Y= 0.98*0.21ln(x) (r^2 =0.75, P <0.01) four days incubation Y= 0.49*0.11ln(x) (r^2= 0.73, P<0.01) 10 days incubation Y= N deposition (g m-2/yr) X= CO2 emission (mg/g/h)	Bragazza et al. (2006)
Peatland	2–20	Nutrient enrichment	Decomposition of litter collected from the field and incubated and constant temperature	12 bogs from 9 European countries	Y= 4.3*2.4ln(x) (r^2=0.61, P=0.01) Y= N deposition (g m-2/yr) X= DOC concentration (mg/g)	Bragazza et al. (2006)
Peatland	2.7 to 8.1 kg N/ha/yr	Nutrient enrichment	Showed N accumulation increases linearly with N deposition	23 ombrotrophic peatlands in Canada	y = 3.50x +0.64, r^2 =0.29, P<0.001 Y= N wet deposition (g m-2/yr) X= N accumulation in soil (g m-2/yr)	Moore et al. 2004
Spruce forest	5 to 30 kg N/ha/yr	Nutrient enrichment N20 flux	showed a significant and positive correlations between increasing N deposition and increasing N2O flux	2 sites in Germany and Ireland	y= 4.7 + 1.4x, r^2 = 0.38, P < 0.001 Y= N wet deposition (mmol m-2) X= N2O flux rates (µg N2O-Nm-2/h)	Butterbach-Bahl et al., 1998

3.3.8. Characterization of Sensitivity and Vulnerability

3.3.8.1. Extent and Distribution of Sensitive and Vulnerable Ecosystems

In general, ecosystems that are most responsive to nutrient enrichment from atmospheric N deposition are those that receive high levels of N loading, are N-limited, or contain species that have evolved in nutrient-poor environments. Species that are adapted to low N supply will often be more readily outcompeted by species that have higher N demand when the availability of N is increased (Aerts, 1990; Tilman and Wedin, 1991; Krupa, 2003). As a consequence, some native species can be eliminated by N_r deposition (Ellenberg, 1985; Falkengren-Grerup, 1986, 1989; Roelofs, 1986; Stevens et al., 2004). Note the terms “low” and “high” are relative to the amount of bioavailable N in the ecosystem and the level of deposition.

The following discussion of sensitive ecosystems is organized into three ecosystem categories: terrestrial, transitional, and aquatic. Case studies are intended to highlight ecosystems and/or regions where there are many publications documenting the effects of N deposition, thus they can provide sufficient data for quantitative risk assessment.

Terrestrial

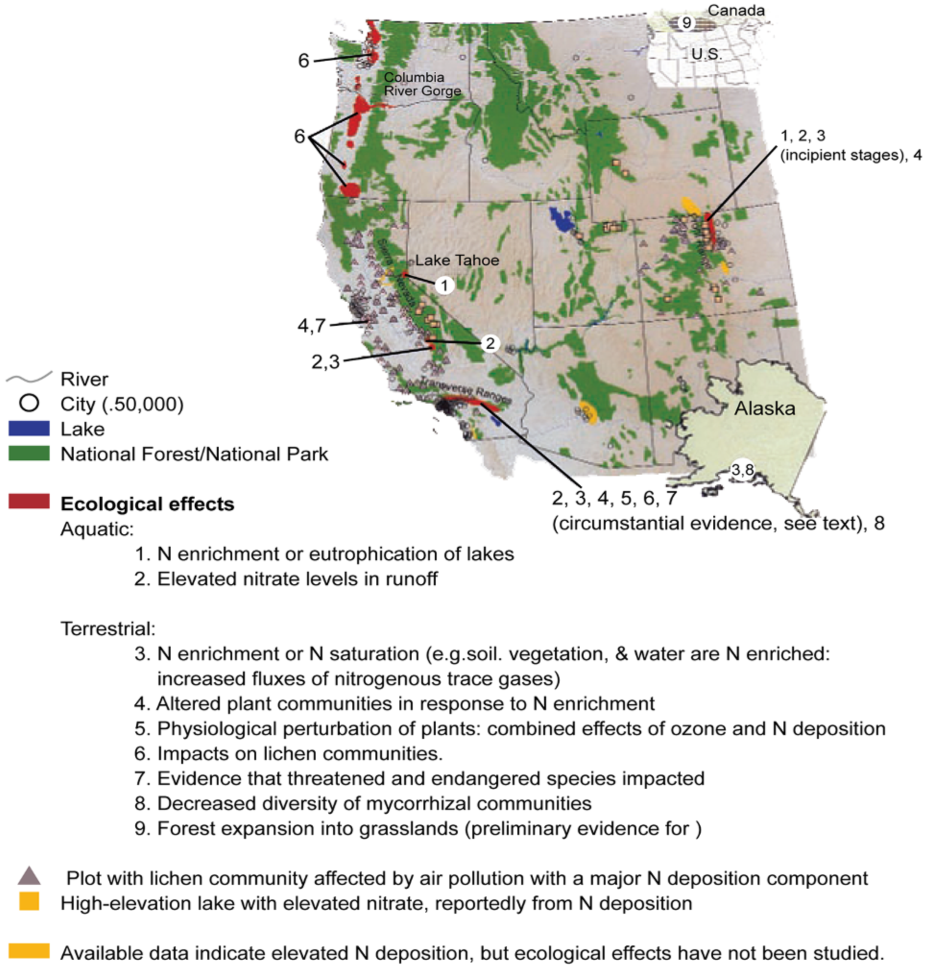
Most terrestrial ecosystems are N-limited, therefore they are sensitive to perturbation caused by N additions (LeBauer, 2008). Little is known about the full extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to adverse impacts caused by nutrient enrichment from atmospheric N deposition. Effects are most likely to occur where areas of relatively high atmospheric N deposition intersect with N-limited plant communities. The factors that govern the vulnerability of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation, rates and form of N deposition, elevation, species composition, length of growing season, and soil N retention capacity.

Regions and ecosystems in the western U.S. where N enrichment effects have been documented in terrestrial ecosystems are shown on Figure 3-51 (Fenn et al., 2003a). The alpine ecosystems of the Colorado Front Range (see case study), chaparral watersheds of the Sierra Nevada, lichen and vascular plant communities in the San Bernadino Mountains (see case study) and the Pacific Northwest, and the southern California coastal sage scrub community are among the most sensitive terrestrial ecosystems.

In the eastern U.S., the degree of N saturation of the terrestrial ecosystem is often assessed in terms of the degree of NO_3^- leaching from watershed soils into ground water or surface water. Stoddard (1994) estimated the number of surface waters at different stages of saturation across several regions in the eastern U.S. Of the 85 northeastern watersheds examined, 40% were in N-saturation Stage 0, 52% in Stage 1, and 8% in Stage 2 (stages are defined in Section 3.3.2.1). Of the northeastern sites for which adequate data were available for assessment, those in Stage 1 or 2 were most prevalent in the Adirondack and Catskill Mountains. Effects on individual plant species have not been well studied in the U.S. More is known about the sensitivity of particular plant communities. Based largely on results obtained in more extensive studies conducted in Europe, it is expected that the more sensitive terrestrial ecosystems include hardwood forests, alpine meadows, arid and semi-arid lands, and grassland ecosystems.

Transitional

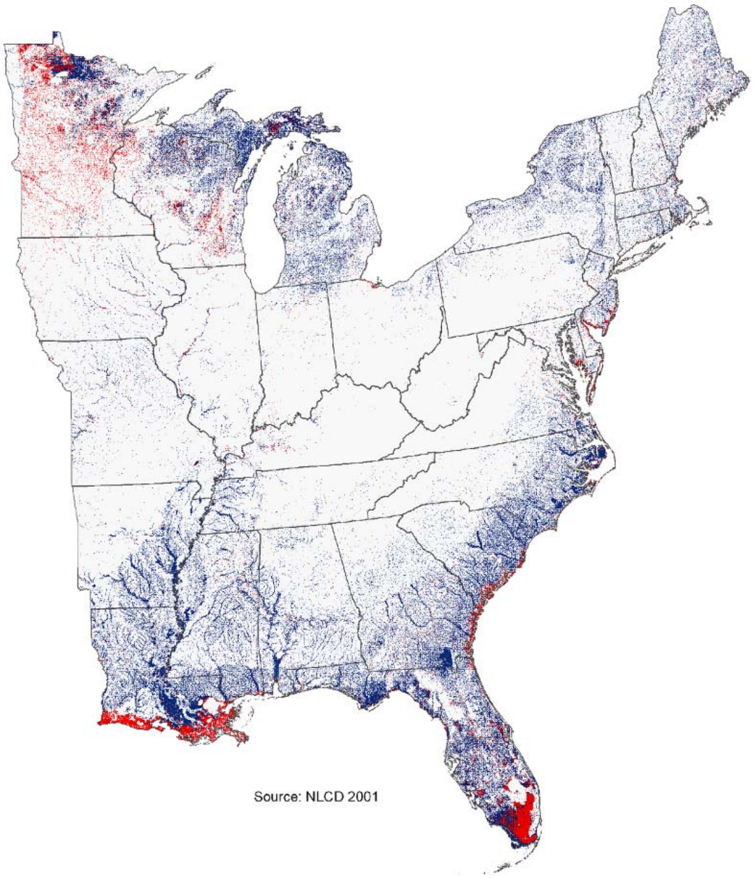
About 107.7 million acres of wetlands are widely distributed in the conterminous U.S., 95 percent of which are freshwater wetlands and 5 percent are estuarine or marine wetlands (U.S. FWS 2005; Figure 3-52). At one end of the spectrum, ombrotrophic bogs are very sensitive to N_r deposition because they receive exogenous nutrients exclusively from precipitation, and the species in them are adapted to low levels of N (Shaver and Melillo 1984, Bridgham et al. 1995, 1996). Intertidal wetlands are at the other end of the spectrum; in these ecosystems marine/estuarine water sources generally exceed atmospheric inputs by one or two orders of magnitude (Morris, 1991). Data are not available with which to evaluate the extent to which wetlands in the U.S. have been affected by nutrient enrichment from N deposition. Wetlands are widely distributed, including some areas that receive moderate to high levels of N deposition.



Source: Fenn et al. (2003a)

Figure 3-51. Map of the western U.S. showing the primary geographic areas where N deposition effects have been reported. Eutrophication effects are more widespread and of greater importance than acidification effects in western North America. Areas where effects of air pollution on lichen communities have been reported in California are represented by pink triangles. The plots in northcentral Colorado where lichen community changes were observed are exposed to emissions of both N and sulfur (S) from two large power plants in Craig and Haydens, Colorado (Peterson and Neitlich, 2001). The areas shown in red in Oregon and Washington (lichen communities affected by N deposition) are kriged data (Geiser and Neitlich, 2007). Only lakes at an elevation greater than 1000 m and with a NO_3 concentration of more than 5 µeq/L (measured in fall surveys or on an annual volume-weighted basis) are shown in this figure. Other high-elevation lakes in the West also had elevated NO_3 concentrations, but were excluded because N sources other than N deposition may have contributed to the elevated concentrations of NO_3.

Peat-forming bog ecosystems are among the most sensitive transitional ecosystems to the effects of N deposition. In the conterminous U.S., peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (EPA, 1993a). In Alaska, these ecosystems are common in poorly drained locations throughout the state.



Source: Data were obtained from the National Land Cover Data (NLCD) (2001) (http://www.mrlc.gov/)

Figure 3-52. Map of location of wetlands in the eastern U.S. Woody wetlands are coded blue and emergent herbaceous wetlands are coded red.

Nutrient concentrations in wetland waters associated with the Great Lakes suggest that coastal Great Lakes wetlands are N-limited. Hill et al. (2006) found that more wetlands were N- than P-limited at each of the five Laurentian Great Lakes. This result is consistent with the apparent N-limitation of most North American marsh lands (Bedford et al., 1999). Nutrient loading to lakeshore wetlands is a concern throughout the lower lakes (Lakes Erie, Ontario, and the southern part of Lake Michigan) and in some localized areas of the upper lakes (Hill et al., 2006). Both agricultural and atmospheric sources of nutrients contribute to this stress.

Coastal marsh ecosystems, unlike bog ecosystems, often receive large N inputs in tidal water, groundwater, and surface runoff. Atmospheric inputs to these systems are important because any N addition has the potential to contribute to eutrophication of coastal marshes and nearby marine and estuarine ecosystems (Paerl, 2002; Galloway, 2003). At many locations, especially along the Atlantic and Gulf coasts, atmospheric N inputs probably contribute to eutrophication problems in coastal marshes either by direct deposition to the wetland or from marine water inputs of N that originated from atmospheric deposition.

Freshwater Aquatic

Aquatic systems in which N has been observed to influence ecological processes either receive extremely high inputs (e.g., Dumont et al., 2005), or have very low initial N concentrations, and respond rapidly to additional inputs (Baron, 2000) Bergström and Jansson, 2006). Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of great concern in lakes and streams that have very low productivity and nutrient levels and that are located in remote areas. In more productive freshwaters, nutrient enrichment from N deposition usually does not stimulate productivity or community changes because P is more commonly the limiting nutrient. Also, in many places with even minor levels of human disturbance, nutrient enrichment with both N and P from non-atmospheric sources is common. Thus, eutrophication effects from N deposition are most likely to be manifested in undisturbed, low-nutrient surface waters such as those found in the higher elevation areas of the western U.S. The most severe eutrophication from N deposition effects is expected downwind of major urban and agricultural centers.

High concentrations of lake or streamwater NO_3^-, indicative of ecosystem saturation, have been found at a variety of locations throughout the U.S., including the San Bernardino and San Gabriel Mountains within the Los Angeles Air Basin (Fenn et al., 1996), the Front Range of Colorado (Baron, 1994) Williams et al., 1996a), the Allegheny Mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch, 1992; Stoddard, 1994, the Adirondack Mountains of New York (Wigington Jr., 1996, and the Great Smoky Mountains in Tennessee (Cook, 1994). All of these regions, except Colorado, received more than about 10 kg N/ha/yr atmospheric deposition of N throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives up to about 5 kg N/ha/yr of total (wet plus dry) deposition (Sullivan et al., 2005), less than half of the total N deposition received at many of these other locations.

High concentrations of NO_3^- in surface waters in the western U.S. are not widespread. NO_3^- concentrations during the fall sampling season were low in most western lakes sampled in the Western Lakes Survey. Only 24 sampled lakes were found to have NO_3^- concentrations greater than 10 µeq/L. Of those, 19 lakes were situated at high elevation, most above 3,000 m (Eilers, 1987). Other effects on aquatic ecosystems in the west are summarized in Table 3-26.

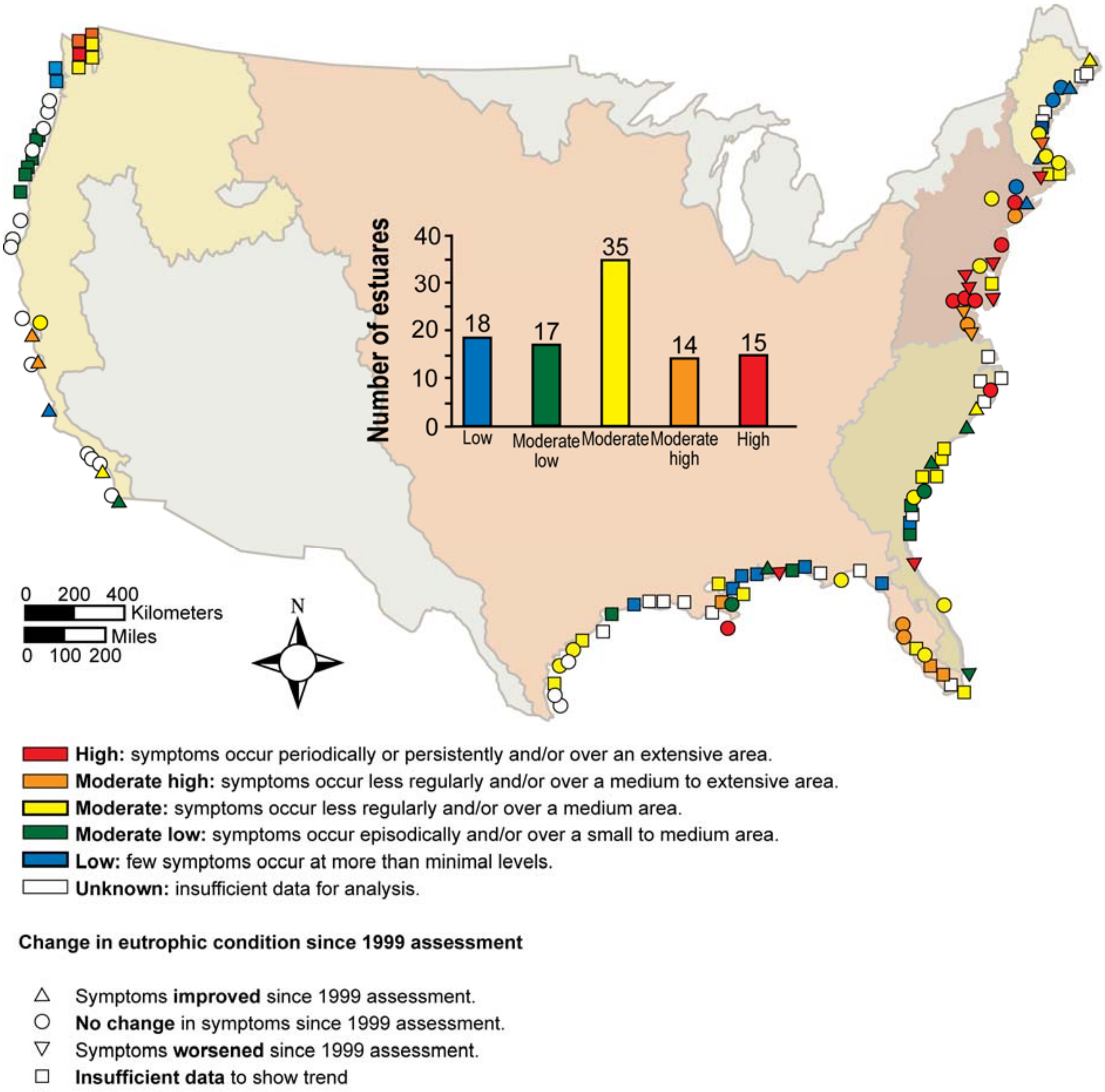
Table 3-26. changes in aquatic ecosystems associated with elevated N loadings in the Western U.S.

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
Effects in Aquatic Systems				
Elevated NO_3^- in runoff; most severe in southern California and in chaparral catchments in the southwestern Sierra Nevada	Transverse ranges of southern California; low-elevation catchments in the Sierra Nevada; high-elevation catchments in the Colorado Front Range	Well-documented response	It is unclear how widespread this phenomenon is outside the ecosystems listed, because there is littler information from low-elevation systems in the Sierra Nevada and elsewhere.	Williams et al. (1996b), Fenn and Poth (1999), Fenn et al. (2003a)
N enrichment and shifts in diatom communities in alpine lakes	Colorado Front Range; Lake Tahoe (California/Nevada border)	Documented for two lakes east of the Continental Divide and Lake Tahoe	These effects seem likely in other N-enriched lakes but have not been investigated.	Baron et al. (2000), Wolfe et al. (2001), Goldman (1988)
Reduced lake water clarity and increased algal growth	Lake Tahoe (California/Nevada border); high-elevation lakes throughout central and southern Sierra Nevada	Well-documented response; N and P deposition believed to be important factors	Lake Tahoe is an unusual case because of its renowned lake clarity; extent of occurrence elsewhere in northern Sierra Nevada is unknown.	Jassby et al. (1994), Sickman et al. (2003)
Increased NO_3^- concentrations in high-elevation lakes	Several regions, mainly downwind of urban centers	Fairly well established from lake surveys, but more data needed for improved definition of frequency and severity	Evidence suggests that urban plumes and agricultural emissions affect lake NO_3^- levels. There is also evidence of impacts on low-elevation lakes.	Figure 2, Sickman et al. (2002)

There is some evidence suggesting that reductions in atmospheric N deposition could decrease the extent of eutrophication in at least some of the Great Lakes. It has generally been believed that the Laurentian Great Lakes are P-limited (Schelske, 1991; Downing and McCauley, 1992; Rose and Axler, 1998). Water quality in the open waters of these lakes has been improving in recent years in response to controls on point sources of P (Nicholls et al., 2001). Work by Levine et al. (1997), however, suggested a more complicated pattern of response to nutrient addition for Lake Champlain. They added nutrients to in situ enclosures and measured indicators of P status, including alkaline phosphatase activity and orthophosphate turnover time. Although P appeared to be the principal limiting nutrient during summer, N addition also resulted in algal growth stimulation. P sufficiency appeared to be as common as P deficiency. During spring, phytoplankton growth was not limited by P, N, or Si, but perhaps by light or temperature (Levine et al., 1997).

Estuarine and Coastal Aquatic

N is an essential nutrient for estuarine and marine fertility. However, excessive N contributions can cause habitat degradation, algal blooms, toxicity, hypoxia (reduced dissolved O_2), anoxia (absence of dissolved O_2), reduction of sea grass habitats, fish kills, and decrease in biodiversity (Paerl, 2002, Valiela and Costa, 1988; Valiela et al., 1990; Boynton et al., 1995; Paerl, 1995, 1997; Howarth, 1996). Each of these potential impacts carries ecological and economic consequences. Ecosystem services provided by estuaries include fish and shellfish harvest, waste assimilation, and recreational activities (Costanza et al., 1997).



Source: Bricker et al. (2007
)

Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia et al., 1986; Howarth, 2006). The national estuary condition assessment conducted by Bricker et al. (2007) found that the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. N over-enrichment is a major environmental problem for coastal regions of the U.S., especially in the eastern and Gulf Coast regions. Of 138 estuaries examined by Bricker et al. (1999) 44 were identified as showing symptoms of nutrient over-enrichment. Estuaries are among the most biologically productive ecosystems on Earth and provide critical habitat for an enormous diversity of life forms, especially fish. Of the 23 estuaries examined in the Northeast, 61% were classified as moderately to severely degraded (Bricker, 1999). Other regions had mixtures of low, moderate, and high degree of eutrophication (See Figure 2-53).

The estuaries with the greatest extent of eutrophication corresponded with conditions related to both the degree of N loading and the inherent sensitivity of the estuary, as influenced by morphology and water flushing dynamics (see Annex C for a discussion of estuarine sensitivity). The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker, 2007).

Figure 3-53. Overall eutrophication condition on a national scale.

Bricker et al. (2007) evaluated the future outlook of the nations estuaries based on population growth and future management plans. They predicted that trophic conditions would worsen in 48 estuaries, stay the same in 11, and improve in only 14 by the year 2020. Between 1999 and 2007, an equal number of estuary systems have improved their trophic status as have worsened. The assessed estuarine surface area with high to moderate/high eutrophic conditions have stayed roughly the same, from 72% in 1999 (Bricker, 1999) to 78% in the recent assessment (Bricker, 2007).

Studies linking changes in estuary nutrient status to atmospheric N deposition have been limited, though it is noted that many states are addressing atmospheric inputs as part of their development of Total Maximum Daily Load plans to address estuarine water quality impairments, including those associated with low dissolved O_2. In an effort to evaluate the contribution of atmospheric N deposition to the future reduction in N loading to estuaries, Castro and Driscoll (Castro, 2002) reported model calculations that suggested that considerable reductions (more than 25%) in atmospheric N deposition will be needed to reduce the contribution made by atmospheric N deposition to the total N loads to their study estuaries in the northeastern U.S. A simulated reduction in atmospheric deposition of 25% of ambient deposition rates reduced the contribution made by atmospheric deposition to the total estuarine N loads by only 1% to 6% (Castro, 2002). In a later study, Driscoll et al. (2003b) estimated that reduction of both mobile N emissions sources and electric utilities would produce an estimated reduction in estuarine N loading in Casco Bay, Maine of 13% (Driscoll et al., 2003). Casco Bay receives the lowest atmospheric and non-atmospheric N loading per unit area of watershed (4 kg N/ha/yr) of the eight estuaries in the northeastern U.S. evaluated by Driscoll et al. (2003) (Figure 3-34).

Case Study: Alpine and Subalpine Communities of the Eastern Slope of the Rocky Mountains

Some alpine plant communities occur in areas that receive moderately elevated atmospheric N deposition; especially those proximal to urban areas (see Annex C for a map). Because alpine plant species are typically adapted to low nutrient availability, they often are sensitive to effects from N enrichment.

Research on N enrichment effects on alpine and subalpine ecosystems in the western U.S. has been limited mainly to studies at the Loch Vale Watershed in Rocky Mountain National Park and the Niwot Ridge Long-Term Ecosystem Research site; both located east of the Continental Divide in Colorado (see review by Burns, 2004). Research has been conducted in this region on both the terrestrial and aquatic effects of nutrient enrichment.

Terrestrial Effects

Changes in biomass production and NO_3^- leaching are indicative of effects on the health and vigor of plants in alpine and subalpine ecosystems. Biomass production responses of alpine communities to increased N deposition are dependent on moisture regimes (Fisk, 1998) and are driven by shifts in species composition. In a fertilization experiment, the addition of 25 kg N/ha/yr during summer caused a community shift towards greater dominance of hairgrass (*Deschampsia sp.*) in wet alpine meadows, but the increase in plant biomass (+67%) and plant N content (+107%) following N fertilization was higher in graminoid-dominated dry meadows than in forb-dominated wet meadows (+53% plant biomass, +64% standing N crop, respectively) (Bowman et al., 1995; Burns, 2004).

Alteration of plant productivity and species richness has been observed in fertilization experiments. Seastedt and Vaccaro (Seastedt, 2001) showed that four years of N addition to alpine vegetation at rates ranging between 100 and 200 kg N/ha (depending on the year) caused marginal increases in plant foliage productivity but reduced species richness. In a follow-up study at Niwot Ridge additions of 20, 40, and 60 kg N/ha/yr (on top of ambient N deposition near 5 kg N/ha/yr) over an 8–year period to a dry alpine meadow led to an increase in plant biomass, and an increase in tissue N concentration at all treatment levels within three years of application. Much of the response was due to increased cover and total biomass of sedges (*Carex spp.*). There was a significant decrease in *Kobresia myosuroides* with increasing N input.

High elevation alpine zones exhibit a relatively low capacity to sequester atmospheric deposition of N because of steep slopes, shallow soils, sparse vegetation, short growing season and other factors (Baron, 1994; Williams et al., 1996a). Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at deposition levels less than 10 kg N/ha/yr (Baron, 1994; Williams and Tonnessen, 2000). The changes in plant species that occur in response to N deposition in the alpine zone can result in further increased leaching of NO_3^- from the soils, because the plant species favored by higher N supply are often associated with greater rates of N mineralization and nitrification than the preexisting species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding, 2006).

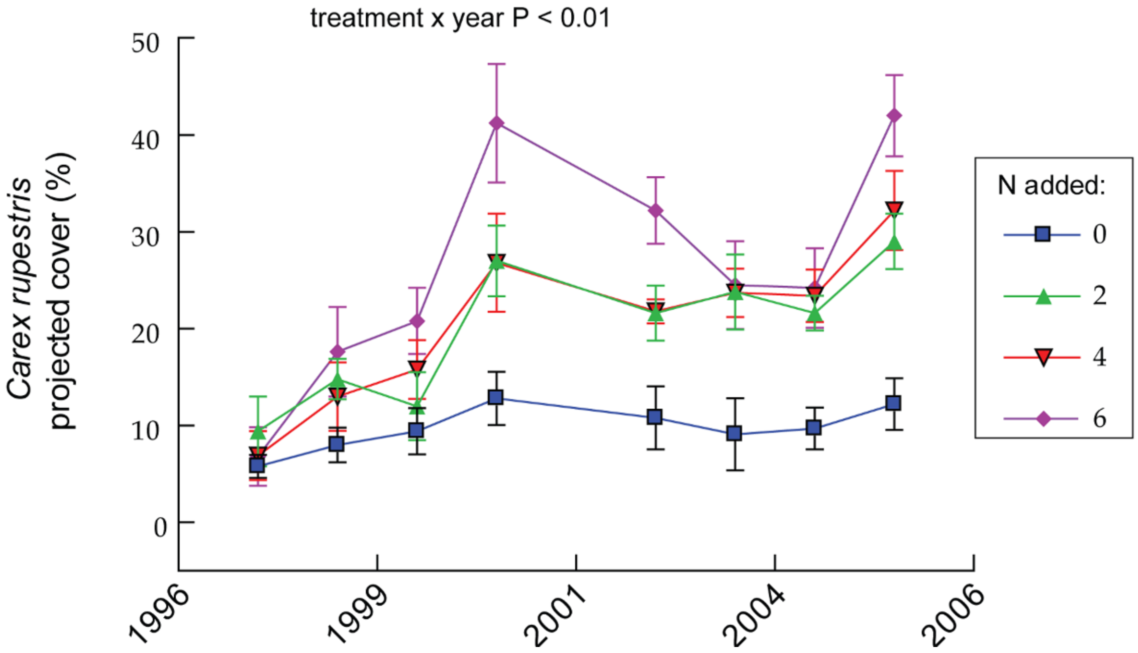
Effects of N_r deposition to alpine terrestrial ecosystems in this region include community-level changes in plants, lichens, and mycorrhizae. Alpine plant communities are sensitive to changes in species composition in response to added N (Bowman, 1995; Seastedt, 2001). Plant species composition likely responds at lower N input levels than those that cause measurable changes in soil inorganic N content. For example, Bowman et al. (2006) conducted a N-addition experiment in the Colorado Front Range with 20, 40, or 60 kg N/ha/yr. Experimental sites were monitored for 8 years along with a control site that received about 5 kg N/ha/yr total ambient deposition. Changes in plant species composition associated with the treatments occurred within 3 years of the initiation of the experiment, and were significant at all levels of N addition.

Using changes of individual species abundance and ordination scores to evaluate critical load, the critical load for total N deposition was estimated for change in individual species to be 4 kg N/ha/yr and for overall community change to be 10 kg N/ha/yr (Bowman et al., 2006). In contrast, increases in NO_3^- leaching, soil solution inorganic NO_3^-, and net nitrification were detectable at levels above 20 kg N/ha/yr (Bowman et al., 2006). These results indicate that changes in plant species composition may be detectable at lower N deposition rates than the level at which the traditional soil indicators signal ecosystem responses to N deposition. This response suggests that changes in species composition are probably ongoing in alpine dry meadows of the Front Range of the Colorado Rocky Mountains at current atmospheric N deposition levels. This research also demonstrated that long-term experimental fertilization plots illustrate a clear response of alpine flora to N addition, including shifts toward graminoid plants that shade smaller flowering species, and accompanying changes in soil N cycling (Bowman et al., 2006).

Changes in alpine plant species composition have also been documented on Niwot Ridge, where increased cover of plant species that are most responsive to N fertilization has occurred in some of the long-term monitoring plots (Korb and Ranker, 2001; Fenn et al., 2003a). These changes have probably developed in response to changes in N deposition. However, the influences of climatic change, particularly changes in precipitation (Williams et al., 1996a), and pocket gopher disturbance (Sherrod and (Seastedt, 2001) could not be ruled out (Fenn et al., 2003a). The altered N cycling provided the potential for replacement of some native plant species by more competitive, faster growing native species (Bowman and Steltzer, 1998; Baron, 2000) Bowman, 2000).

Aquatic Effects

Rocky Mountain National Park has been the site of research addressing the effects of N deposition on algal species abundance in freshwater lakes. Wolfe et al. (2001) analyzed sediments from Sky Pond and Lake Louise, two small alpine lakes located at more than 3300 m elevation on the east slope of the Colorado Front Range in Rocky Mountain National Park. Prior to 1900, the diatom flora was typical of oligotrophic Rocky Mountain lakes, dominated by such species as *Aulacoseira distans*, *A. perglabra*, *Fragilaria pinnata*, *F. construens*, and various *Achnanthes* spp. The mesotrophic planktonic species *Astrionella formosa* and *Fragilaria crotonensis* were present in trace frequencies, but became common elements of the diatom flora during the 20th century. Between 1950 and 1970, *A. formosa* became the dominant taxa in both lakes. It is known from studies in other locations as an opportunistic alga that responds rapidly to disturbance and nutrient enrichment (Renberg et al., 1993; Anderson et al., 1995; Reavie and Smol, 2001). This shift in diatom species is apparently the result of environmental stimulation, rather than recent colonization, as evidenced by the presence of these mesotrophic taxa in the older sediment record.



Source: Bowman et al. (2006)

Figure 3-54. Changes in plant species composition associated with N addition treatments in an alpine dry meadow of the Colorado Front Range. Within 3 years of the initiation of the experiment, statistically significant changes in the cover of Carex rupestris occurred at all treatment levels.

Additional corroborative evidence for the linkage between atmospheric N deposition and the observed diatom shifts in these alpine lakes is provided by the results of laboratory (Interlandi and Kilham, 1998) and in-lake (McKnight et al., 1990) N addition experiments. In both sets of experiments, growth of *A. formosa* and *F. crotonensis* was accelerated by experimental N addition. The post-1950 period of rapid shifts in diatom species composition in Sky Pond and Lake Louise corresponded with intensification of agricultural practices, animal husbandry, and population growth in adjacent regions to the east of Rocky Mountain National Park (Wolfe et al., 2001). Nevertheless, N deposition at that time was estimated to be low, probably less than 2 kg N/ha/yr (Baron, 2006).

Case Study: Chesapeake Bay

Chesapeake Bay is the largest estuary in the U.S. and one of the most sensitive to N inputs (Bricker, 1999; Howarth, 2007). Eutrophication effects have been pronounced in Chesapeake Bay (Howarth, 2007) and it is perhaps the best known example in the U.S. of human activities leading to accelerated estuarine eutrophication and its associated negative effects. In the recent national assessment of eutrophic conditions in estuaries, the Chesapeake Bay stands out as a system with both physical features and N loading levels that make it particularly vulnerable to eutrophication (Bricker, 2007).

The role of atmospheric N deposition in estuary eutrophication in the U.S. was ignored until Fisher and Oppenheimer (1991) suggested that it could constitute up to 40% of the total N inputs to the Chesapeake Bay. Although their analysis was preliminary, and has been updated by more conservative estimates (e.g., Boyer et al., 2002; Boyer and Howarth, 2002), it served to focus attention on the role of atmospheric deposition as an important contributor to the overall budget of estuaries in the eastern U.S. N inputs to the Chesapeake Bay have increased substantially over the last 50 to 100 years. The increase is attributed to rapid acceleration of the use of chemical fertilizers in agriculture, the increasing human population density and associated wastewater discharge, and rising atmospheric N emissions within the airshed and consequent deposition within the Chesapeake Bay watershed. Atmospheric deposition of N is currently estimated to contribute about one-fourth of the total N loading to Chesapeake Bay (Boyer et al. 2002; Howarth, 2007).

Human activities have increased the susceptibility of the Chesapeake Bay to the effects of atmospheric N deposition. For example, the filling in of wetlands and deforestation for agricultural and urban development, have reduced the ability of natural ecosystem processes to remove or trap nutrients, thereby further accelerating nutrient delivery to the bay. In addition, diseases and over-harvesting led to a dramatic decline of the once highly abundant eastern oyster, seriously reducing the natural filtering of algae and other organic matter from the water column.

As a result of these changing conditions, eutrophic symptoms intensified in the Chesapeake Bay from the mid-1950s to the mid-1980s. The most apparent symptoms were (1) high production of algae, (2) increasingly turbid water, (3) major declines in SAV abundance and species, and (4) increasingly worsening anoxia and hypoxia (Boesch et al., 2001). The recent national estuary condition assessment (Bricker, 2007) reported that chlorophyll *a*, dissolved O_2, nuisance/toxic algal blooms, and SAV rated "high" in Chesapeake Bay in terms of severity of effects associated with eutrophication. In addition, macroalgae and toxic algal bloom conditions have worsened since the previous national assessment in 1999 (Bricker, 1999; Bricker, 2007).

Concentrations of chlorophyll *a* in the surface mixed layer have increased tenfold in the seaward regions of the bay and one-and-one-half- to twofold elsewhere, paralleling estimates of increased loading of N and P to the bay since 1945 (Harding and Perry, 1997).

SAV began to decline as a result of nutrient enrichment during the mid-1960s, disappearing entirely from the Patuxent and lower Potomac Rivers. By 1980, many areas of the bay that once contained abundant SAV beds had none or only very small remnants left (Orth and Moore, 1984). Research indicated that the major driving factor in the decline of SAV was nutrient enrichment, which was causing excessive growth of algae in the water column and on SAV leaf blades (epiphytic algae). This algal growth decreased light availability to the submerged plants to the point that they could not survive (Kemp et al., 1983; Twilley et al., 1985).

There is an annual cycle of O_2 *depletion* in the Chesapeake Bay that begins as the water starts to warm in spring, and O_2 depletion accelerates during and following the spring freshet. The spring accumulation of algal biomass is more than sufficient to create conditions for O_2 depletion and summer anoxia (Malone, 1991, 1992). Hypoxia (very low dissolved O_2 concentration ~ < 2mg/L) and anoxia (absence of dissolved O_2) generally occur from May through September, with the most severe conditions observed in mid-summer. Seasonal hypoxia has been a feature of the Chesapeake Bay since deforestation during the colonial period (Cooper and Brush, 1991; Malone, 1991), but evidence suggests an increase in the extent of the problem in recent decades (Officer, 1984) Malone, 1991). Estuarine eutrophication is sometimes accompanied by increases in the populations of species of algae, often cyanobacteria that produce toxins. Such chemicals can affect people, fish, shellfish, and other organisms. Blooms of algae that produce toxins in Chesapeake Bay have become more extensive over approximately the past decade (Bricker, 2007).

In 1983, EPA, District of Columbia, and states of Virginia, Maryland, and Pennsylvania signed the first Chesapeake Bay Agreement, which established the Chesapeake Bay Program—a voluntary government partnership that directs and manages bay cleanup efforts. Scientific findings from the program led to the signing of the second Chesapeake Bay Agreement in 1987, in which it was agreed to reduce by 40% the N and P entering the Chesapeake Bay by the year 2000. Point source reductions have been most successful, especially for P. Between 1985 and 1996, emissions from P point sources were reduced by 58% and N by 15%. Nonpoint source reductions have been slower, largely because nonpoint sources of nutrients are more difficult to control. Nonpoint source emissions of N and P have been reduced by only 7% and 9%, respectively (Boesch et al., 2001). Strategies to reduce nonpoint source nutrients include changes such as adoption of better agricultural practices, reduction of atmospheric N deposition, enhancement of wetlands and other nutrient sinks, and control of urban sprawl.

Case Study: San Bernardino

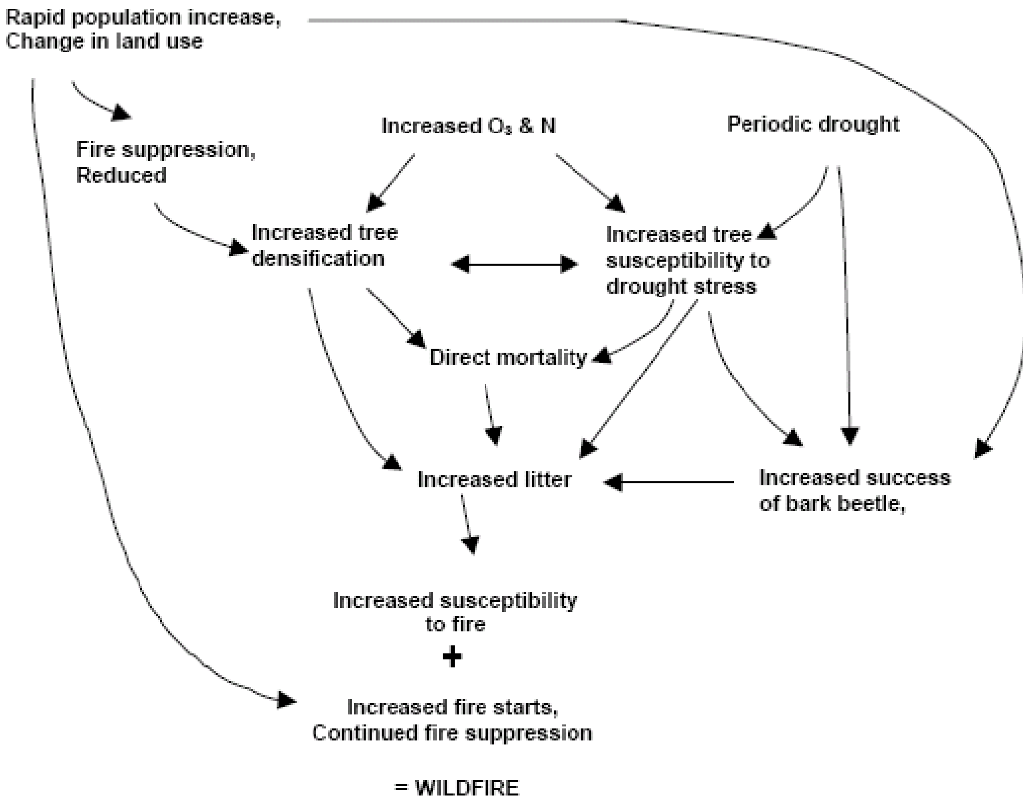
The San Bernardino Mountains lie east of the Los Angeles Air Basin in California. Pollutants generated in the greater LA metropolitan area are transported 60–100 km downwind and affect mid-elevation forests in the San Bernardino Mountains and the San Gorgonio Class I Wilderness area. The primary source of air pollution is fossil fuel combustion. Approximately half of the air pollution in the LA air basin is generated from mobile sources including trucks, trains, cars, ships, and buses (South Coast Air Quality Management District). On the western end of the San Bernardino Mountains, nearly half of the N deposition is in reduced forms (Fenn and Poth, 2004), most of which is believed to originate from dairy farms in the Chino/Norco area.

In the San Bernardino Mountains, a wide variety of N species (NO, NO_2, HNO_3, HNO_2, NO_3^-) are deposited to vegetation and soil surfaces, in gaseous, wet, and dry forms. Ammonium (NH_4 +) can also be transported moderate distances from feedlots for cattle and poultry (Bytnerowicz, 2002). Along a west to east gradient in the San Bernardino Mountains, throughfall N deposition goes from averaging 71 kg N/ha/yr at Camp Paivika (nearer to the pollutant sources), to 9 kg N/ha/yr at Barton Flats (farther from the sources), 45 km east of Camp Paivika (Breiner et al., 2007, Fenn et al. 2008). These throughfall measurements were made using ion exchange resin columns that measure total NO_3^- and NH_4^+ deposition from precipitation, plus fog or dry deposition that has been scavenged by the overstory pine canopy and then washed through the canopy (Fenn and Poth 2004). Throughfall N deposition using this method is also available for seven other sites within the San Bernardino Mountains (Fenn et al. 2008).

Several key ecological endpoints in the mixed conifer forests of the San Bernardino Mountains have been linked to anthropogenic N deposition. Because air pollution has been high since 1945 in the LA air basin (Lee et al., 2003), N deposition is in excess of plant and microbial demand (Fenn et al., 1996). The cardinal symptom of excess N is the export of high NO_3^- levels in streamwater (see 3.3.2.1), which is well demonstrated for areas with N deposition above 17 kg/ha/yr in the San Bernardino and San Gabriel Mountains (Breiner et al., 2007; Fenn and Poth; 1999; Michalski et al., 2004; Riggan et al., 1985, Fenn et al. 2008). Other indicators of excess N in the ecosystem include lowered litter C:N and elevated emissions of NO and N_2O from the soil (see 3.3.4.2, which have been observed at the more polluted sites in the San Bernardino Mountains (Fenn et al. 1996; Fenn & Poth 2001; Fenn et al. 2008). Lichen communities in the San Bernardino Mountains have also been dramatically changed by the disappearance of up to 50% of the species that occurred in the region in the early 1900s, due to N pollution (Fenn et al 2003, (Nash, 1999). A disproportionate number of the locally extinct lichen species are cyanolichens. N deposition has also been tentatively linked to reduction in fine root biomass in ponderosa pine (*Pinus ponderosa* C. Lawson) at three sites (Grulke et al. 1998, Fenn et al. 2008). However, ozone is also believed to contribute to decreased C allocation to fine roots (Grulke et al 1998), and could be a confounding factor (see below). Recently, Fenn et al. 2008 have used the linkages between N deposition and effects described above to calculate empirical and simulated (i.e. DayCent, Simple Mass Balance for N as a nutrient) critical loads for N deposition for California mixed conifer forests.

The effects of high N deposition in the forests of San Bernardino Mountains are compounded by the high ozone exposures that have occurred throughout the past 65 years. For example, from west to east,

O_3 concentrations were high at Camp Paivika (80 ppb/hr, averaged over 24 hr, from April 15 through October 15, from 1993 through 1995; Grulke et al., 1998), moderately high (72 to 74 ppb/hr) 5 km further east near Rim Forest, and moderate (62–64 ppb/hr) 45 km east of Camp Paivika at Barton Flats. Both O_3 exposure and N deposition reduce foliar retention (Grulke and Balduman, 1999) and alter tissue chemistry of both needles and litter (Poth and Fenn, 1998). In addition, confounding factors such as drought and fire suppression add to the complexity of ecosystem response (Arbaugh et al., 2003; Minnich et al., 1995; Takemoto et al., 2001). Extensive crown injury measurements have also been made, linking ambient O_3 exposure data to chlorotic mottle and needle retention (Arbaugh et al., 1998). Ozone exposure and N deposition reduce carbon allocation to stems and roots (Grulke et al., 1998a, 2001), further predisposing trees to drought stress, windthrow, root diseases, and insect infestation (Takemoto et al., 2001). Recently, Grulke et al. 2008 reported that various lines of phenomenological and experimental evidence indicate that N deposition and ozone pollution contribute to the susceptibility of forests to wildfire in the San Bernardino Mountains by increasing stress due to drought, weakening trees, and predisposing them to bark beetle infestation. Figure 3-55shows the multiple factors contributing to susceptibility to wildfires in the San Bernardino Mountains.



Source: Grulke et al. (2008)

Figure 3-55. Diagram of multiple factors contributing to forest susceptibility to wildfire.

3.3.9. Ecosystem Services

This evidence reviewed in this ISA supports that N_r deposition affects ecosystem services in the following categories (defined by Hassan et al. 2005)(Hassan, 2005):

- Supporting: nutrient cycling, biodiversity
- Provisioning: forest yields, fishing yields in estuaries
- Regulating: climate (e.g. C sequestration, N_2O emission, CH_4 flux), water quality, fire frequency and intensity
- Cultural: swimming, boating, biodiversity

At this time, no peer-reviewed publication has focused on the ecosystem services affected by N deposition. However, some valuation studies have addressed the effects of N enrichment from multiple sources (see Annex F). In general, both ecosystem structure and function play essential roles in providing goods and services (Daily, 1997). Ecosystem processes provide diverse benefits including absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance and climate, and fixation of solar energy (Westman, 1977; Daily, 1997; World Resources Institute, 2000). These ecological benefits, in turn, provide economic benefits and values to society (Costanza et al., 1997; Pimentel et al., 1997). Goods such as food crops, timber, livestock, fish, and drinking water have market value that can be easily quantified. The values of ecosystem services such as flood-control, wildlife habitat, cycling of nutrients, and removal of air pollutants are more difficult to measure (Goulder and Kennedy, 1997).

Particular concern has developed within the past decade regarding the consequences of decreasing biological diversity (Hooper and Vitousek, 1997; Chapin et al., 1998; Ayensu et al., 1999; Wall, 1999; Tilman, 2000). Human activities that decrease biodiversity also alter the complexity and stability of ecosystems, and change ecological processes. In response, ecosystem structure, composition and function can be affected (Table 3-27) (Pimm, 1984; Tilman and Downing, 1994; Tilman, 1996; Chapin et al., 1998; Levlin, 1998; Peterson et al., 1998; Daily, 1999; Wall, 1999). Biodiversity is an important consideration at all levels of biological organization, including species, individuals, populations, and ecosystems. Human-induced changes in biotic diversity and alterations in the structure and functioning of ecosystems are the two most dramatic ecological trends of the past century (Vitousek, 1997; EPA, 2004), and the deposition of nutrient N from the atmosphere contributes to both.

Table 3-27. Primary Goods and Services Provided by Ecosystems

Ecosystem	Goods	Services
Coastal Ecosystems	Fish and shellfish Fish meat (animal feed) Seaweeds (for food and industrial use) Salt Genetic resources	Moderate storm impacts (mangroves, barrier islands) Provide habitat and breeding areas/hatcheries/nurseries for wildlife (marine and terrestrial) Maintain biodiversity Dilute and treat wastes Provide harbors and transportations routes Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreations
Forest Ecosystems	Timber Fuel wood Drinking and irrigation water Fodder Non timber products (vines, bamboos, leaves, etc.) Food (honey, mushrooms, fruit, and other edible plants; game) Genetic resources	Remove air pollutants, emit O_2 Cycle nutrients Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization) Maintain biodiversity Sequester atmospheric carbon Moderate weather extremes and impacts Generate soil Provide employment Provide human and wildlife habitat Contribute aesthetic beauty and provide recreation
Freshwater	Drinking and irrigation water Fish Hydroelectricity Genetic resources	Buffer water flow (control timing and volume) Dilute and carry away wastes Cycle nutrients Maintain biodiversity Provide aquatic habitat Provide transportation corridor Provide employment Contribute aesthetic beauty and provide recreation
Grassland Ecosystems	Livestock (food, game, hides, and fiber) Drinking and irrigation water Genetic resources	Maintain array of watershed functions (infiltration, purification, flow control, and soil stabilization) Cycle nutrients Remove air pollutants and emit O_2 Maintain biodiversity Generate soil Sequester atmospheric carbon Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreations

Source: World Resources Institute (2000).

3.4. Other welfare effects

This section includes the non-acidification effects of sulfur and direct phytotoxic effects of gas-phase NO_X and SO_X on vegetation. Materials and structures damage caused by NO_X and SO_X is addressed in Annex E.

3.4.1. Non-acidification Effects of Sulfur

As discussed in Section 3.2, a number of environmental effects are associated with S deposition, in particular soil and water acidification. However, S deposition also contributes to nutrient enrichment, toxicity, and has secondary effects on the cycling and bioavailability of Hg, a highly neurotoxic contaminant. High concentrations of SO_2 can harm vegetation by causing foliar injury, decreasing plant growth, and eliminating sensitive plant species, although atmospheric concentrations of SO_2 are seldom high enough to cause these effects on vegetation at ambient air pollution levels in the U.S. The biogeochemical cycling of S is closely linked with the cycling of other important elements, including C, N, P, Al, and Hg. Therefore, S deposition can influence the cycling of these elements in ways that influence nutrient availability or contaminant toxicity. In particular, current research suggests that S deposition influences the cycling of Hg in transitional and aquatic ecosystems by stimulating SO_4^{2-}-reducing bacteria, which are responsible for the bulk of Hg methylation, a key process that increases the bioavailability of Hg.

3.4.1.1. Biological Role of Sulfur

Effects on Plants

S is an essential plant nutrient. Low dosages of S serve as a fertilizer, particularly for plants growing in S-deficient soil (Hogan, 1998). A certain level of foliar $SO_4^{2-}$is necessary for adequate plant S nutrition (Johnson, 1998; Marschner, 1995, and S deficiency has been shown to occur at foliar SO_4^{2-} levels below 80 µg/g in *Pinus radiata* (Turner, 1980). Nevertheless, the annual increment of S in vegetation is usually small compared to atmospheric deposition and leaching fluxes. Plants require similar levels of S and P, but S is generally available in much higher concentrations in soil. Storage of S in vegetation is of minor significance in the retention or loss of S in most forests (Mitchell, 1992; Johnson, 1998).

Atmospheric deposition is an important component of the S cycle. This is true not only in polluted areas where atmospheric deposition is very high, but also in areas of low S deposition. Biochemical relationships between S and N are involved in plant protein synthesis and metabolism. S deficiency reduces NO_3 reductase and glutamine synthetase activity. N uptake in forests, therefore, could be loosely regulated by S availability, but SO_4^{2-} additions in excess of needs do not necessarily lead to injury (Turner, 1980; Hogan, 1998). Current levels of S deposition throughout much of the United States exceed the capacity of most plant communities to immobilize the deposited S (Johnson, 1984; Lindberg, 1992). S excesses associated with acidic deposition have been found (Shriner, 1978; Meiwes, 1981); Johnson et al., 1982

S deficiency in forest soil is rare, but has been reported in remote areas that receive very low levels of atmospheric S deposition and that have inherently low S levels in soil (Kelly, 1972) (Turner, 1990; Turner, 1977; Turner, 1990) Schnug, 1997). In such cases, atmospheric S deposition might be taken up by vegetation, with little SO_4^{2-} leaching. Within areas of the U.S. influenced by acidic deposition, this is not expected to be a common phenomenon. To some extent, plant uptake of S is determined by the availability of N. This is because most S in plant tissue is in protein form, with a specific S:N ratio (Turner, 1990; Turner, 1977; Turner, 1990; Johnson, 1982)

Sulfur plays a critical role in agriculture, and is an essential component of fertilizers (Ceccotti, 1997). It is particularly important for plants growing in S-deficient soil (Hogan, 1998). The most important source of S to vegetation is SO_4^{2-}, which is taken up from the soil by plant roots (Marschner, 1995). There are few field demonstrations of foliar SO_4^{2-} uptake (Krupa, 1986; Krupa, 1999; EPA, 2004). Rather, SO_4^{2-} in throughfall is often enriched above levels in precipitation. The relative importance of the contribution of foliar leachate versus prior dry-deposited SO_4^{2-} particles to this enrichment is difficult to quantify (Cape, 1992). The major factor controlling the movement of S from the soil into vegetation is the rate of release through microbial decomposition of S from organic to inorganic forms (May, 1972)EPA, 1982, 1993; Marschner, 1995).

Sulfur deposition can also have direct effects on plants via nutrient enrichment pathways. Sulfur is an essential nutrient for protein synthesis in plants. Adequate S supply for sustaining plant health is 0.01% to 0.05% in soils (Nriagu, 1978). SO_4^{2-} is the dominant form of bioavailable S in soils. Plants can also utilize volatile S compounds such as SO_2 in the atmosphere to fulfill nutrient requirements (Rennenberg, 1984). This S is directly available for diffusive uptake through the leaf surface to support plant growth (Jager, 1980, and can also become bioavailable in the soil for plant root uptake (Moss, 1978). However, excess S inputs via atmospheric deposition can be toxic to plants and result in delayed flowering, reduced growth, and mortality (Smith, 1981; Rennenberg, 1984; Roelofs, 1991) ; Smolders and Roelofs, 1996). Plants that have exhibited reduced growth due to S toxicity have also been observed to have reduced molybdenum (Mo) uptake and increased copper (Cu), manganese (Mn), and zinc (Zn) uptake (Gupta and Munro, 1969; Gupta and Mehla, 1980). The threshold level of S toxicity is variable among species (Mudd and Kozlowski, 1975).

Koch et al. (1990) found that hypoxia and high levels of sulfide (>1 mM) limited wetland plant growth by inhibiting nutrient uptake. Sulfide toxicity to plants (e.g., *Carex* spp. *Juncus acutiflorus*, *Galium palustre, Gramineae*) has also been observed in wetland mesocosm experimentally enriched with SO_4^{2-} (Lamers et al., 1998). Biomass regrowth was significantly reduced for these species for both 2 and 4 mmol/L SO_4^{2-} treatments (Lamers et al., 1998). Van der Welle (2007) also showed that increased SO_4^{2-} loading had negative effects on aquatic macrophytes (*Stratiotes aloides* and *Elodea nuttallii*), via sulfide toxicity. Though *S. aloides* was native to the study region (The Netherlands) of Van der Welle et al.

(2007), it is considered a noxious invasive plant in the U.S. However, *E. nuttallii* is native to the U.S., widely distributed across 33 states, and is considered threatened in Kentucky and a species of concern in Tennessee (http://plants.usda.gov/). Negative impacts from elevated rates of atmospherically deposited SO_4^{2-} on this species could be of concern. It is important to note, however, that the SO_4^{2-} concentrations reported in these studies were much higher than would generally be expected to occur in regions of the U.S. exposed to elevated atmospheric S deposition.

Iron (Fe) concentrations can influence the level of sulfide toxicity in wetland sediments (Smolders et al., 2001; Lamers et al., 2002). Free sulfide produced through SO_4^{2-} reduction is able to bind with Fe, forming insoluble Fe sulfide (FeS). If sufficient Fe is present, this complexation can reduce or eliminate sulfide toxicity to plants by removing the free sulfide from solution. Van der Welle et al. (2007) confirmed the role of Fe in buffering against sulfide toxicity to plants by observing no toxic effects when sufficient Fe was available to precipitate free sulfide.

However, the formation of FeS can disrupt, or compete with, Fe phosphate ($FePO_4$) complexation, resulting in P release and potential undesirable eutrophication effects on downstream receiving waters (Caraco et al., 1989; Smolders et al., 2003). Iron(III) hydroxides and iron(III) phosphates are reduced in anaerobic soils and highly insoluble FeS is formed, increasing phosphate (PO_4^{3-}) mobility and bioavailability in surface waters (Smolders et al., 2006). This process has been termed "internal eutrophication" since P is mobilized from within the system and is not contributed from an external source (Roelofs, 1991). Increased nutrient availability via SO_4^{2-}-induced P release from wetland sediments can result in changes in aquatic vegetation community composition. Rooted aquatic macrophytes can be out-competed by non-rooting floating species and filamentous algae (Smolders et al., 2003). If Fe is available in high enough concentrations, it can prevent P release from saturated soils with high S loading by providing adequate Fe to bind with sulfide without releasing P (Van Der Welle et al., 2007).

The observation that NO_3^- addition decreases P release in wetland enclosures provides further indication that S-induced P release is related to redox conditions and microbial dynamics in the soil profile (Lucassen et al., 2004). Sufficiently high NO_3^- concentrations can prevent SO_4^{2-} reduction, and subsequent interruption of Fe-P binding, by maintaining redox status above that suitable for SO_4^{2-} reduction (Lucassen et al., 2004). In the absence of a sufficient supply of NO_3^- to act as a redox buffer, SO_4^{2-} will undergo reduction and potentially trigger the internal eutrophication mechanism described above (Lucassen et al., 2004). It is important to note that the majority of research on the topic of internal eutrophication of has occurred in Dutch peatlands that have historically experienced much larger N loading than those in the U.S., making it difficult to extrapolate these findings to U.S. systems.

Effects on Methane-producing Microbes

Increased atmospheric S deposition and its impacts on microbial community structure can also affect methane (CH_4) emissions from saturated soils. Early investigation into the effects of elevated pore water SO_4^{2-} concentrations on CH_4 emissions from wetland soils involved the application of a single large dose of SO_4^{2-} (Fowler, 1995). Methane production was observed to be suppressed (40% less than the control) three weeks after the addition of SO_4^{2-}. This was followed by a 4–week recovery period, after which CH4 production had returned to pre-treatment levels. These results led to the hypothesis that large single addition of SO_4^{2-}, as applied by Fowler (Fowler, 1995), only stimulate SO_4^{2-}-reducing bacterial (SRB) activity for a short time. Fowler concluded that studies that more closely approximated long-term SO_4^{2-} loading, as with atmospheric S deposition, were necessary. Dise and Verry (2001) and Gauci et al. (2002) showed that smaller and more numerous SO_4^{2-} additions sustained CH_4 emission suppression in wetland soils. These studies more closely approximated SO_4^{2-} enrichment associated with acidic deposition. These results provided support to the hypothesis that continuous elevated SO_4^{2-} deposition, as encountered in areas affected by acidic deposition, contributes to sustained suppression of CH_4 emissions from wetland soils.

Gauci et al. (2004) considered both methods of SO_4^{2-} addition (a single large dose versus numerous small doses) in the same experiment. Rates of SO_4^{2-} addition ranged between 15 and 100 kg S/ha/yr to wetland soils previously exposed to 4 kg S/ha/yr of atmospheric S deposition. They observed that CH_4 emissions from these wetland soils were almost equally suppressed under each treatment, and that each treatment experienced the same CH_4 emission "recovery" as found in the single-dose Fowler et al. (1995) study. The two main conclusions from Gauci et al. (2004) were that 15 kg S/ha/yr is either at or above the rate of S deposition required to achieve maximum CH_4 emission suppression, and that a single large dose of S has similar effects on CH_4 emission suppression as do numerous smaller doses. The authors observed that CH_4 emissions from treated soils recovered to levels that were observed from untreated soils during the period of plant senescence. This led to the hypothesis that SRB will out-compete CH_4 producing bacteria under conditions of elevated S deposition and durSing vigorous plant growth when available C substrate is limited, but that root exudates and root degradation during the period of plant senescence provides adequate substrate to sustain both methanogenic and SRB bacteria populations. Although the suppression of CH_4 emissions can fluctuate based upon plant growth cycles, elevated S deposition is considered to shift microbial community structure in favor of SRB over methanogenic bacteria, reducing annual CH_4 emissions from saturated soils (Granberg, 2001). However, climate change simulations suggest that increased soil temperature may override the suppressive effect that elevated S deposition has on CH_4 emissions (Granberg, 2001; Gauci, 2004).

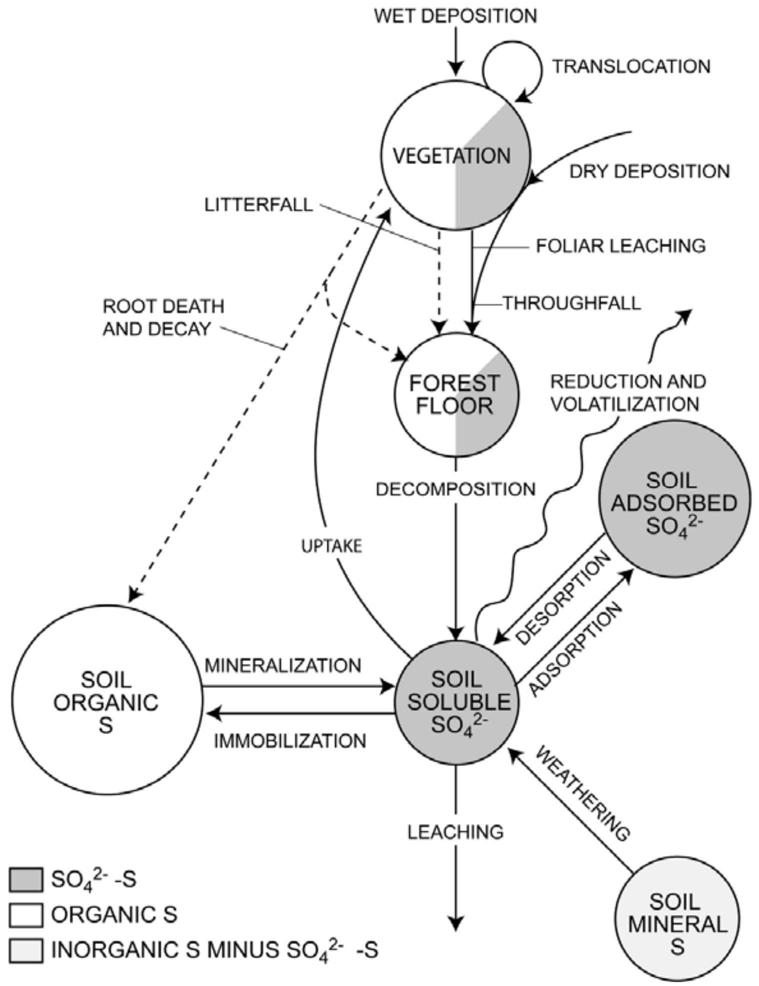
3.4.1.2. Cycling and Storage of Sulfur

Terrestrial Ecosystems

Considerable effort was devoted in the 1980s to the computation of S budgets for watersheds and forest plots, with the objective of evaluating S retention and release. These budgets were subject to complications from fluxes that could not be measured directly, such as dry deposition and weathering, but they generally indicated net S retention at sites south of the line of glaciation — a result attributed to net adsorption of SO_4^{2-} (Rochelle et al., 1987; Cappellato et al., 1998). During the 1990s, little or no decrease in SO_4^{2-} concentration occurred in streams in the Ridge and Blue Ridge physiographic provinces, despite regional decreases in atmospheric deposition of S (Webb et al., 2004), and no evidence of S addition from mine drainage. This lack of response in stream chemistry has been generally attributed to a shift in S equilibrium between the adsorbed and solution phases under conditions of decreased atmospheric inputs of SO_4^{2-}. This interpretation is supported by a decrease in concentrations of adsorbed SO_4^{2-} from 1982 to 1990 in a Piedmont soil in South Carolina that received decreasing levels of S deposition during this period (Markewitz et al., 1998). This same soil also experienced an increase in adsorbed SO_4^{2-} from 1962 to 1972 (Markewitz et al., 1998). The only published S budget more recent than 1992 for an unglaciated site in the U.S. (Castro, 2000) also suggested a net release of SO_4^{2-}. This upland Maryland watershed released 1.6 times more SO_4^{2-} than measured in throughfall in 1996–97.

Numerous S budgets were compiled in the 1980s for glaciated sites, and results generally indicated that inputs approximately equaled outputs on an annual basis (Rochelle and Church, 1987). The observation of little or no S retention at glaciated sites was attributed to relatively low SO_4^{2-} adsorption capacity in soils. Balanced S budgets in glaciated regions implied that decreases in atmospheric deposition of S would lead directly to decreases in SO_4^{2-} leaching. The strong correlation between recent decreases in both atmospheric S deposition and SO_4^{2-} concentrations in surface waters is widely recognized to be a result of this direct linkage (Stoddard, 2003). Nevertheless, considerable evidence also indicates that S inputs in glaciated ecosystems do not behave conservatively, but instead are cycled in part through microbial and plant biomass (David et al., 1987; Alewell and Gehre, 1999;(Likens, 2002). As a result, large quantities of S are stored in organic forms within the soil. David et al. (1987) found that annual S deposition (wet plus dry) at a site in the central Adirondack region of New York was about 1% of the organic S pool in the soil. Houle et al. (Houle, 2001) estimated that annual S deposition at 11 sites in North America ranged from 1% to 13% of the organic S pool in soil.

The S cycle in forest ecosystems can be represented as a series of input, uptake, and output terms (Figure 3-56). Some of the fluxes illustrated in this schematic drawing can be measured in the field, including wet deposition, litterfall, and throughfall. Other fluxes must be calculated or estimated, which involves considerable uncertainty (Johnson, 1998).



Source: Johnson (1984).

Figure 3-56. Representation of the S cycle in forest ecosystems.

Perhaps the most important uncertainty concerns the amount of dry deposition, which can be substantial (Lindberg, 1990).

Atmospheric deposition is an important part of the S cycle, including in areas that are not exposed to appreciable air pollution levels. In fact, although agricultural S and geologic S (especially associated with mining activities) can be locally important or dominant, atmospheric S inputs may constitute the major source of S input to many terrestrial ecosystems (Probert, 1983; Johnson, 1998).

Much of the organic S stored in soil is in C-bonded forms that are relatively unreactive, but can be oxidized by bacteria or mineralized to SO_4^{2-} under oxic conditions, which are typically found in moderately well drained to well drained soils (Johnson, 1998). Carbon-bonded S in forest soils can be found in a variety of organic S compounds, including amino acids, sulfolipids, and sulfonic acids. Carbon-bonded S can also be found in humic material in the form of aliphatic and aromatic structures

(Likens, 2002). Furthermore, strong correlations have been shown between levels of atmospheric deposition of S and concentrations of S in soil (Driscoll et al., 2001; Novák et al., 2005). Long-term increases in concentrations of total S in soils that are at least partially attributable to increases in organic S have also been documented (Knights, 2000; Lapenis, 2004), although the study of Houle et al. (Houle, 2001) did not find a relation between these factors. A Swedish "clean roof" study also provides some insight into the role of organic S in possibly delaying chemical recovery from acidification due to S deposition (Mörth, 2005). After 9 years of application of pre-industrial levels of S deposition, the amount of SO_4^{2-} in runoff still exceeded inputs by 30%. Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

Thus, research on the effects of atmospheric S deposition on soils has indicated pronounced changes in soils from sustained SO_4^{2-} leaching, and accumulation of S through physical/chemical adsorption and biological assimilation. The recent evidence of net loss of S from soils at a number of sites is likely a response to decreased atmospheric inputs. The gradual loss of previously accumulated S contributes to continued SO_4^{2-} leaching. Uncertainties in estimates of ecosystem fluxes such as weathering and dry deposition, and complications in discerning the effects of desorption from mineralization make it difficult to predict when S outputs will no longer exceed inputs as levels of S deposition continue to decline. Research based on experimental reduction of S inputs suggests that this process will occur on a decadal time scale (Martinson, 2005; Mörth, 2005). The long-term role of C-bonded S adds further uncertainty because enhancement of S mineralization by a warming climate could also affect S retention and release (Knights, 2000)Driscoll et al., 2001). This process can be microbially catalyzed, and bacteria are generally more active at higher temperature.

Transitional Ecosystems

Transitional ecosystems exert important controls on watershed S budgets, especially in watersheds that contain extensive wetland development. Sulfur storage in wetland soils provides an important buffering system that restricts chronic SO_4^{2-} leaching to surface waters. Input-output studies of bogs in Massachusetts (Hemond, 1980), Ontario (Urban and Bayley, 1986), and Minnesota (Urban and Eisenreich, 1988) suggested more than 50% retention of atmospheric S inputs. However, oxidation of S that was previously stored in wetland soils can provide an important episodic source of SO_4^{2-} to downstream surface waters. Thus, the presence of wetlands in a watershed can either temporarily increase or decrease the flux of SO_4^{2-} to surface waters, and these differences are largely determined by changes in hydrology and redox conditions in wetland soils. Overall, wetlands act as sinks for S because of microbial SO_4^{2-} reduction and sequestering of reduced S as sulfide minerals and organic S.

Changes in S flux that are controlled by processes in transitional ecosystems can have important effects on surface water chemistry. For example, reduction of SO_4^{2-} in sediments by assimilatory and dissimilatory processes is an important source of acid neutralizing capacity (ANC) to lakes having long hydraulic residence time, and a likely source also to beaver ponds and wetlands. In-lake ANC production is mostly due to S retention from microbial SO_4^{2-} reduction (Schindler, 1986; Brezonik et al., 1987; Turner, 1990). It is unlikely, however, that the changes in S flux caused by wetlands and ponds in a watershed would be large enough to have any direct non-acidification effects on biota. More likely, the major non-acidification effects of wetland influence on S cycling relate to changes in Hg methylation in wetland soils. This is discussed in Section 3.4.1.4. Other changes can also occur, including enhanced release of N and P from wetland soils.

Some of the organic S in wetlands can be converted to reduced S gasses, including dimethylsulfide and hydrogen sulfide (under acidic conditions), and released to the atmosphere. Up to 30% of the atmospheric deposition of S in remote areas may be derived from release of reduced S gasses from wetlands (Nriagu, 1987). Thus, wetland processes can have important effects on local atmospheric S deposition and trace gas emissions.

Aquatic Ecosystems

In aquatic ecosystems that are sensitive to acidification from atmospheric S deposition, SO_4^{2-} is generally highly mobile within the ecosystem. Acid-sensitive streams tend to be relatively fast-flowing, high-gradient, low-order streams that exhibit high SO_4^{2-} mobility. Acid sensitive lakes tend to be relatively small, headwater lakes with short hydraulic residence times (weeks to months). In such streams and lakes, most of the SO_4^{2-} contributed by inflowing ground and surface waters is directly flushed through the ecosystem and emerges as outflow.

However, larger streams, streams that flow through series of ponds (i.e., beaver ponds) or lakes, and especially larger lakes, tend to have longer hydraulic residence, and provide opportunity for microbial S reduction in sediments. This S reduction can have important effects on the concentration of SO_4^{2-} in drainage water, and results in the generation of ANC. The importance of sediment reactions to the acid-base chemistry of surface water depends mainly on the flux rate of material across the sediment-water interface and the amount of time that water remains in contact with the sediment (Kelly, 1987) Baker and Brezonik, 1988; Turner, 1990). In some lakes having long water residence times, about half of the input SO_4^{2-} is retained in lake sediments (Kelly, 1987; Baker and Brezonik, 1988).

Sulfur is an essential nutrient for algae and planktonic bacteria. Nevertheless, S concentration in most lakes is well above the limiting concentration for algal productivity, and therefore biotic S uptake in the water column is not a quantitatively important part of the S cycle in acid-sensitive lakes (Turner, 1990).

3.4.1.3. Export of Sulfur

Terrestrial Ecosystems

In order for atmospherically deposited S to exert influence on drainage water, with the range of associated environmental effects that can occur, it must be exported as SO_4^{2-} from the soil. If the incoming S in atmospheric deposition is retained in the vegetation or soil compartments, it will not be available to affect soil water or surface water downstream within the watershed. In areas of S deposition, almost all deposited S moves into the soil and can then be exported from the terrestrial ecosystem or adsorbed on soil. In most parts of the U.S., most deposited S is exported in drainage water. In much of the southeastern U.S., however, S adsorption on soil substantially limits S export (See discussion in Annex B).

Transitional Ecosystems

When saturated, wetland soils act as sinks for incoming S via SO_4^{2-} reduction. Sulfide is produced through this process and sequestered in anoxic wetland sediments (Mitsch and Gosselink, 2000). However, it has been observed that wetlands can act as sources of SO_4^{2-} to downstream drainage waters during storm events that follow prolonged periods of drought (Dillon and LaZerte, 1992; Devito and Hill, 1999; Eimers, 2002; Jeffries et al., 2002; Laudon et al., 2004; Mitchell, 2006). The mechanism has been described as follows. SO_4^{2-} is produced through oxidative processes in wetland sediments when they are exposed to atmospheric O_2 as the water Table falls during periods of drought. This newly formed SO_4^{2-} is mobile, and therefore can be flushed from the wetland into streams or lakes when the water table rises as more typical hydrologic conditions resume. This flush of SO_4^{2-} can result in episodic acidification of downstream surface waters (Laudon et al., 2004) and potentially prolong the chemical recovery of surface water ANC as S deposition declines (Aherne et al., 2006).

Much of the supporting research on this topic has been performed within the boreal watersheds of Ontario, Canada (Dillon and LaZerte, 1992; Devito and Hill, 1997; Jeffries et al., 2002; Aherne et al., 2004; Laudon et al., 2004). A Sphagnum-conifer wetland within the Plastic Lake watershed in Ontario was determined to be a source of SO_4^{2-} to downstream drainage waters after extended periods of summertime drought (Dillon and LaZerte, 1992). Comparisons of stream water chemistry were made between the wetland inlet and the wetland outlet, which drains a watershed consisting entirely of upland soils. The results showed little difference between SO_4^{2-} concentrations in the wetland inlet and outlet during typical hydrologic conditions. However, SO_4^{2-} concentrations in the outlet increased by up to a factor of five during storm events that followed extended periods of drought. This occurred during 4 separate years.

The majority of the study watersheds in the Plastic Lake region of Ontario, Canada have consistently exported more SO_4^{2-} than was atmospherically deposited on an annual basis over an 18–year period (Eimers, 2002). This observation suggests either the existence of an internal watershed SO_4^{2-} source, or an underestimation of S deposition. It is possible that dry deposition is underestimated (Likens et al., 1990; Edwards et al., 1999), but a variety of potential watershed sources of additional S have also been proposed in areas that are sensitive to atmospheric S deposition, including:

- weathering of S-containing minerals (Baron, 1995)
- desorption of SO_4^{2-} previously adsorbed to soils when S deposition was higher (Driscoll et al., 1995; Mitchell, 1996)
- mineralization of S previously incorporated into organic matter (Driscoll et al., 1998)
- drought-related oxidation and release of S stored in wetlands and riparian soils (Dillon and LaZerte, 1992; Dillon et al., 1997)

Underestimation of dry deposition was not considered to be a significant issue for the Canadian study watersheds (Eimers, 2002). Furthermore, mineral weathering is not considered a significant source of SO_4^{2-} in that region, due to the low S content of the bedrock (Neary et al., 1987). Reoxidation and mobilization of S stored in wetland sediments was considered the most likely explanation for the observed higher SO_4^{2-} outputs for those watersheds that contain a significant proportion of wetland. Other mechanisms, including increased soil SO_4^{2-} desorption and/or increased S mineralization in response to decreased S deposition inputs, may explain the SO_4^{2-} input/output imbalance observed in watersheds containing little or no wetland area (Alewell and Gehre, 1999; Eimers, 2002). Jeffries et al. (1995, 2002) determined that within the Turkey Lakes watershed in western Ontario wetland, reoxidation and SO_4^{2-} remobilization mechanism can delay lake acidification recovery by as much as 6 years.

Wetland S transformations have been incorporated into state-of-the-science modeling to better describe climate-induced acidification effects on lake water chemistry (Aherne et al., 2004, 2006). A wetland component to the MAGIC model was developed and tested for its ability to predict observed stream water SO_4^{2-} fluxes from the Plastic Lake watershed (Aherne et al., 2004). This model was then used to investigate acidification recovery under two different climate scenarios: (1) an “average climate” scenario consisting of long-term (most recent 20 years) monthly precipitation and runoff and (2) a “variable climate” scenario that included sequential repetition of the measured monthly precipitation and runoff for the preceding 20 years. The average climate scenario did not include any significant drought periods, whereas the variable climate scenario included several periods of summer drought.

Model results under the average climate scenario suggested that chemical recovery of lake water would occur, with ANC reaching 40 μeq/L by 2020 and 50 μeq/L by 2080. However, the variable climate scenario projected that recovery would be greatly reduced. ANC recovery by 2080 was estimated to only reach 2.6 μeq/L. The authors acknowledged that reiterating the past 20 years of climate under the variable climate scenario was somewhat arbitrary. Nevertheless, results suggested that climate effects on the cycling of S can modify chemical recovery of lake water from acidification in watersheds that are wetland-influenced.

Aquatic Ecosystems

Export of S from surface waters is controlled primarily by retention in sediments through microbial SO_4^{2-} reduction. In-stream and in-lake biological demand for S is generally a very small component of the S input levels in areas affected by atmospheric S deposition. Sulfur reduction can be an important process regulating S export from aquatic ecosystems, mainly in waters that exhibit long hydraulic retention. Sulfur reduction in lake and pond sediments can also be closely associated with Hg methylation. Therefore, the dynamics of S storage and export can influence the bioavailability of Hg to fish, piscivorous wildlife, and humans who consume large quantities of fish.

3.4.1.4. Sulfur and Methylation of Mercury

Hg has long been established to be a potent neurological, reproductive, and developmental toxin that accumulates at progressively higher concentrations in higher trophic levels (biomagnification). For the protection of human health, the USEPA set the fish tissue criterion for MeHg at 0.3 μg/g. This has resulted in 2,436 fish consumption advisories for Hg in 2004, 2,682 in 2005 and 3,080 in 2006. Forty-eight states, 1 territory, and 2 tribes have issued mercury advisories. Eighty percent of all advisories have been issued, at least in part, because of mercury. Most of the new Hg advisories issued in 2005 and 2006 were in Wisconsin (293), Michigan (46), New York (36) and Minnesota (32). In 2005, American Samoa, Kansas, Oklahoma and Utah started issuing Hg advisories, and Iowa started in 2006. In 2006, a total of 14,177,175 lake acres and 882,963 river miles were under advisory for mercury. As of July 2007, 23 states have issued statewide advisories for mercury in freshwater lakes and/or rivers.

The biogeochemical cycle of Hg is closely tied to that of sulfur (S), and the presence of SO_4^{2-} in wetlands and lake sediments is essential for entry of Hg into the food web. Hg is taken up by living organisms, and bioaccumulates, in the methylmercury (MeHg) form. SRB are the main agent of Hg methylation in the environment, and changes in SO_4^{2-} deposition have been shown to result in commensurate changes in both Hg methylation, and Hg levels in fish.

Effects of Mercury in Aquatic Biota

Adverse effects of Hg, including behavioral, reproductive, neurochemical, and hormonal effects, have been demonstrated in piscivorous mammals and birds (USEPA, 1996; Scheuhammer et al., 2007), and MeHg has been shown to be the form in which Hg accumulates in tissue of fish and piscivorous species (Bloom, 1992; Becker and Bigham, 1995; Harris et al., 2003; Scheuhammer et al., 2007). Exposure of fish and wildlife to Hg occurs primarily through the diet. Top predatory, especially piscivorous, animals feeding on aquatic food chains are at greatest risk for Hg accumulation and toxicity (Scheuhammer et al., 2007). Wildlife living in inland lake habitats tends to accumulate higher tissue concentrations of Hg than those living in coastal habitats (Frederick et al., 2002; Evers et al., 2005).

Available data suggest that numerous wild populations of fish, birds, and mammals experience MeHg exposures that are high enough to cause substantial reproductive, behavioral or health impairment. Reproduction is the component of response that appears to be most affected (Scheuhammer et al., 2007). In fish, exposure to MeHg can affect growth, reproductive ability, morphological characteristics, and feeding efficiency. Examples of studies documenting the effects of MeHg on fish include Friedmann et al. (1996), who investigated the effects of low-level (0.137 µg Hg/g) and high-level (0.987 µg Hg/g) dietary Hg concentrations (as MeHg) on hatchery juvenile walleye (*Stizostedion vitreum*). These experimental Hg exposures were chosen to reflect dietary Hg concentrations commonly encountered in North American lakes and streams. Results showed impaired fish growth and impaired gonad development in males. Fjeld et al. (1998) exposed grayling (*Thymallus thymallus*) embryos to varying concentrations of MeHg (0.16, 0.8, 4.0, and 20 µg Hg/L) during their first 10 days of development. This exposure resulted in body tissue MeHg concentrations of 0.09, 0.27, 0.63, and 3.80 µg Hg/g respectively. Morphological deformities were observed in fish exposed to the highest level of MeHg. Samson and Shenker (2000) also observed morphological disturbance in zebrafish (*Danio rerio*) at embryonic MeHg exposure levels of 20 and 30 µg CH_3HgCl/L. Other fish such as mummichog (*Fundulus heteroclitus*) and rainbow trout (*Oncorhynchus mykiss*) have also been observed to suffer teratogenic effects such as cyclopia, tail flexures, cardiac malformations, jaw deformities, twinning, and axial coiling from embryonic MeHg exposure (Samson and Shenker, 2000). Fish survival and subsequent population status can be jeopardized as a result of exposure to MeHg. Fathead minnows (*Pimephales promelas*) showed impaired feeding efficiency after exposure to both 6.79 and 13.57 µg $HgCl_2$/L (Grippo and Heath, 2003). Reduced feeding efficiency and competitive ability was also observed in grayling exposed to 0.8 to 20 µg Hg/L as embryos (Fjeld et al., 1998).

Role of Sulfur in the Biogeochemical Cycle of Mercury

The global cycle of Hg has atmospheric, aquatic, edaphic, and biotic components. In the atmosphere, Hg is transported locally, regionally, and globally, depending on speciation. Both elemental and oxidized forms are found in soil and aquatic environments, but the oxidized form is more prevalent. MeHg is the form that is found in tissues (Figure 3-57). SRB are the main agent of Hg methylation in the environment. Although Hg methylation in watersheds has been shown to occur through other processes, their contribution to MeHg loads is negligible in comparison to that of SRB-mediated methylation. Addition of SO_4^{2-} has been demonstrated to stimulate mercury methylation by SRB in studies spanning scales from the culture of isolated bacteria, to the experimental amendment of entire lakes. Those studies have included addition of SO_4^{2-} at rates corresponding to observed deposition.

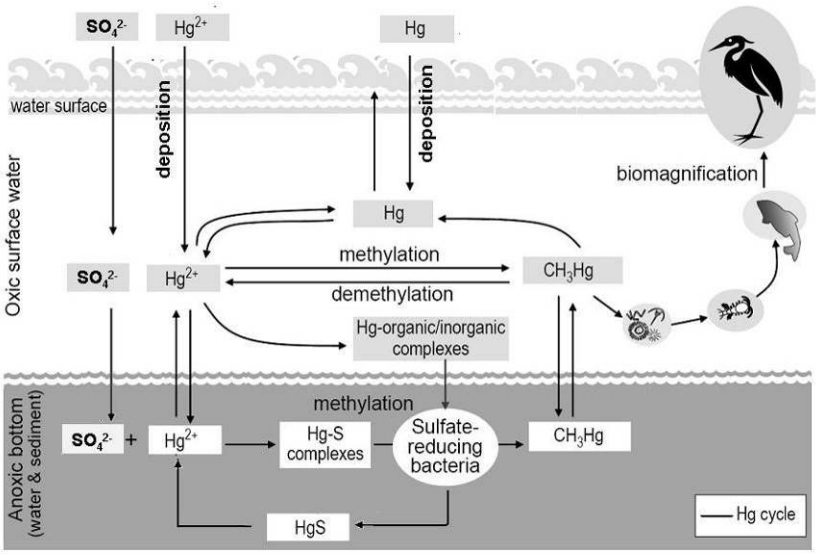
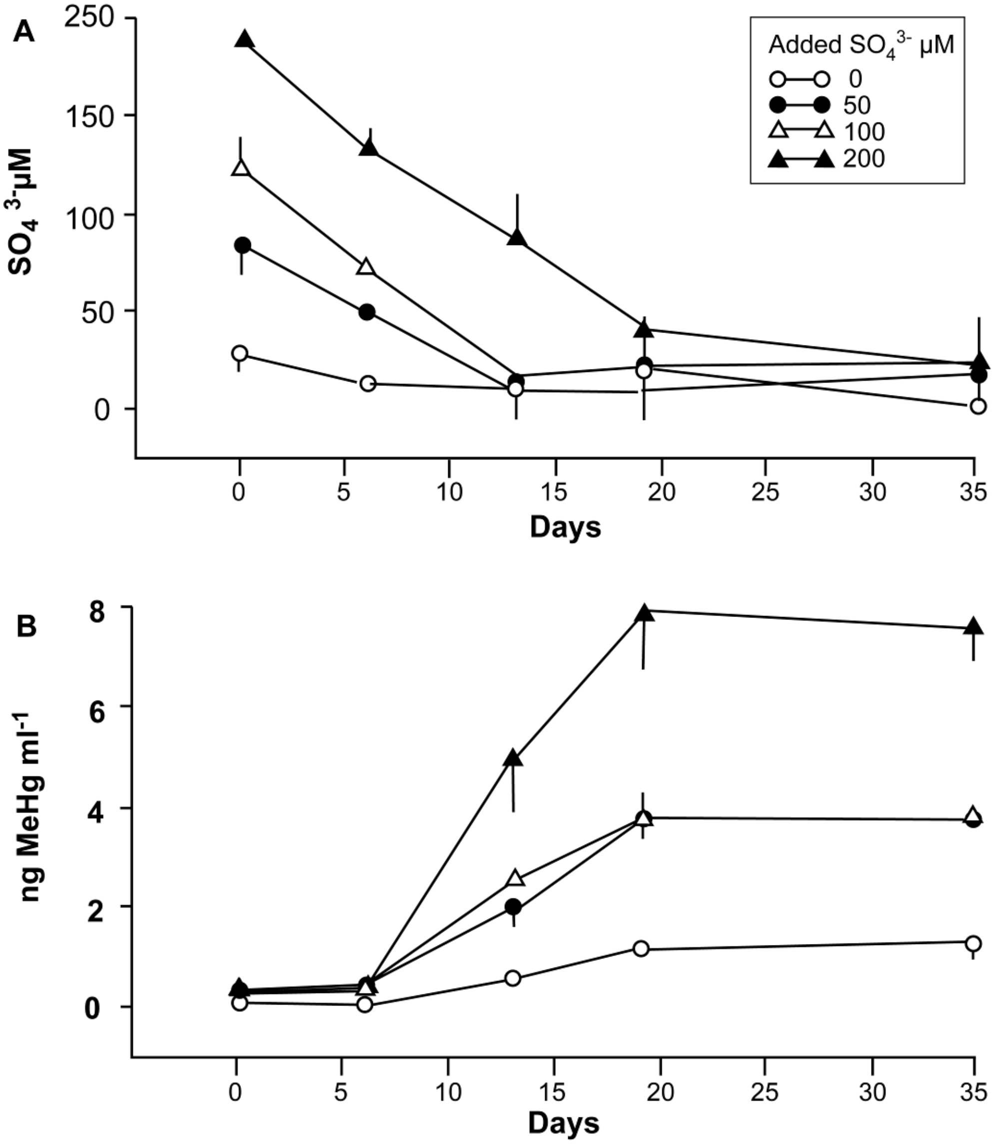


Figure 3-57. Simplified cycle of Mercury, showing the role of Sulfur. Arrows are not proportional with actual rates.

SRB are commonly found in anoxic wetland and lake bottom sediments (Compeau, 1985; Gilmour, 1991; Gilmour, 1992). Under increased SO_4^{2-} availability, their number and activity increase. The mechanisms for Hg methylation, as mediated by SRB, have been discussed by Choi et al. (Choi, 1994), Ekstrom et al. (Ekstrom, 2003), and Ekstrom and Morel (Ekstrom, 2004). Abiotic mechanisms responsible for Hg methylation have been discussed by Weber (Weber, 1993), Hintelmann and Evans (Hintelmann, 1997), and Siciliano et al. (Siciliano, 2005). Studies demonstrating the response of SRB-mediated methylation to SO_4^{2-} in pure cultures include King et al. (King, 2000), Benoit et al. (2001a), and Benoit et al. (2001b). This response has also been established in samples of soil and sediments (Compeau, 1985; Gilmour, 1992) Harmon et al., 2004), and in experimental manipulations in wetlands and lakes (Branfireun et al., 1999; Branfireun et al., 2001; Benoit et al., 2003; Frost et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006; Watras, 2006)Wiener et al., 2006).

Evidence regarding the importance of SRB in MeHg production was provided by Compeau and Bartha (Compeau, 1985), and Gilmour et al. (Gilmour, 1992), who showed that MeHg production was substantially reduced with addition of a known SRB inhibitor (Na_2MoO_4). This is also in agreement with observations of SRB-mediated Hg methylation in salt marsh sediments (Compeau, 1985). The work of Gilmour et al. (Gilmour, 1992) considered anoxic lake bottom sediments, rather than wetland sediments. However, anoxia is also common in freshwater wetland sediments, where SO_4^{2-} addition has also been observed to enhance Hg methylation (Branfireun, 1999; Harmon, 2004; Jeremiason, 2006). Accumulation of sulfidic forms of S in sediments, also resulting from SRB activity, has been shown to diminish the availability of S to SRBs, and thus net Hg methylation (Gilmour et al., 1998; Benoit et al., 1998; Benoit et al., 2001; Benoit et al., 1999a; Benoit et al., 1999b; King et al., 2001).

Gilmour et al. (1992) investigated MeHg production within anoxic sediments of a reservoir located in central Massachusetts. Elevated MeHg production with SO_4^{2-} addition was measured in both experimental laboratory slurries (Figure 3-58b) (Gilmour, 1992) and intact sediment cores. The background SO_4^{2-} concentration in the experimental sediment slurries was 60 μeq/L. SO_4^{2-} additions of 0, 100, 200, and 400 μeq/L were applied to these samples in the presence of 50 mg/L of Hg as HgCl2. The rate of production and the final concentration of MeHg increased in proportion to the initial SO_4^{2-} concentration. Furthermore, SO_4^{2-} concentrations decreased during the experiment (Figure 3-58a); Gilmour, 1992), suggesting that SO_4^{2-} reduction had occurred. MeHg production within isolated lake bottom sediment cores was also enhanced across a gradient of SO_4^{2-} addition (3 to 1040 μmol sodium SO_4^{2-} [Na_2SO^4]; Figure 3-59). Sediment MeHg production was most enhanced when SO_4^{2-} concentration was above about 60 μeq/L, with increased production from a pre-treatment background MeHg concentration of 0.26 ng/g to approximately 7.0 to 8.5 ng/g. These results suggest maximum MeHg production at SO_4^{2-} concentrations between about 200 and 400 μeq/L, although optimal conditions for methylation are likely to vary with other factors that influence SO_4^{2-} reduction. SO_4^{2-} concentrations in the range of these experiments (about 60 to 200 μeq/L) are often found in waters affected by S deposition in the U.S.



Source: Gilmour et al. (Gilmour, 1992).

Figure 3-58. (A) SO$_4^{2-}$ and (B) methylmercury (MeHg) concentrations as a function of time in sediment slurries made from Quabbin Reservoir littoral sediments. Each delta point represents the average value from three separate incubations and the associated standard error.

Interacting factors

Many studies have also shown an association between low lake water pH and high Hg concentrations in fish (Grieb et al., 1990; Suns and Hitchin, 1990; Driscoll et al., 1994; Kamman et al., 2004). Hrabik and Watras (Hrabik, 2002) found that decreases in fish Hg concentration in an experimentally de-acidified lake basin exceeded those in the reference lake basin by a factor of two over a 6–year period of experimental de-acidification. The association between low pH and high Hg accumulation in fish suggests a response of methylation to pH, but although SRB activity does respond to pH (Kelly, 2003), quantification of the interactive effects of pH with SO_4^{2-} in the environment has only been tentative.

Other interacting factors, mainly Fe, P, and dissolved organic matter, have been identified, but very incompletely quantified (Munthe et al., 2007; Watras and Morrison, 2008). Driscoll et al. (2007) developed indicators of Hg sensitivity using two stratified, random-probability surveys of northeastern lakes combined with the survey data sets of Chen et al. (2005). This analysis showed that lakes with Hg levels above the EPA criterion of 0.3 µg/g in yellow perch had significantly higher dissolved OC, and lower pH, ANC, and total P than lakes with fish Hg concentrations below 0.3 µg/g (Driscoll et al., 2007). Based on the probability surveys, they calculated that about 20% of lakes in the region had total P concentrations above 30 µg/L and yellow perch Hg concentrations below 0.3 µg/g. In the remaining 80% of lakes, 75% had yellow perch Hg concentrations exceeding 0.3 µg/g when surface water dissolved OC levels exceeded 4.0 mg C/L, a pH of less than 6.0, or an ANC of less than 100 µeq/L. Most Hg in the water column of freshwaters is bound to organic matter, either to dissolved OC or to suspended particulate matter. Therefore, total Hg and MeHg concentrations are often positively correlated with dissolved OC in lake waters (Mierle and Ingram, 1991; Driscoll et al., 1994; EPA, 1996). Dissolved OC, in turn, has an important influence on pH. Thus, several interrelated factors seem to affect Hg loading in tissue. For example, Driscoll et al. (1995) found one or more yellow perch exceeding the 0.5 µg/g action level in 14 of 16 Adirondack study lakes despite wide ranges in pH (to above 7) and ANC (to above 200 µeq/L) (Mierle, 1990). Driscoll et al. (1994) concluded that the most obvious factor regulating the concentration and availability of both total Hg and MeHg in Adirondack lakes is dissolved OC. They found increased fish Hg concentrations with increasing dissolved OC up to dissolved OC concentrations of about 8 mg/L, followed by lower concentrations in the highly dystrophic Rock Pond (dissolved OC = 26 mg/L). They hypothesized that dissolved OC may bind with MeHg at very high dissolved OC concentration, limiting the bioavailability of the Hg. In addition, calculations made by Driscoll et al. (1995) with the Hg Cycling Model suggested that increases in dissolved OC result in increasing concentrations of Hg in biota, but decreases in the bioconcentration factor of Hg in fish tissue. Because the transport of Hg to Adirondack lakes appeared to be linked to dissolved OC production from wetlands within the watersheds of the study lakes, Driscoll et al. (1995) concluded that dissolved OC is important in regulating Hg concentrations in the lakes, and ultimately the supply to fish. In a peatland experiment testing the effects of various sources of organic C, Mitchell et al. (2008) demonstrated that while SO_4^{2-} is required for methylation of Hg, the addition of some sources of C greatly enhanced the process. The combinations of C and SO_4^{2-} additions that enhanced methylation in the experiment corresponded to the combinations present in MeHg ‘hot spots’ within watersheds that include peatlands.

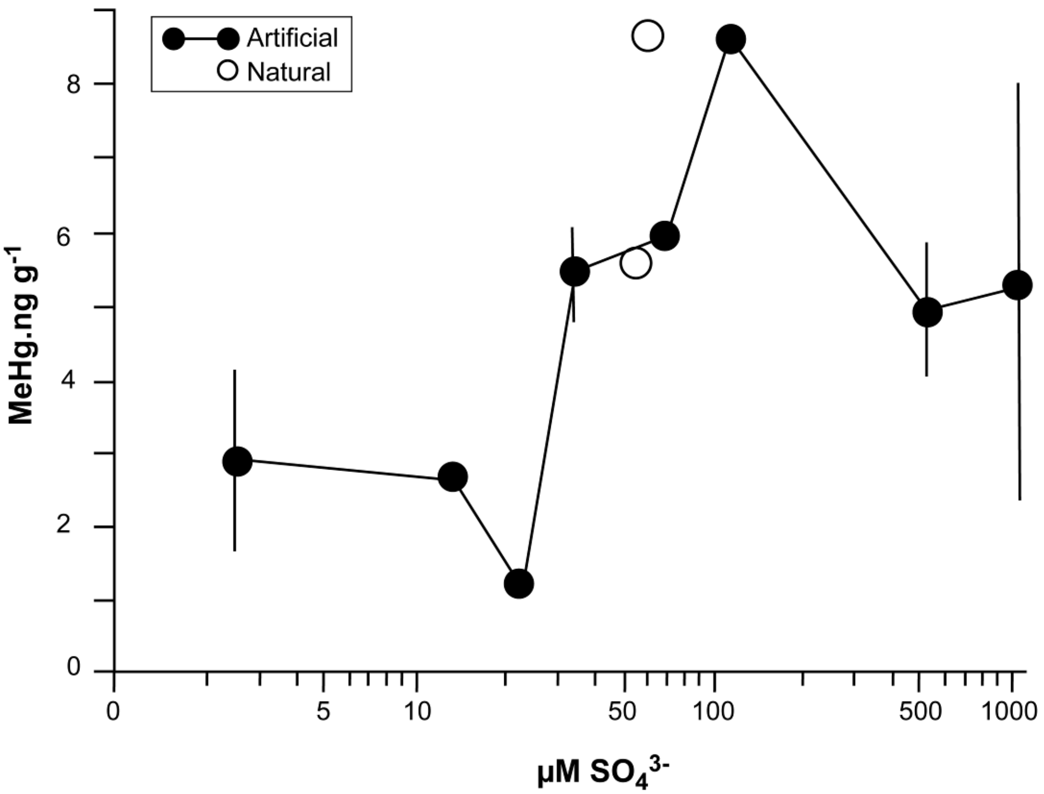


Figure 3-59. Methylmercury produced in sediment cores incubated two weeks under artificial lake water containing 3–1040 µM Na_2SO_4. Error bars represent standard error between two replicate cores. Data from cores incubated under natural water are shown individually. The average MeHg concentration in unamended Purgee sediments sampled in July was 0.26 ± 0.01 ng/g (n = 2).

Several researchers have suggested that the export of Hg from terrestrial watersheds to lakes may be controlled in large part by the nature of watershed soils and the transport of naturally occurring organic acids (Mierle, 1990; Meili, 1991; Mierle and Ingram, 1991; Engstrom et al., 1994). This suggestion is based partly on the fact that dissolved organic matter strongly binds with Hg, and partly on the observed positive correlation between Hg accumulation in lake sediments and the ratio of the watershed area to the lake area in relatively undisturbed watersheds ($r^2 = 0.91$; $r^2 = 0.91$) (Engstrom et al., 1994). Engstrom et al. (1994) concluded that Hg export from the terrestrial watershed to lake water may be explained by factors regulating the export of fulvic and humic matter and by watershed area. They based this conclusion on the close correlation between Hg concentration and humic matter in surface waters, the observation that peak concentrations of both Hg and dissolved organic matter tend to occur during periods of high runoff, and the experimental determination that Hg transport occurs primarily in upper soil horizons.

Ecosystems Characteristics Conducive to Methylation

S deposition is most likely to result in enhanced Hg methylation in regions that receive relatively high levels of atmospheric Hg and S deposition and that exhibit characteristics conducive to methylation. These include low ANC and low pH surface waters, with large upstream or adjoining wetlands (Scheuhammer and Blancher, 1994; Chen et al., 2005; Scheuhammer et al., 2007). Such sensitive ecosystems are prevalent in portions of the northeastern U.S. and southeastern Canada. Studies of Hg concentration in feathers, blood, and eggs of the common loon (*Gavia immer*) indicate decreasing concentrations from west to east in this region (Evers et al., 1998, 2003). This pattern is in general agreement with patterns of deposition of both Hg and S.

Wetland environments have been shown to be significant areas of MeHg production and sources of export to downstream receiving waters (St. Louis et al., 1994). Wetland MeHg production has been measured at rates 26 to 79 times higher than in upland areas of a Canadian boreal forest (wetland: 1.84 to 5.55 mg/ha/yr$^-$; upland: 0.07 mg/ha/yr) (St. Louis et al., 1994). Watersheds containing 14.0% to 16.3% wetland yielded 5 to 14 times more MeHg than upland catchments that lacked wetlands (St. Louis et al., 1994). In the same region, St. Louis et al. (1996) found that all watersheds were net sinks for total Hg, but that watersheds containing wetlands regularly exported MeHg (St. Louis et al., 1996). However, MeHg export from these watersheds was not directly proportional to percent wetland coverage, indicating that other variables are also involved in the major processes that regulate MeHg production and export. In particular, the level of atmospheric Hg deposition and the acid-base chemistry of drainage water may be important.

Branfireun et al. (1996) measured highest peat and pore water MeHg concentrations in wetland areas that exhibited characteristics of a poor fen environment (i.e., interaction with nutrient-poor ground water). St. Louis et al. (1996) observed that high water yield resulted in high MeHg export. Thus, the proportion of upland to wetland land area within a watershed was not the only control on MeHg export, but wetland type and annual water yield also played important roles (St. Louis et al., 1996).

As noted by Munthe et al. (2007), multiple hydrological, chemical, and biological characteristics of watersheds determine the movement of Hg between compartments. With regards to MeHg, however, the chemical and biological characteristics of the lake compartment may be more critical: comparing two remote lakes, one a seepage lake, and the other a drainage lake, Watras and Morrison (2008) found that although wetland MeHg export was the dominant external source of MeHg to the drainage lake, in-lake methylation remained four- to seven-fold greater than loading from the wetland. Likewise, Harris et al. (2007) demonstrated, using traceable stable isotopes of Hg in a whole ecosystem experiment, that nearly all of the increase in fish MeHg came from Hg deposited to the lake surface, with less than 1% of Hg deposited to the watershed being exported to the lake, in any form.

Regardless, methylation of Hg occurs in anoxic sediments that contain a sufficient C source to support SO_4^{2-}-reducing bacterial activity along with an adequate supply of SO_4^{2-} for SRB-mediated SO_4^{2-} reduction. These conditions are found in lake and pond bottom sediments (Gilmour, 1992), freshwater wetland sediments (Branfireun et al., 1999; Harmon et al., 2004; Jeremiason et al., 2006), and salt mash sediments (Compeau, 1985). Such wetland systems, expected to exhibit high levels of Hg methylation, can be found throughout the U.S.

In a 1998 preliminary national survey of 106 sites from 21 basins across the U.S., Krabbenhoft et al. (1999) examined the relations of total Hg and MeHg in water, sediment and fish, and concluded that wetland density was the single most important factor controlling MeHg production at the basin scale. Four study basins along the east coast of the U.S. had the greatest methylation efficiency, while nationwide, sub-basins characterized as mixed agriculture and forest cover types had the highest methylation efficiency. A recent study of biological Hg hotspots in the northeastern U.S. and southeastern Canada (Evers et al., 2007) analyzed more than 7,300 observations of Hg levels in seven species from three major taxonomic groups to quantify the spatial heterogeneity in tissue Hg concentrations. Using published effect thresholds for Hg tissue concentrations, they identified five known and nine possible biological Hg hotspots. They reported that two of the biological hotspots, located in the Adirondack Mountains of New York and south-central Nova Scotia, occur in areas with relatively low to moderate atmospheric Hg deposition and high landscape sensitivity, as determined by the abundant forest and wetland cover as well as the acidic surface water conditions (Evers et al., 2007). Using data collected by the Northeastern Ecosystem Research Cooperative (NERC) initiative (Evers and Clair, 2005) to examine the link between Hg deposition and biotic Hg, Driscoll et al. (2007) concluded that “forested regions with a prevalence of wetland and unproductive surface waters,” which are common in the northeastern US, “promote high concentrations of Hg in freshwater biota.” In contrast, in a study of over 600 randomly selected streams and rivers throughout the western U.S., Peterson et al. (2007) found little relationship between fish tissue Hg concentrations and surface water pH, SO_4^{2-}, or dissolved OC. They attributed the lack of a relationship to the fact that low pH (<7) and high dissolved OC systems were rare in the West. The major factors controlling fish tissue Hg concentrations in western streams and rivers were fish size and feeding group, not water chemistry. Likewise, a 1999 survey of high altitude western lakes with both low Hg and low MeHg (Krabbenhoft et al., 2002) identified high pH and elevated rates of photo-demethylation as the likely causes for low net methylation. Water clarity and high sunlight exposure were cited as sources of enhanced photo degradation of MeHg.

S deposition and MeHg in fish

As shown by Harris et al. (2007), the response of fish MeHg to changes in Hg deposition can occur on a time scale of less than a year. In their comprehensive synthesis of information on all elements of the connection between environmental Hg loading, and Hg in fish, Munthe et al. (2007) concluded that several interacting factors are expected to affect the speed and magnitude of the changes in fish contamination that result from changes in Hg loading. As indicated previously, numerous studies have ascertained that SO_4^{2-} supply is a principal driver of MeHg production, and Hrabik and Watras (Hrabik, 2002) showed that decreased deposition of both Hg and SO_4^{2-} are followed by MeHg decrease in fish. Drevnick et al. (Drevnick, 2007), however, were able to establish an explicit linkage between S deposition and fish Hg, by verifying that even in the absence of change in Hg deposition, changes in S deposition alone result in commensurate changes in MeHg accumulation in fish.

3.4.1.5. Summary

The most important non-acidification effect of S deposition in areas of the U.S. that receive high levels of S deposition is the influence of S supply on Hg methylation. The extent of methylation governs the bioavailability of Hg to biota. High concentrations of MeHg in fish can constitute an important health concern for people who consume large quantities of fish and can affect the health and reproduction of piscivorous wildlife, including the common loon, bald eagle (*Haliaeetus leucocephalus*), and river otter (*Lutra canadensis*). Hg methylation occurs mostly in wetland soils and bottom sediments of lakes and ponds. S deposition to these ecosystems can enhance S reduction and Hg methylation processes. Although S can also be directly toxic to terrestrial vegetation, levels of S in ambient air pollution and levels of S deposition commonly found in the U.S. are generally not high enough to cause substantial direct adverse effects on plants.

3.4.1.6. S Nutrient Enrichment Case Study: Interactive Effects of S and Hg in Little Rock Lake, WI

Little Rock Lake is an 18–ha precipitation-dominated seepage lake located in a forested and undisturbed catchment of northcentral Wisconsin. The extensive experimental work conducted at Little Rock Lake was described by Hrabik and Watras (2002). The research at Little Rock Lake provides considerable insight into the interactions of S and Hg in the lake, and also bioaccumulation of Hg in fish in freshwater ecosystems.

In 1984, the lake was divided into two basins by placing an impermeable curtain across a narrow lake section. One of the basins was experimentally acidified from pH 6.1 to 4.7 by mixing H_2SO_4 into the surface water over a period of 6 years (Watras, 1989). The other basin was left undisturbed to serve as a reference. Beginning in 1990, the treated basin was left to de-acidify naturally.

Hg accumulation in yellow perch showed significant declines in fish in both the experimental and reference basins between 1994 and 2000, commensurate with declines in atmospheric deposition of Hg.

Fish Hg concentrations in the experimental basin were 57% higher in 1994 than in 2000, whereas concentrations were 36% higher in the reference basin (Hrabik, 2002). The authors determined that half of the decrease in fish Hg concentration was attributable to lakewater de-acidification and the other half was associated with regional declines in atmospheric Hg deposition. In the reference basin, which had higher pH and exhibited a lower rate of de-acidification, 15% of the decrease in fish Hg concentration was due to de-acidification (Hrabik, 2002).

These findings were consistent with the hypothesis that SO_4^{2-} and newly added Hg synergistically contribute to enhanced bioaccumulation of Hg in fish. In subsequent analyses, Watras et al. (Watras, 2006) found that maximum CH_3Hg^+ concentrations in hypolimnetic waters were directly correlated with the SO_4^{2-} deficit (mean epilimnetic SO_4^{2-} concentration - minimum hypolimnetic SO_4^{2-} concentration) and they observed a correlation between CH_3Hg+ and lakewater SO_4^{2-} concentrations. The tracking of external loads of Hg and S, and internal loads of Hg and CH_3Hg^+ suggested a tight biogeochemical connection among atmospheric deposition, SO_4^{2-} reduction, and Hg methylation. However, these relationships did not fully explain the observed large inter-annual variability in CH_3Hg+ accumulation. The variability appeared to be influenced by OC, terrestrial runoff and temperature.

The results from the Little Rock Lake acidification experiment suggest that S deposition plays an important role in the accumulation and methylation of Hg in freshwater ecosystems, and that acid deposition and Hg deposition have a disproportionately larger effect together than either would have separately (Watras, 2006).

3.4.2. Direct Phytotoxic Effects of Gaseous N and S on Vegetation

This section is intended to provide a brief overview of the exposure and phytotoxic effects of gaseous N and S compounds on vegetation. This recognizes that the major focus of this review is the effect of acidifying deposition and N deposition on ecosystems. However, direct effects of gaseous N and S could augment the effects of deposition on vegetation and effects of gaseous N and S may occur in some areas.

The effects of gaseous pollutants such as SO_2, NO_2, NO, HNO_3 and O_3 on vegetation have been studied since the 1950s and 1960s. Methodologies have been developed to study these effects in the lab, greenhouse, and in the field. The methodologies to study gaseous pollutants effects on vegetation have been recently reviewed in the O_3 AQCD (EPA, 2006). A thorough description of the methodologies used to expose vegetation to gaseous pollutants can be found in Section AX9.1 of the O_3 AQCD (EPA, 2006) and Section 9.2 in the 1993 NO_2 AQCD (EPA, 1993).

Uptake of gaseous pollutants in a vascular plant canopy is a complex process involving adsorption to surfaces (leaves, stems, and soil) and absorption into leaves. These pollutants penetrate into leaves primarily in gaseous form through the stomata, although there is evidence for limited pathways via the cuticle. Pollutants must be transported from the bulk air to the leaf boundary layer in order to get to the stomata. Although the transport of pollutants through a boundary layer into the stomata region is known to be important, and even rate limiting in many cases of low wind velocity, its description has been defined from aeronautical concepts and usually relates to smooth surfaces that are not typical of leaf-surface morphology; however, it is nearly the only treatment available (Gates, 1968). Once through the boundary layer, the gas must enter the leaf through the stomata. The entry of gases into a leaf is dependent upon the physical and chemical processes of gas phase and surfaces as well as the stomatal aperture. The aperture of the stomata is controlled largely by the prevailing environmental conditions, such as humidity, temperature, and light intensity. When the stomata are closed, as occurs under dark or drought conditions, resistance to gas uptake is very high and the plant has a very low degree of susceptibility to injury (Figure 3-60). The stomatal control of uptake of gaseous pollutants is described in more detail in AX9.2 of the O_3 AQCD (EPA, 2006a) and Section 9.3.1.5 of the oxides of N AQCD (EPA, 1993a). It should be noted that unlike higher plants, mosses and lichens do not have a protective cuticle barrier to gaseous pollutants, a major reason for their sensitivity to gaseous S and N.

3.4.2.1. Direct Phytotoxic Effects of SO_2 on Vegetation

It has been known since the early 1900s that exposure of plants to SO_2 can cause damage and death (Wislicenus, 1914). The large sources of SO_2 were ore smelters. Sulfides in the ore were oxidized during smelting and resulted in large releases of SO_2. Emissions from large ore smelters in the U.S. and Canada resulted in large areas denuded of vegetation surrounding these facilities (Swain 1949; Thomas 1951). Much of the damage to the vegetation was due to acute effects of high concentrations of SO_2. However, as early as 1923 researchers recognized that SO_2 might reduce plant growth without acute symptoms of foliar injury (Stoklasa, 1923). In the 1950s through the early 1980s, there was much research on the effects of lower levels of SO_2 as well as the interaction with other pollutants such as O_3 and NO_2. Since then, there has been much less research on the effects of SO_2 on vegetation, especially in the U.S., due to the decreasing ambient concentrations of SO_2. The effects of SO_2 on vegetation are summarized below.

Currently, SO_2 is the only criteria pollutant with a secondary NAAQS distinct from the primary standard. This standard is to protect acute foliar injury resulting from SO_2 exposure. The standard is a 3–h average of 0.50 ppm and was promulgated in 1970 to protect against acute foliar injury in vegetation. The last AQCD for ecological effects of SO_X was completed in 1982 and concluded that controlled experiments and field observations supported retaining this secondary standard (EPA, 1982a,b).

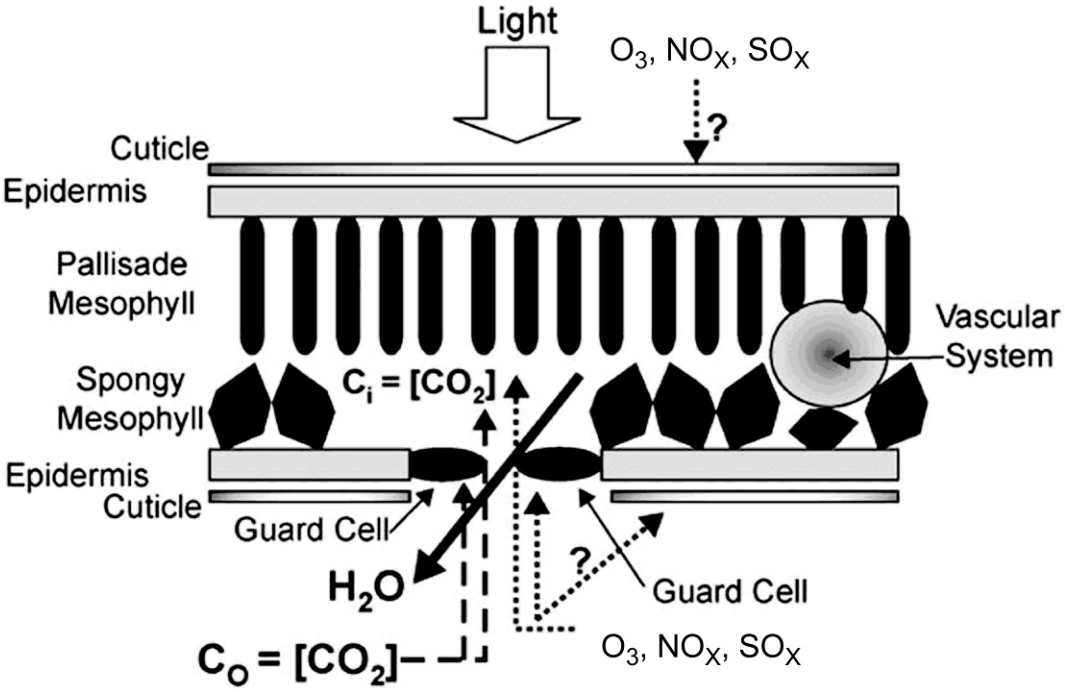


Figure 3-60. The microarchitecture of a dicot leaf. While details among species vary, the general overview remains the same. Light that drives photosynthesis generally falls upon the upper (adaxial leaf surface. CO_2, SO_X, NO_X, and O_3 gases generally enter through the stomata on the lower (abaxial) leaf surface, while water vapor exits through the stomata (transpiration).

Acute foliar injury usually happens with hours of exposure, involves a rapid absorption of a toxic dose and involves collapse or necrosis of plant tissues. Another type of visible injury is termed chronic injury and is usually a result of variable SO_2 exposures over the growing season. After entering the leaf, SO_2 is converted to sulfite and bisulfite, which may be oxidized to SO_4^{2-}. SO_4^{2-} is about 30 times less toxic than sulfite and bisulfite. The conversion of sulfite and bisulfite to SO_4^{2-} results in net H^+ production in the cells. Kropff (1991) proposed that the appearance of SO_2-induced leaf injury was likely due to a disturbance of intracellular pH regulation. Kropff (1991) pointed out several studies that the pH of homogenates only shifted towards greater acidity when plants were lethally damaged from long-term SO_2 exposures (Grill 1971; Jager and Klein, 1977; Thomas et al., 1944). The appearance of foliar injury can vary significantly between species and growth conditions affecting stomatal conductance. Currently there is not regular monitoring for SO_2 foliar injury effects in the U.S.

Besides foliar injury, long-term lower SO_2 concentrations can result in reduced photosynthesis, growth, and yield of plants. These effects are cumulative over the season and are often not associated with visible foliar injury. As with foliar injury, the effects of foliar injury vary among species and growing environment. The 1982 SO_2 AQCD summarized the concentration-response information available at the time (EPA, 1982a). Effects on growth and yield of vegetation were associated with increased SO_2 exposure concentration and time of exposure. However, that document concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Because of falling ambient SO_2 concentrations and focus on O_3 vegetation effects research, few studies have emerged to better inform a metric and levels of concern for effects of SO_2 on growth and productivity of vegetation.

Since the 1982 SO_2 AQCD was published, several studies have investigated a number of different effects of SO_2 effects on plants. Most recent research has been performed in areas of Europe where ambient SO_2 concentrations are generally higher than in the U.S. A brief summary of some of the major studies are presented in Table 3-28.

SO_2 is considered to be the primary factor causing the death of lichens in many urban and industrial areas, with fruticose lichens being more susceptible to SO_2 than many foliose and crustose species (Hutchinson et al., 1996). Damage caused to lichens in response to SO_2 exposure includes reduced photosynthesis and respiration, damage to the algal component of the lichen, leakage of electrolytes, inhibition of N fixation, reduced K^+ absorption, and structural changes (Farmer et al., 1992; Belnap et al., 1993; Hutchinson et al., 1996). Significant reductions in lichen photosynthesis have been measured at concentrations as low as 91 ppb over 2–4 hours (Huebert et al., 1985, Sanz et al. 1992). Damage to the algal component of the thallus is evidenced by its discoloration. The entire thallus dies soon after algal cells are damaged (Hutchison et al., 1996). At higher levels, SO_2 deactivates enzymes by chemical modification leading to reduced metabolic activity and loss of membrane integrity (Zeigler 1975 and 1977: Nieboer et al. 1976). It also binds to the central metal atoms of enzymes, adversely affecting membrane function and cell osmolality. In addition, SO_2 competitively inhibits carbonate (HCO_3) and phosphate (H_2PO_4) interactions with enzymes (Hutchison et al., 1996). Low pH increases the toxicity of SO_2 action (Farmer et al., 1992). The toxic effects of atmospheric deposition of SO_2 are lessened when lichen are attached to a substrate, typically bark or rock, having high pH or superior buffering capacity (Richardson and Cameron, 2004). Van Herk (2001) evaluated relationships between bark pH and air pollution levels as two significant variables affecting epiphytic lichen composition, and concluded that bark pH was the primary factor regulating the distribution of acidophilic species in The Netherlands. In studies of unpolluted areas, differences in bark chemistry also affect the presence and distribution of epiphytes (Farmer et al., 1992). Indirect effects on bark pH, caused by acidification and high SO_2 concentrations, also affect lichen distribution (Farmer et al., 1992).

3.4.2.2. Direct Phytotoxic Effects of NO, NO_2 and Peroxyacetyl Nitrate (PAN)

It is well known that in sufficient concentrations nitric oxide (NO) and NO_2 can have phytotoxic effects on plants through decreasing photosynthesis and inducing visible foliar injury (EPA, 1993a). The

1993 NO_X AQCD concluded that concentrations of NO_2 or NO in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (EPA, 1993a). Since the 1993 AQCD, very little new research has been done on these phytotoxic effects to alter this conclusion. However, it is known that these gases alter the N cycle in some ecosystems, especially in the western U.S., and contributing N saturation (Fenn et al., 2003a;(Bytnerowicz, 1996). See Section *3.3* for a discussion of the nutrient effects of N.

In general, NO and NO_2 enters leaves through stomata (Saxe, 1986). However, it has also been shown that the leaf cuticle may be an important receptor for NO_2 and there is evidence of transport of NO and NO_2 across isolated cuticles (Lendzian and Kerstians, 1988). Several studies have demonstrated that plant canopies can directly assimilate N in the form of NO_2, but canopy uptake of NO_2 is generally small relative to total plant uptake (Hanson et al 1989, Norby et al, 1989; nussbaum et al 1993; Ammann et al 199; segschneider et al 1993; vallano and sparks 2008; von ballmoos et al 1993). After entering the leaves, NO_2 dissolves in the extracellular water of the sub-stomatal cavity to form HNO_2 and HNO_3, which then dissociate to form nitrite, NO_3^-, and protons (Bytnerowicz et al, 1998a). Both cell and tonoplast membranes contain ATP-dependent H^+ pumps and the tonoplast pumps are strongly inhibited by NO_3^- (Bytnerowicz et al, 1998a). If extra protons are deposited in vacuoles of the plant cells during normal cellular regulation, then additional acidity will occur in combination with additional NO_3^-. This combination can cause disruptions in cellular control (Taylor and MacLean, 1970). NO_3^- and nitrite are metabolized to amino acids and proteins through a series of enzymatic reactions mainly involving NO_3^- and nitrite reductases (Amundson and MacLean 1982). The effectiveness of plants to reduce NO_3^- and nitrite to amino acids and proteins determines the potential of the plant to detoxify NO and NO_2 (Wellburn, 1990). Reduction of NO_3^- takes place outside of the chloroplast while the reduction of nitrite is coupled with the light reactions of photosynthesis. Therefore, when leaves are exposed to NO and NO_2 in the dark, highly phytotoxic levels of nitrite accumulate and may lead to greater toxicity to NO and NO_2 at night (Amundson and MacLean, 1982). Exposure to NO produces both NO_3^- and nitrite in the leaves, but the rate of NO_3^- accumulation is much slower than nitrite. Thus, plants exposed to high NO could be at risk to elevated concentrations of nitrite (Wellburn, 1990). More detailed information on the cellular effects of NO and NO_2 can be found in the 1993 NO_X AQCD.

The functional relationship between ambient concentrations of NO or NO_2 and a specific plant response, such as foliar injury or growth, is complex. Factors such as inherent rates of stomatal conductance and detoxification mechanisms and external factors, including plant water status, light, temperature, humidity, and the particular pollutant exposure regime, all affect the amount of a pollutant needed to cause symptoms of foliar injury. Plant age and growing conditions, and experimental exposure techniques also vary widely among reports of experimental exposures of plants to NO_2. An analysis conducted in the 1993 NO_X AQCD of over 50 peer-reviewed reports on the effects of NO_2 on foliar injury indicated that plants are relatively resistant to NO_2, especially in comparison to foliar injury caused by exposure to O_3 (EPA, 1993a). With few exceptions, visible injury was not reported at concentrations below 0.20 ppm, and these occurred when the cumulative duration of exposures extended to 100 hours or longer. At 0.25 ppm, increased leaf abscission was reported on navel orange trees (*Citrus sinensis* L), but only after exposures in excess of 1000 hours (Thompson et al. 1970). Green bean plants used as bio-indicators of NO_2 injury in Israel developed foliar injury symptoms when ambient concentrations exceeded 0.5 ppm (Donagi and Goren 1979). Only when concentrations exceeded 1 ppm did injury occur on most plants in less than one day (EPA, 1993a).

Reductions in rates of photosynthesis have been recorded in experimental exposures of plants to both NO and NO_2, but usually at concentrations significantly higher than would normally be encountered in ambient air. For example, Sabaratnam et al. (1988) reported that soybean (*Glycine max*) exposed 7 hours/day for 5 days showed an increase in photosynthetic rates at a concentration of 0.2 ppm, but a reduction in net photosynthesis at a concentration of 0.5 ppm. Short-term exposures of soybean to 0.6 ppm NO_2 for 2 to 3 hours also had no effect on net photosynthesis (Carlson 1983). Most plants appear to be more susceptible to NO than to NO_2, as shown by Saxe (1986b), who exposed a variety of horticultural plants raised in greenhouses (species of *Hedera*, *Ficus*, *Hibiscus*, *Nephrolepis*, and *Dieffenbachia*) to both NO and NO_2. Saxe (1986b) reported that reductions in net photosynthesis occurred at doses of NO that were 22 times less than that for NO_2. However, these reductions in net photosynthesis required concentrations as high as 1 ppm NO for 12 hours to elicit a response in these plants.

Hundreds of studies have been conducted on the effects of NO_2 on growth and yield of plants mostly performed in the 1970s and 1980s. These studies varied widely in plant species, growing conditions, exposure equipment, concentrations, durations, exposure regimes, and environmental conditions during exposures. No clear dose-response relationships for exposure to NO_2 and reductions in growth and/or yield of plants have emerged from these experiments. Readers are referred to the analysis of over 100 studies conducted in the 1993 NO_x AQCD. A few key studies are highlighted in this section. Several plant species appear to be susceptible to reductions in growth by relatively low concentrations of NO_2 (less than 0.2 ppm), particularly when exposed during low-light conditions. For example, nearly continuous exposure to 0.1 ppm NO_2 for eight weeks significantly reduced growth of Kentucky blue grass (*Poa pratensis* L) (Ashenden and Williams 1979; Whitmore and Mansfield 1983). Eight species of tree seedlings were exposed to 0.1 ppm NO_2 for six hours/day for 28 days, resulting in reduced shoot or root growth in two species, white ash (*Fraxinus americana* L.) and sweetgum (*Liquidambar styraciflua* L.), reduced height growth in two clones of loblolly pine (*Pinus taeda* L.), and no effects on the other species (Kress and Skelly 1982). No effects of NO_2 at 0.1 ppm or lower were observed on numerous other species, including potato (*Solanum tuberosum* L.), black poplar (*Populus nigra* L.), radish (*Raphanus sativus* L.), soybean, or peas (*Pisum sativum* L.) (EPA, 1993a). No effects of NO_2 were observed on soybeans grown in field plots subjected to a series of 10 episodic exposures averaging 0.4 ppm for 2.5 or

3 hours (Irving et al. 1982). Numerous studies have reported negative effects on growth of a variety of plants exposed to 0.5 ppm NO_2 and above (EPA, 1993a), but these concentrations are unrealistically high relative to current ambient levels of NO_2.

The 1993 NOx AQCD reviewed the extensive literature on the effects of NO_2 in combination with other gaseous air pollutants, particularly SO_2 and O_3 and concluded that combinations of pollutants can cause reductions in photosynthesis or foliar injury at concentrations lower than those associated with NO_2 acting alone, but the plant responses occur at concentrations much higher than are found in ambient air (EPA, 1993a). In addition, the presence of NO_2 in combination studies did not produce symptoms different from those caused by the dominant pollutant, either SO_2 or O_3, so that a plant response produced by combinations of NO_2 with other air pollutants in the field would be difficult, if not impossible, to distinguish from those of the other single pollutants (EPA, 1993a).

Since the 1993 NOx AQCD was completed most new research on NO_2 exposure to vegetation has taken place in Europe and other areas outside the US. For example, foliar NO_3 reductase activity was increased in Norway spruce (*Picea abies*) trees growing in near a highway with average exposures of about 0.027 ppm compared to trees growing 1300 meters away from the highway with NO_2 exposures less than 0.005 ppm (Ammann et al. 1995). This was consistent with other studies on Norway spruce in the field and laboratory (Ballomoos et al. 1993; Thoene et al 1991). Muller et al (1996) found that the uptake rate of NO_3 by roots of Norway spruce seedlings was decreased by the exposure to 0.1 ppm of NO_2 for 48 hours. Similarly, soybean plants grown in Australia had decreased NO_3 uptake by roots and reduced growth of plants exposed to 1.1 ppm of NO_2 for 7 days (Qiao and Murray, 1998). In a Swiss study, poplar cuttings exposed to 0.1 ppm for of NO_2 for approximately 12 weeks resulted in decreased stomatal density and increased specific leaf weight, but did not result in other effects such as leaf injury or a change in growth (GunthardtGoerg, 1996). However, NO_2 enhanced negative effects of ozone, including leaf injury, on these poplars when the pollutants were applied in combination (Gunthardt-Goerge et al 1996)(GunthardtGoerg, 1996 007D.

Peroxyacetyl nitrate (PAN) is a well-known photochemical oxidant, often co-occurring with O_3 during high photochemical episodes, which has been shown to cause injury to vegetation (See reviews by Cape, 2003, 1997; Kleindienst, 1994)(Smidt, 1994; Temple, 1983). Acute foliar injury symptoms resulting from exposure to PAN are generally characterized as a glazing, bronzing, or silvering of the underside of the leaf surface; some sensitive plant species include spinach, Swiss chard, lettuces, and tomatoes. Petunias have also been characterized as sensitive to PAN exposures and have been used as bioindicators of in areas of Japan (Nouchi et al., 1984). Controlled experiments have also shown significant negative effects on the net photosynthesis and growth of petunia (*Petunia hybrida* L.) and kidney bean (*Phaseolus vulgaris* L.) after exposure of 30 ppb of PAN for four hours on each of three alternate days (Izuta et al., 1993). As mentioned previously, it is known that oxides of N, including PAN, could be altering the N cycle in some ecosystems, especially in the western U.S., and contributing N saturation (Fenn et al., 2003a; Bytnerowicz, 1996) see Section 3.3). However, PAN is a very small component of N deposition in most areas of the US. Although PAN continues to persist as an important component of photochemical pollutant episodes, there is little evidence in recent years suggesting that PAN poses a significant risk to vegetation in the U.S.

3.4.2.3. Direct Phytotoxic Effects of HNO_3

Relatively little is known about the direct effects of HNO_3 vapor on vegetation. It has been established that HNO_3 has a very high deposition velocity compared to other pollutants and may be an important source of N for plants (Hanson, 1991; Vose, 1990; Hanson, 1992). This deposition could contribute to N saturation of some ecosystems close to sources of photochemical smog (Fenn, 1998). For example, in mixed conifer forests of the Los Angeles basin mountain ranges HNO_3 has been estimated to provide 60% of all dry deposited N (Bytnerowicz, 1999b; Bytnerowicz, 1999a).

Norby et al. (Norby, 1989) reported that exposure of 75 ppb of HNO_3 for one day increased nitrate reductase activity in red spruce foliage. In another study, foliar nitrate reductase activity was also increased in California black oak (*Quercus kelloggi*), canyon live oak (*Quercus chrysolepis*) and pondersosa pine (*Pinus ponderosa*) seedlings exposed to HNO_3 concentrations of 65 to 80 ppb for 24 hours (Krywult, 1997). Because the induction of nitrate reductase activity is a step in a process leading to the formation of organic N compounds (amino acids), the nitrate from HNO_3 could function as an alternated source of N for vegetation (Callanni et al 1999). However, in plants under stress, the reduction of nitrate to amino acids consumes energy needed for other metabolic processes.

At high ambient concentrations HNO_3 can cause vegetation damage. Seedlings of ponderosa pine and California black oak subjected to short-term exposures from 50–250 ppb of HNO_3 vapor for 12 hours showed deterioration of pine needle cuticle at 50 ppb in light (Bytnerowicz et al, 1998b). Oak leaves appeared to be more resistant to HNO_3 vapor, however, with 12-h exposures in the dark at 200 ppb producing damage to the epicuticular wax structure (Bytnerowicz et al, 1998b). The observed changes in wax chemistry caused by HNO_3 and accompanying injury to the leaf cuticle (Bytnerowicz et al, 1998b) may predispose plants to various environmental stresses such as drought, pathogens and other air pollutants. Because elevated concentrations of HNO_3 and ozone co-occur in photochemical smog (Solomon et al. 1998), synergistic interactions between the two pollutants are possible (Bytnerowicz et al, 1998a).

It has been suspected that HNO_3 may have caused a dramatic decline in lichen species in the Los Angles basin (Nash, 1999). The suggestion was strengthened by transplant of *Ramalina* lichen species from clean air habitats (Mount Palomar and San Nicolas Island) to analogous polluted habitats in the Los Angeles basin and repeatedly observing death of the lichens over a few weeks in the summer

(Boonpragob, 1991). Associated with this death was massive accumulation of H+ and NO_3^- by the lichen thalli (Boonpragob, 1989). Recently, Riddell et al. (2008) exposed the healthy *Ramalina menziesii* thalli to moderate (8–10 ppb) and high (10–14ppb) HNO_3 in month-long fumigations and reported a significant decline in chlorophyll content and carbon exchange capacity compared to thalli in control chambers. Thalli treated with HNO_3 showed visual signs of bleaching and by day 28 were clearly damaged and dead. The damage may have occurred through several mechanisms including acidification of pigments and cell membrane damage (Riddell, 2008). The authors concluded that *Ramalina menziesii* has an unequivocally negative response to HNO_3 concentrations common to ambient summer conditions in the Los Angeles air basin and it is very likely that HNO_3 has contributed to the dissappearance of this sensitive lichen species from the Los Angeles air basin, as well as other locations with arid conditions with high deposition loads (Riddell, 2008).

Table 3-28. Summary of recent studies of SO_2 exposure to plants.

Species	Exposure (Concentration, Duration [hours, days])	Endpoint(s)	Results	Reference
Scots pine (*Pinus sylvestris L.*); Norway spruce (*Picea abies (L.) Karst.*)	0, 50, 100, 150, 155 ppb SO_2 in growth chambers simulating natural weather in Finland in early June. The SO_2 concentrations represented the range of hourly SO_2 concentrations in the vicinity of industrial areas in Finland.	Concentrations of carbohydrates and secondary components	Exposure to SO_2 (100 and 155 ppb) reduced concentrations of glucose and fructose and increased concentrations of sucrose in pine needles. By contrast, one spruce clone had more glucose and fructose and less sucrose in needles exposed to 100 ppb SO_2, but in other spruces no changes in sugar concentrations were detected in different SO_2 exposures (50–155 ppb). Exposure to SO_2 had no effects on concentrations of monoterpenes in pine or spruce needles. Concentration of total resin acids was significantly smaller in needles exposed to the greatest concentration of SO_2 (155 ppb), but no changes were detected in other exposures (50–150 ppb) in either tree species. Concentrations of palustric and neoabietic acids were affected by SO_2 in needles of pine (155 ppb SO_2) and clonal spruces (100 ppb SO_2). Exposure to SO_2 did not affect foliar concentration of total phenolics in pine and spruce seedlings. In exposure to 0, 50, 100 and 150 ppb SO_2, total phenolic concentration of spruce roots increased linearly with elevated SO_2 exposure level. By contrast, one spruce clone had decreased concentrations of phenolics in roots after exposure to 155 ppb SO_2.	Kainulainen et al. (Kainulainen, 1995)
Scots pine (*Pinus sylvestris L.*); Norway spruce (*Picea abies (L.) Karst.*)	Mature trees growing at a polluted (32 ppb SO_2) and low pollution (1 ppb SO_2) sites in Finland. In addition, seedlings were placed in the chambers and open-field plots in mid-Sept. 1991 and fumigated 8 hours daily, 5 days a week from 19 September to 15 Nov 1991 and from 19 May to 12 Oct 1992. Mean pollutant concentrations in the fumigated chambers during the 8–h exposure periods were 5–6 ppb SO_2 and 7–8 ppb NO_2. The mean pollutant concentrations not receiving the particular pollutant were ~2 ppb SO_2 and 5 ppb NO_2.	Response of needle sulphur and N concentrations	Elevated concentrations of S were found in mature pine and spruce trees at polluted sites. The response of mature Scots pine to SO_2 differed from that of mature Norway spruce. The greater increase in the needle total S concentrations of pine suggested more abundant stomatal uptake of SO_2 compared to spruce. Mature pine was able to assimilate SO_4^{2-} derived from SO_2 into organic S more effectively than mature spruce at the high S and N deposition sites, whereas both pine and spruce seedlings accumulated S under NO_2+SO_2 exposure.	Manninen et al. (Manninen, 2000)
Mature red spruce (*Picea rubens Sarg.*)	Branches were fumigated in late summer of 1990 and 1991 in Canada. Four SO_2 treatment levels (0, 100, 200, 400 ppb)	Net photosynthesis, stomatal conductance, visible foliar injury	Net photosynthesis and stomatal conductance were found to decrease in direct proportion with cumulative foliar SO_2 absorption. Needle injury was observed in sun branches exposed to 200 and 400 ppb of SO_2 in 1990. Net photosynthesis was depressed by SO_2 regardless of branch position. Foliage subjected to high level SO_2 did not recover from SO_2 damage 1 year after treatment: needles had fallen off twigs and twig length of new foliage was reduced.	Meng et al. (Meng, 1994

Species	Exposure (Concentration, Duration [hours, days])	Endpoint(s)	Results	Reference
Scots pine (*Pinus sylvestris L.*); Norway spruce (*Picea abies (L.) Karst*.)	Open-air experiment, Finland- trees were exposed to F, N and S pollutants individually, or in mixtures, by spraying F and N compounds in aqueous solution and fumigating plants with gaseous SO_2, for 5 months in each of 3 consecutive growing seasons. SO_2 concentration among the trees varied between 35 and 140 ppb SO_2, depending on velocity and direction of the wind. Exact concentrations of SO_2 were not reported.	Visible symptoms, pollutant concentrations, ultrastructure of seedlings	Visible injury symptoms were most pronounced in combination exposures and whenever F was applied. Visiblesymptoms correlated well with needle pollutant concentrations. Exposure to F increased needle F contents particularly when F was applied with SO_2 or NH_4NO_3. This suggests that a reduction in N or SO_2 emissions, in F polluted areas, could improve the condition of conifers via decreased accumulation of phytotoxic F in the needles. Norway spruce needles accumulated 2–10 times as much S and F as those of Scots pine. In both species, exposure to SO_2 increased significantly the amount of cytoplasmic vacuoles, suggesting detoxification of excess sulphate or low pH. All exposures enhanced the accumulation of lipid bodies. Both visible symptoms and ultrastructural changes pointed to the more pronounced sensitivity of Norway spruce compared to Scots pine.	Wulff et al. (Wulff, 1996)
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst*.) European Silver Fir (*Abies alba Mill*.).	Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years.	Shoot length, leaf surface area, dry weight	Fumigation with SO_2 alone caused insignificant decreases of shoot length, total dry weight, and needle surface of spruce and fir. Fir trees fumigated with SO_2 in combination with O_3 showed lower rates of productivity compared to filtered control treatments. Beech was not as affected by SO_2 than with O_3 or SO_2 + O_3.	Billen et al. (Billen, 1990)
Norway spruce (*Picea abies* (*L*.))	Weekly concentrations of SO_2, (averaging 3–42ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years.	Ectomycorrhizal (EM) frequency, fine root structure, distribution of short roots	SO_2 resulted in higher percentages of non-mycorrhizal short root tips, and decreased number of living short roots. EM percentage decreased by 38% on SO_2 exposed roots.	Blaschke (Blaschke, 1990)
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst.*) European Silver Fir (*Abies alba Mill*.).	Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers in Hohenheim, Germany, for almost five years	Visible injury	In Jan to Feb 1985, after long frost, SO_2 treated fir showed development of tip necrosis, showing SO_2 inhibits frost resistance. No clear visible effects were found due to SO_2 alone on beech or spruce.	Arndt et al. (Arndt, 1990)
European Beech (*Fagus sylvatica L.*), Norway Spruce (*Picea abies (L.) Karst.*) European Silver Fir (*Abies alba Mill*.).	Root samples taken in five-year Hohenheim Long Term Experiment in Germany from 2 tree groups. Each group of trees consisted of three younger (10–year-old) and five older (13–year-old) trees. Weekly concentrations of SO_2, (averaging 3–42 ppb) and O_3 (10–90 ppb) was applied to trees in open-top chambers.	Fine root and mycorrhizae production	In beech seedlings, SO_2 and SO_2 +O_3 resulted in reduced fine root production by 35% and 55%, respectively. SO_2 had no clear effect on fine root production in fir. SO_2 increased fine root production in spruce by 31%, but significantly reduced relative frequency of mycorrhizae (~20).	Wollmer and Kottke (Wollmer, 1990)
Norway spruce (*Picea abies L. Karst.*) and fir seedlings (*Abies aiba Mill*.)	One- and two- year old seedlings exposed to low levels of SO_2 and O_3 in open-top chambers in five year experiment 1983 through 1988 in Hohenheim, Germany. SO_2 concentrations averaged weekly between 3–42 ppb and O_3 concentrations were between 10–90 ppb.	Visible symptoms, photosynthesis, transpiration	The twigs did not exhibit any visible sign of injury due to SO_2 treatments. Exposure of fir to SO_2 alone or in combination with O_3 resulted in a significant decrease in photosynthesis and transpiration. No changes either in photosynthesis or transpiration were found in spruce under fumigation with $S0_2$ alone.	Schweizer and Arndt (Schweizer, 1990)
Black sage (*Salvia mellifera*) CA sagebrush (*Artemisia californica*) Eastern Mojave buckwheat (*Eriogonum asciculatum*) CA brittlebush (*Encelia californica*)	SO_2 fumigation over 10 weeks, at 0, 50, 200, and 500 ppb, California	Number of inflorescences	Decreased inflorescences were observed at 50 ppb SO_2 for black sage, and at 200 ppb SO_2 for California sagebrush, Eastern Mojave buckwheat, and California brittlebush, with progressive declines as SO_2 concentration increased.	Westman et al. (Westman, 1985)
Timothy grass (*Phleum pratense*)	Exposure to 120 ppb SO_2 for 40 days.	Leaf production, leaf senescence, dry weight (LAR), leaf-area ratio, specific leaf area (SLA)	Diminished leaf production and increased leaf senescence in seedlings exposed to 120 ppb SO_2 at 35 days. Exposure to 120 ppb SO_2 in seedlings over 40 days resulted in a 62% reduction in the dry weight of roots and 51% reduction in the dry weight of shoots, as well as a significant decline in leaf-area ratio and specific leaf area by the end of the experiment.	Mansfield and Jones (Mansfield, 1985)
Mixed native prairie grassland	Exposed grasses to a control (~7 ppb) and three elevated levels of SO_2 (~21, 37, 64 ppb) over 5 year study.	Root and rhizome S concentrations, biomass, primary productivity, lichen cover, population	Year-to-year S accumulation did not appear to occur over the 5–year course of the treatment, though progressive increases in root and rhizome S concentrations were observed seasonally. No significant negative effects on either above-ground net primary productivity or below-ground biomass dynamics in grasses were observed, except a decrease in biomass for *Bromus japonicus*. Lichen cover declined after 1 year of exposure at the low treatment level.	Laurenroth and Milchunas Laurenroth
Faba bean (*Vicia faba L)*	Experiment done in 3 different years (1986, 1986, 1988). Seasonal mean elevated exposures of SO_2 were 58 ppb in 1985, 22 ppb in 1986 and 26 ppb in 1988. Ambient concentrations were 6 ppb in 1985, 3 ppb in 1986 and 3 ppb in 1988.	Yield, leaf injury	Exposure to elevated SO_2 resulted in leaf injury in all three years. SO_2 exposure reduced yield by 17% in 1985, 7% in 1986 and 9% in 1988.	Kropff (Kropff, 1990)

Chapter 4. Summary and Conclusions

The previous chapters present the policy-relevant science pertaining to the emissions, atmospheric transformation and transport, deposition and ecological effects of NO_X and SO_X. Ecological effects are divided into the broad categories of ecosystem type which are typically studied: terrestrial, wetlands, freshwater aquatic, and estuarine aquatic. Several NO_X and SO_X chemical species were considered because of their complex multi-phase and multi-species in both the atmosphere and the biosphere. For example, the atmospheric chemistry of NO_X and SO_X would be incomplete, for the purposes of this ISA, if only gas-phase compounds were considered; therefore, descriptions of current ambient concentrations and deposition amounts related to the particulate forms of N and S are given in Chapter 2. Similarly, the roles of other atmospheric pollutants, including Hg, O_3, NH_3, and ammonium ion, and their interactions with NO_X and SO_X in the atmosphere and production of demonstrable welfare effects are also considered.

4.1. Source to Dose

4.1.1. Relevant Chemical Families and Constituent Species

NO_X is the name given to the family of chemical species containing oxidized N, chief among which is N_2O, NO_2, HNO_3, and PAN in the gas phase. And because it has a prominent role in moving N from the atmosphere to the biosphere, particulate nitrate is included in this ISA as well even though it is not a member of the oxidized N family of species as typical defined. Some of these oxidized N species are directly emitted; others are formed as secondary products from the emitted species. Similarly, SO_X is the name for the family of chemical species containing oxidized S, including SO, SO_2, SO_3, and S_2O; however, of these gas-phase species, only SO_2 is present in concentrations relevant for atmospheric chemistry and environmental exposures. In addition, and as was the case with the NO_X family of species, particulate SO_4^{2-} is included in this ISA because of its dominant role in transferring S species from the atmosphere to the biosphere. Furthermore, this ISA includes extensive treatment of the reduced N chemical species NH_3 and NH_4 — together given the chemical family name NH_X — because NH_X can play a crucial role controlling the transfer of total N and S to the biosphere on many levels of spatial extent. The most salient points from the foregoing chapters are summarized below.

4.1.2. Emissions and Atmospheric Concentrations

Total anthropogenic NO and NO_2 emissions in the U.S. in 2001 were ~23.19 Tg. Combustion chemistry at EGUs contributed ~22% of these total and transportation-related sources, ~56%. Ambient annual NO_X concentrations have decreased ~35% in the period 1990–2005 to current annual average concentrations of ~15 ppb.

Biogenic NO_X sources are substantially smaller than anthropogenic ones and include biomass burning, lightning, and soils. The NO and N_2O emitted from soils as intermediate products from denitrification can evolve either naturally or as stimulated by addition of N containing fertilizers to crops and other soil management practices. N_2O, another member of the oxides of N family of chemicals, is also a minor contributor to total U.S. GHG emissions: ~6.5% on a Tg CO_2e basis in 2005, and its U.S. emissions decreased ~3% in the period 1990–2005, though there remains considerable interannual variation in this value.

Concentrations of NO_2 in the CONUS from uncontrollable sources in the U.S. and elsewhere in the world are <300 ppt over most of the CONUS and <100 ppt in the eastern U.S. on an annual average basis. The 24-h ambient NO_2 concentrations in CMSAs where most of the regulatory monitors are located and where most anthropogenic emissions originate were, on average, <20 ppb with a 99 percentile value <50 ppb for the years 2003–2005. Annual-average NO_2 concentrations over the CONUS are calculated to be <5 ppb for nearly all urban and rural and remote sites.

On a national scale, energy production at EGUs accounted for ~66% of total SO_2 emissions in the U.S. in 2001-2002; ~5% of total SO_2 is emitted by transportation-related sources, with on-road vehicles accounting for ~40 % of the transportation fraction, and off-road diesel and marine traffic together accounting for the remainder. Ambient annual SO_X concentrations have decreased ~50% in the period 1990–2005 and now stand at ~4 ppb for both aggregate annual and 24-h average concentrations nation-wide.

Annual-average policy-relevant background SO_2 concentrations in the U.S. from uncontrolled sources here and elsewhere in the world are <10 ppt over most of the CONUS, or <1% of observed SO_2 concentrations everywhere except areas in the Pacific Northwest where geogenic SO_2 sources are particularly strong.

NH_3 emissions are chiefly from livestock and from soils as stimulated by addition of N-containing fertilizers to crops and other soil management practices. Confined animal feeding operations and other intensified agricultural production methods over a period of many decades have resulted in greatly increased volumes of animal wastes high in N; 30 to 70% of these wastes may be emitted as NH_3. This increase in NH_3 emissions, and the consequent increase in NH_4^+ concentration and deposition, correlates well with the local and regional increases in agricultural intensity. However, there remain no reliably consistent estimates of national average NH_3 concentrations owing to three complex issues: (1) the high spatial and temporal variability in NH_3 emissions; 2) the high uncertainty in the magnitude of those emissions; and (3) the lack of real-time, ambient level NH_3 monitoring techniques. Nonetheless, U.S. national NH_3 emissions totals have been calculated taking into account these three drivers of uncertainty; for 2001-2002 that national NH_3 emissions total was ~4.08 Tg/yr.

4.1.3. Deposition of N and S

Increasing trends in urbanization, agricultural intensity, and industrial expansion during the previous 100 years have produced a nearly 10-fold increase in N deposited from the atmosphere. NO_X, chiefly from fossil fuel combustion, often dominates total N pollution in the U.S. and comprises ~50 to 75% of the total N atmospheric deposition.

For the period 2004–2006, the routine monitoring networks report the mean N deposition in the U.S. was greatest in the Ohio River Valley, specifically in the states of Indiana and Ohio, with values as high as 9.2 and 9.6 kg N/ha/yr, respectively. N deposition was lower in other parts of the East, including the Southeast and in northern New England. In the central U.S., Kansas and Oklahoma reported the highest deposition, 7.0 and 6.5 kg N/ha/yr, respectively.

N deposition primarily occurred in the form of wet NO_3 and NH_4, followed with decreasing amounts of dry HNO_3, dry NH_4^+, and dry NO_3. Although deposition in most areas of the U.S. occurred in wet form, there were some exceptions, including parts of California where N deposition was primarily dry. Data are very sparse for the central U.S. between the 100th meridian and the Mississippi River; but, where available, N deposition values there are lower than most of the Eastern U.S., ranging from 4.1 to 5.3 kg N/ha/yr.

For the period 2004–2006, mean S deposition in the U.S. was greatest east of the Mississippi River with the highest deposition amount, 21.3 kg S/ha/yr, in the Ohio River Valley where most recording stations reported three-year averages >10 kg S/ha/yr. Numerous other stations in the East reported S deposition >5 kg S/ha/yr. Total S deposition in the U.S. west of the 100th meridian is relatively low, with all recording stations reporting less than 2 kg S/ha/yr and many reporting less than 1.0 kg S/ha/yr.

S was primarily deposited in the form of wet SO_4^{2-} followed in decreasing order by a smaller proportion of dry SO_2 and a much smaller proportion of dry SO_4^{2-}. However, these S data in the western U.S., like those for N deposition, are derived from networks with many fewer nodes in the West than in the East.

N from atmospheric deposition is estimated to comprise 10 to 40% of the total input of N to many coastal estuaries, and could be higher for some. Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape, are then computed using measurements of wet and dry N deposition where these are available, and then interpolated with or without a set of air quality model predictions.

Atmospheric inputs of reactive N directly to the surface of coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to >50% of external N loadings to these systems: 11, 5.6, and 5.6 kg N/ha/yr for the northeast Atlantic coast of the U.S., the southeast Atlantic coast of the U.S., and the eastern Gulf of Mexico, respectively.

Atmospheric N loads to great waters and estuaries in the U.S. are estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the Catherines-Sapelo estuary (Castro, 2003) at the highest end.

At Chesapeake Bay, where N and S deposition and ecological effects have been extensively studied, total atmospheric deposition of atmospheric NO_3 is estimated to contribute from 20 to 30% of total N and 14% of the NH_4^+ loadings to the Bay.

4.1.4. Field Sampling and Analysis

The instrumentation deployed at present in the routine regulatory monitoring networks for determination of gas-phase NO_X and SO_2 concentrations are likely adequate for determining compliance with the current NAAQS. But all these methods have important limitations which make them inadequate for fully characterizing the state of the atmosphere at present, the complex heterogeneity of N and S deposition across the landscape, and the roles of atmospheric N and S in driving observed biological effects.

- Routine NO_2 measurements by CL (the Federal Register Method) are contaminated by unknown and varying concentrations of higher-order oxidized N species, including gas-phase HNO_3, important as in itself for N deposition to the biosphere and also as a precursor to pNO_3. Moreover, dry deposition of NO, NO_2, and PANs is not measured, but could be as much as 30% of total dry oxidized N deposition in areas near strong NO_X sources.
    - The present-day ambient annual avg SO_2 concentrations are very near or even below the operating limit of detection of most of the FRM monitors in the largest regulatory. This produces irresolvable uncertainty in these data which may be important for environmental effects since they can be affected in some cases at these current low concentrations.
    - Routine field sampling techniques for NH_3 are at present limited to integrated values—from several days to one week—because higher frequency semi-continuous methods are not yet sufficiently robust to deploy in regulatory networks. Estimates for the contribution of NH_3 to the total N deposition budget range as high as 30% of total N, and perhaps the dominant source of reduced N.

  - Routine regulatory sampling and analysis for particulate-phase NO_3^-, SO_4^{2-}, and NH_4^+ are subject to positive and negative errors, chiefly from the loss or production of constituent species on the surface of the filter used for the long time-integrated measurement.

- The coverage of the networks is very thin over large expanses of the interior U.S. and especially so west of the 100th meridian. This assessment concludes that this lack of monitored sites increases the likelihood that significant deposition is now occurring at current atmospheric concentrations where no measurements are available, as predicted in numerical experiments with large-scale, first-principles models of atmospheric chemistry and physics and deposition or measured at some few selected special sites.

4.2. Acidification

Oxides of N and S act together to cause acidification of ecosystems. The principal factor governing the sensitivity of terrestrial and aquatic ecosystems to acidification deposition is geology. Watersheds of acid-sensitive lakes and streams have geologic formations with low base cation supply (Bricker, 1989; Stauffer, 1990; Stauffer, 1991; Vertucci, 1993; Sullivan, 2007). Other factors contribute to the sensitivity of soils and surface waters to acidifying deposition, including topography, vegetation, soil chemistry, land use, and hydrologic flowpath. Regional and ecosystem vulnerability to acidification is from sensitivity and exposure to atmospheric loading of NO_X and SO_X.

4.2.1. Terrestrial

In the 1982 AQCD for SO_X (U.S. EPA, 1982), foliar and root uptake pathways for sulfur oxides were described in detail, as well as the role of S as a nutrient. Though small amounts of SO_2 may be beneficial, it was understood that large amounts and high frequency of SO_2 exposure and S deposition can be detrimental in the long term. At that time, there were no documented observations or measurements of changes in natural terrestrial ecosystems that were directly attributed to acidic precipitation. This did not necessarily indicate that no change was occurring.

The 1993 AQCD for NO_X (U.S. EPA, 1993) documented few cases in which excessive atmospheric N deposition was linked to soil acidification, although the process of soil acidification was already well understood. Since the preparation of these assessments, direct links between NO_X and SO_X deposition and many adverse affects associated with ecosystem loading have been reported.

4.2.1.1. Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to terrestrial ecosystems. The strongest evidence for a causal relationship comes from studies of forested ecosystems, with supportive information on other plant communities, including shrubs and lichens Section 3.2.2.1. Grasslands are likely less sensitive to acidification than woodlands. Soil acidification occurs in response to inputs of sulfuric acid and nitric acid; the effect can be neutralized by weathering or base cation exchange. Soil acidification is a natural process, but is often accelerated by acidifying deposition. Acidifying deposition is important in decreasing concentrations of exchangeable base cations in soils. The limited mobility of anions associated with naturally derived acidity (organic acids and carbonic acid) controls the rate of base cation leaching from soil under conditions of low atmospheric deposition of S and N. Because inputs of S and N in acidifying deposition provide anions that are more mobile in the soil environment than anions of naturally derived acids, these mineral acid anions can accelerate natural rates of base-cation leaching.

Nitrification is mediated by autotrophic bacteria that derive energy by reducing NO_3^- to NH_4^+. Nitrification produces acidity in the form of HNO_3 as a byproduct, which contributes to the acidification of soils and surface waters.

There are three useful indicators of chemical changes and acidification effects on terrestrial ecosystems, with consistency and coherence seen among multiple studies (see Table 4-1) Soil Base Saturation, Aluminum Concentration, and C:N Ratio.

- Soil base saturation is the concentration of exchangeable bases as a percent of the total soil cation exchange capacity. Once base saturation decreases to a critical level (~15-20%), inputs of H_2SO_4 and HNO_3 are increasingly buffered by the release of inorganic Al through cation exchange.

- Al is toxic to some tree roots. Plants affected by high inorganic Al concentrations in soil solution often have reduced root growth, which restricts the ability of the plant to take up water and nutrients, especially calcium (Parker, 1989).

- The C:N ratio of soil is used to indicate alterations to the N biogeochemical cycle. If the ratio falls below about 20 to 25, nitrification is stimulated and net nitrification and associated production of acidity occurs in soils.

Table 4-1. Studies on chemical indicators of acidification to terrestrial ecosystems.

Reference	Indicator
Soil Base Saturation	
Reuss (1983)	If base saturation is less than 15–20%, exchange ion chemistry is dominated by inorganic Al.
Cronan and Grigal (1995)	Base saturations below about 15% in the soil B-horizon could lead to effects from Al stress.
Lawrence et al. (1995)	Base saturation decreases from 30% to 20% in the upper soil B-horizon showed decreases in diameter growth of Norway spruce.
Bailey et al. (2004)	At Ca saturation less than 2% and Mg saturation less than 0.5% in the upper soil B-horizon, sugar maple mortality was observed.
Aluminum Concentrations	
Johnson et al. (1991) Joslin and Wolfe (1992)	In soils with base saturation below about 20%, base cations reserves are so low that Al exchange dominates.
Eagar et al. (1996) Cronan and Grigal (1995)	There is a 50% risk of negative effects on tree growth if the molar ratio of Ca to Al in soil solution was 1.0. 100% risk for negative effects on growth at a molar ratio below 0.2.
Johnson et al. (1994; , 1994)	Ca:Al ratios above 1.0 over the course of 4 years were found in a forest stand experiencing high mortality.
DeWitt et al. (2001)	Ca:Al ratios below 0.5 in a Norway spruce stand showed reduced Mg concentrations in needles in the third year.
C:N Ratio	
Aber et al. (2003) Ross et al. (2004)	Increased effects of nitrification occur only in soil with C:N ratio below about 20–25.

4.2.1.2. Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in terrestrial biota. The strongest evidence for a causal relationship comes from studies of terrestrial systems exposed to elevated levels of acidifying deposition that show reduced plant health, reduced plant vigor, and loss of terrestrial biodiversity. In multiple studies, consistent and coherent evidence shows that acidifying deposition can affect terrestrial ecosystems by causing direct effects on plant foliage and indirect effects associated with changes in soil chemistry (Section 3.2.2.2). Biological effects of acidification on terrestrial ecosystems are generally attributable to aluminum toxicity and decreased ability of plant roots to take up base cations. There are several indicators of stress to terrestrial vegetation (see Table 3-3), including percent dieback of canopy trees, dead tree basal area (as a percent), crown vigor index, and fine twig dieback.

Species Level

- Changes in soil chemistry (e.g., depletion of soil base cations, Al toxicity to tree roots, leaching of base cations into drainage water) have contributed to high mortality rates and decreasing growth trends of red spruce trees (*Picea rubens*) in some areas of the Eastern U.S. over the past three decades (see Red Spruce, Section 3.2.2.2).

- Acidifying deposition, in combination with other stressors, is a likely contributor to the decline of sugar maple (*Acer saccharum*) trees that occur at higher elevation, in some portions of the eastern U.S., on geologies dominated by sandstone or other base-poor substrate, and that have base-poor soils (see Sugar Maple, Section 3.2.2.2).

- Lichens and bryophytes are among the first species affected by acidifying deposition in the terrestrial ecosystem. Effects of SO_2 on lichens include reduced photosynthesis and respiration, damage to the algal component of lichen, leakage of electrolytes, inhibition of N fixation, reduced potassium absorption, and structural changes.

- Data are insufficient to draw general conclusions for other species.

Community Level

- Species loss and reduced biodiversity of forests, shrubs, and meadow plant communities may occur in response to acidifying deposition; however, such effects are likely more related to the nutrient enrichment effects of N deposition.

4.2.1.3. Regional Vulnerability and Sensitivity

There has been no systematic national survey of terrestrial ecosystems to determine the extent and distribution of terrestrial ecosystem sensitivity to the effects of acidifying deposition. However, one preliminary national evaluation estimated that ~15% of forest ecosystems in the U.S. exceeds the estimated critical load of wet and dry deposition of S and N by > 250 eq/ha/yr (McNulty, 2007).

Forests of the Adirondack Mountains of New York, Green Mountains of Vermont, White Mountains of New Hampshire, the Allegheny Plateau of Pennsylvania, and high-elevation forest ecosystems in the southern Appalachians are the regions most sensitive to terrestrial acidification effects from acidifying deposition (Section 3.2.4.2). It is unknown if terrestrial acidification in these areas is continuing, or if recovery is occurring in response to recent reductions in acidifying deposition.

4.2.2. Aquatic

In the 1982 AQCD for SO_X (EPA, 1982), evidence on acidifying deposition and its role in the acidification of aquatic ecosystems was assessed. The most vulnerable regions were identified, including the Adirondack Mountains of New York. Significant changes occurred in aquatic ecosystems with increasing acidity, particularly as the pH decreases below ~ 5.5. It was concluded that: a) changes in community structure occur at all levels in the food web; b) bacterial decomposition is reduced and fungi that feed on organic debris may become dominant in aquatic communities; c) organic matter accumulates rapidly, tying up nutrients and limiting nutrient mineralization and cycling; d) phytoplankton productivity may be reduced because of changes in nutrient cycling and increased acidity; e) biomass and total productivity of benthic macrophytes and algae may increase, in part because of increased lake transparency; and f) species diversity and total numbers of species of aquatic plants and animals (especially invertebrates and fish species) are reduced, and acid-tolerant species predominate.

The 1993 AQCD for NO_X (EPA, 1993) reflected a substantial increase in our knowledge of the role of N deposition in the acidification of aquatic ecosystems. This was especially the case with respect to episodic acidification, which is far more common than chronic acidification and has been well documented for streams and lakes in the Eastern U.S. The most well-known examples are in the Adirondack and Catskill Mountains of the Northeast, as well as in the Great Smoky Mountains of the Southeast. Instances of episodic acidification were also reported in the Western U.S. but to a much lesser extent than in the East.

Biogeochemistry and Chemical Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in biogeochemistry related to aquatic ecosystems. The strongest evidence for a causal relationship comes from studies of changes in surface water chemistry including concentrations of SO_4^{2-}, NO_3^-, sum and surplus of base cations, ANC, inorganic Al, Ca, and surface water pH (see Section 3.2.2.1. Surface water chemistry integrates the sum of upstream soil and water processes and reflects the results of watershed-scale terrestrial effects of S and N deposition, including N saturation, forest decline, and soil acidification (Stoddard, 2003). In many cases, surface water chemistry indicates the effects of acidification on biotic species and communities found in fresh water ecosystems.

The status of surface water chemistry can be examined and reported as chronic chemistry or episodic chemistry. Chronic chemistry refers to annual average conditions, which are often represented as summer and fall chemistry for lakes, and as spring baseflow chemistry for streams. Episodic chemistry refers to conditions during rainstorms or snowmelt when proportionately more drainage water is routed through upper soil horizons, which tend to provide less neutralizing of atmospheric acidity as compared with deeper soil horizons. Surface water chemistry has lower pH and ANC during storm runoff or snowmelt than during baseflow conditions. One of the most important effects of acidifying deposition on surface water chemistry is the short-term change in chemistry that is termed “episodic acidification.” Some streams may have chronic or average chemistry that is suitable for aquatic biota, but be subject to occasional episodic acidification with lethal consequences. Episodic declines in pH and ANC are nearly ubiquitous in drainage waters throughout the Eastern U.S., caused partly by acidifying deposition and partly by natural processes.

Acidification effects on aquatic biota are often evaluated using measures of either Al or pH. ANC is also used because it is an indicator of buffering capacity (although ANC does not relate directly to the health of biota). The usefulness of ANC lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca, and inorganic Al.

Sulfate, Nitrate, and Base Cations

Changes in water chemistry resulting from acidifying deposition typically include changes in SO_4^{2-}, NO_3^-, and base cation concentrations. Each plays an important role in the acid-base chemistry of water; none are directly toxic at concentrations commonly encountered in surface waters Table 4-2.

- Sulfate is the primary inorganic anion found in most acid-sensitive waters. Continued decreases in S emissions should cause further decreases in SO_4^{2-} concentrations in surface waters. However the rate of decrease in surface water SO_4^{2-} concentrations may be delayed as accumulated S leaches from watershed soils in some regions of the country, especially the Blue Ridge Mountains.

- The importance of NO_3^- as an agent of acidification varies by region, but is particularly important during periods of high hydrologic flow from soils to streams, such as those that occur during snowmelt and rain runoff. The relationship between N deposition and surface water NO_3^- concentration is complex and involves the terrestrial and aquatic cycling of N and other elements. NO_3^- contributes to the acidity of many lakes and streams in the eastern U.S. However, there is no apparent relationship between recent trends in N deposition and trends in NO_3^- concentrations in these surface waters (in contrast to observed responses for S deposition and SO_4^{2-} concentrations). This suggests that the time scales of N saturation may be longer than previously considered (e.g., centuries, rather than decades). Nevertheless, long-term retention of N deposited in forested regions and consequent dampening of deposition effects on surface waters is unlikely to continue (Aber, 2003).

- Decreases in base cation concentrations in Eastern U.S. surface waters over the past two to three decades are ubiquitous and are closely tied to trends in SO_4^{2-} concentrations. Rates of base cation depletion have been similar to those for SO_4^{2-} plus NO_3^- in most areas (Shenandoah National Park is a notable exception). Decreasing trends in base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but may indicate either lower base cation leaching rates in soils or depletion of base cations from the soil system.

Acid Neutralizing Capacity, Aluminum, and pH

Acidification of surface water causes changes in ANC, Al concentration, and pH. Low pH and high inorganic Al concentration can be directly toxic to aquatic biota Section 3.2.3.

- ANC reflects the difference between base cations and anions of strong acids in solution; it is the most widely used measure of acid sensitivity, acidification, and chemical recovery of surface waters in response to changes in acidifying deposition. Acidic waters are defined as those having ANC equal to or below zero. Waters with ANC of < 50 µeq/L are considered "extremely acid-sensitive" (Schindler, 1988), and are vulnerable to episodic acidification (DeWalle, 1987; Eshleman, 1988). Lake and stream ANC values decreased throughout much of the 20th century in a large number of acid-sensitive lakes and streams throughout the Eastern U.S. Since ~1990, the ANC of many affected lakes and streams has increased slightly. The number of acidic surface waters has decreased in some areas of the Northeast, but not in the mid-Appalachian Mountains.

- Dissolved inorganic Al is an important chemical indicator of the effects of acidifying deposition on surface water because it is toxic to aquatic life and generally does not leach from soils in the absence of acidification. When pH falls below approximately 5.5, inorganic Al generally becomes a greater health risk to biota. Limited data suggest that acid-sensitive regions of the Northeastern U.S. have elevated inorganic Al concentrations in surface waters induced by years of acidifying deposition, posing a threat to aquatic life. Concentrations have decreased slightly in some surface waters in the northeastern U.S. during the last two decades in response to decreased levels of acidifying deposition.

- The pH of freshwater streams and lakes is a common measure used to link acidification to adverse effects on aquatic biota. Decreases in pH below values of 6.0 typically result in species loss of benthic invertebrates, plankton species, and fish. A number of synoptic surveys indicated loss of species diversity and absence of several fish species in the pH range of 5.0 to 5.5. If pH decreases to lower values, there is a greater likelihood that more aquatic species could be lost without replacement, resulting in decreased richness and diversity.

Table 4-2. Studies on chemical indicators of acidification in surface water.

Reference	Indicator
Sulfate	
Driscoll et al. (2001)	Acidifying deposition at Hubbard Brook Experimental Forest in New Hampshire contributed to a nearly four-fold increase in stream SO_4^{2-} concentration between 1850 and 1970.
Stoddard et al. (2003)	Widespread decreasing trends in SO_4^{2-} concentrations were documented by EPA during the period 1990–2000 in the Eastern U.S. including New England lakes (1.77 µeq/L/yr), Adirondack lakes (2.26 µeq/L/yr), Appalachian streams (2.27 µeq/L/yr), and Upper Midwest lakes (3.36 µeq/L/yr).
Nitrate	
Driscoll and Newton (1985)	NO_3^- concentrations in 20 Adirondack lakes in the early 1980 averaged 12% of SO_4^{2-} concentrations.
Lovett et al. (2000)	Baseflow NO_3^- concentrations in 1994–97 were an average of 37% of SO_4^{2-} concentrations in 39 Catskill streams.
Murdoch and Stoddard (1993)	During high-flows in Catskill streams NO_3^- concentrations periodically equaled or exceeded SO_4^{2-} concentrations.
Webb et al. (2004)	Average concentrations of NO_3^- in most southeastern streams tend to be considerably less than SO_4^{2-} concentrations.
Cook et al. (1994)	Very high NO_3^- concentrations in streamwater were documented at high elevations in the Great Smoky Mountains in North Carolina.
Base Cations	
Likens et al. (1996)	Approximately linear increasing relationship between concentrations of base cations and SO_4^{2-}+ NO_3^- concentrations in Hubbard Brook streams from 1964 to 1969, then a reversal in 1970 and a decreasing trend up to 1994.
Lawrence et al. (1998)	Decreasing concentrations of base cations at a rate that exceeded decreases in concentrations of SO_4^{2-}+ NO_3^- in Catskill Mountain streams from 1984 to 1997.
Acid Neutralizing Capacity	
Sullivan et al. (2006)	Model simulations suggest that none of the lakes in the Adirondack target lake population were chronically acidic or had ANC less than 20 µeq/L under preindustrial conditions. By 1980, there were hundreds of such lakes.
Stoddard et al. (2003)	Tendencies during the 1990s toward increasing surface water Gran ANC in all glaciated regions of the Eastern U.S. (i.e., New England, Adirondacks, Northern Appalachian Plateau) and Upper Midwest; and decreasing Gran ANC in the Ridge/Blue Ridge province.
Surface Water Aluminum	
Gensemer and Playle (1999)	Found that organically complex aluminum (organic Al) can occur in surface waters as a result of natural soil and hydrologic processes, but this form of Al is not harmful to aquatic life.
Gensemer and Playle (1999)	Demonstrated that inorganic Al has been found to be toxic to plant and animal species throughout the food web.
Baldigo et al. (2007)	20% mortality of young-of-the-year brook trout during a 30–day period with a median inorganic Al concentration of 2 µmol/L. 90% mortality occurs over 30 days with a median inorganic Al concentration of 4.0 µmol/L.
Lawrence et al. (2007)	49 of 195 streams (25%) in the Western Adirondack region had inorganic Al concentrations above 2.0 µM during August base flow.
pH	
Haines and Baker (1986) Baker et al. (1990a)	pH values for biological effects have been summarized for a variety of aquatic organisms; common threshold values for pH are 5.0, 5.5, and 6.0.
Charles et al. (1989) Sullivan et al. (1990) Cumming et al. (1992; , 1994)	25 to 35% of the Adirondack lakes larger than 4 ha have acidified since preindustrial time. An estimated 80% of the Adirondack lakes that had pH less than 5.2 in the mid-1980s were inferred to have experienced large declines in pH and ANC since the previous century. About 30 to 45% of the lakes with pH between 5.2 and 6.0 have also acidified.
Gbondo-Tugbawa et al. (2002)	PnET-BGC modeling at Hubbard Brook estimated that past stream pH (circa 1850) was probably about 6.3, compared with just above 5.0 in 2000.
Stoddard et al. (2003)	An increase in the hydrogen ion concentration of Appalachian streams (0.08 µeq/L/yr) and Upper Midwest lakes (0.01 µeq/L/yr) was reported. No trends were found in New England lakes or Appalachian streams in this study.

4.2.2.1. Biological Effects

The evidence is sufficient to infer a causal relationship between acidifying deposition and changes in aquatic biota. The strongest evidence for a causal relationship comes from studies of aquatic systems exposed to elevated levels of acidifying deposition that support fewer species of fishes, macroinvertebrates, and diatoms (Section 3.2.3.2). Although there are few studies of the response of higher trophic levels to pH changes resulting from acidifying deposition, piscivorous birds are known to be affected by acidifying deposition. Consistent and coherent evidence from multiple species and studies shows that acidification can result in the loss of acid-sensitive species, and more species are lost with greater acidification. Biological effects are linked to changes in water chemistry including ANC, Al, and pH. Decreases in ANC and pH and increases in inorganic Al concentration contribute to declines in taxonomic richness of zooplankton, macroinvertebrates, and fish. Chemical changes can occur over both long- and short-term time scales, with additional effects on biological systems. Short-term (hours or days) episodic changes in water chemistry can have biological effects, including reduced fish condition factor, changes in species composition, and declines in aquatic species richness across multiple taxa, ecosystems and regions.

Species

- Logistic regression modeling showed that the occurrence of two piscivorous birds (common loons and common mergansers) is positively related to the pH of lakes in the Algoma region of Ontario. Model estimates suggested that the number of lakes projected to be suitable for supporting breeding pairs and broods of these bird species increased with increasing lake pH.

- High levels of acidification (to pH values below 5) virtually eliminate all mayflies, crustaceans, and mollusks from some streams.

- In general, populations of salmonid fish are not found at pH levels less than 5.0, and smallmouth bass (*Micropterus dolomieu*) populations are usually not found at pH values less than 5.5 to 5.2.

- Twenty percent mortality of young-of-year brook trout were documented during a 30-day period with a median inorganic Al concentration of 2 µmol/L (Baldigo, 2007). It was estimated that 90% mortality would occur over 30 days with a median inorganic Al concentration of 4.0 µmol/L.

Community

Community-level effects were observed in the Adirondacks and Shenandoah National Park where taxonomic richness is lower in lakes and streams having low ANC and pH.

- Decreases in pH and increases in inorganic Al concentrations have reduced the species richness of plankton, invertebrates, and fish in acid-affected surface waters.
- In the Adirondacks, a positive relationship exists between the pH and ANC in lakes and the number of fish species present in those lakes. A number of synoptic surveys indicated suggested loss of species diversity and absence of several sensitive fish species in the pH range of 5.0 to 6.0 (Section 3.2.4.4).
- In Shenandoah National Park streams, the fish species richness decreased with decreasing stream ANC. On average, richness is lower by one fish species for every 21 μeq/L decrease in ANC (Section 3.2.4.5).
- Short-term episodes of acidification are particularly harmful to aquatic biota. Early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults. Episodes are most likely to affect biota if the water had pre-episode pH above 5.5 and minimum pH during the episode of less than 5.0. Episodic acidification can have long-term adverse effects on fish populations.

Regional Vulnerability and Sensitivity

The effects of acidifying deposition have been assessed by several national surveys since the 1980s, including the National Surface Water Survey and the National Stream Survey in the mid-1980s, the Wadeable Streams Assessment (WSA) in 2004, EPA's Long-Term Monitoring program beginning in 1983, and Temporally Integrated Monitoring of Ecosystems probability surveys beginning in 1991. These surveys indicate that acidifying deposition has acidified surface waters in the southwestern Adirondacks, New England uplands, low-silica eastern Upper Midwest, forested Mid-Atlantic Highlands, and Mid-Atlantic Coastal Plain (Section 3.2.4.2).

The Northeast and mountainous West of the U.S. contain many of the surface waters most sensitive to acidification. Levels of acidifying deposition in the West are low in most areas, acidic surface waters are rare, and the extent of chronic surface water acidification that has occurred to date has been very limited. However, episodic acidification does occur. In both the West and the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt. On average, spring ANC values of acid-sensitive surface waters in New England, the Adirondacks, and the northern Appalachian Plateau were about 30 μeq/L lower than summer values between 1990 and 2000. This implies that lakes and streams in these regions would need to recover to chronic ANC values above ~30 μeq/L or more before they could be expected not to experience acidic episodes (Stoddard, 2003).

In 2004, the EPA conducted a national WSA survey and found that, overall, less than 1% of the 1,020,000 km of stream in the target population was acidic due to acidifying deposition. No acidic streams were observed in the Mountainous West, Xeric West, Upper Midwest, Northern Plains, Southern Plains, or Temperate Plains ecoregions. Streams that were acidified from acidifying deposition were found in the Northern Appalachians (2.8% of 96,100 km of stream), and the Southern Appalachians (1.8% of 287,000 km). Very low ANC (0 to 25 μeq/L) streams, likely exposed to episodic acidification, were found in the Northern Appalachians (2.7% of 96,100 km of stream), the Coastal Plain (6.3% of 119,000 km), and the Mountainous West (0.6% of 204,000 km). Stream surveys were not conducted in the Adirondacks or New England.

It is important to address surface water recovery in response to reduced acidifying deposition over the past few decades. The following summarizes recent regional trends in acidification recovery.

- About one-quarter to one-third of the lakes and streams that were chronically acidic during summer in the 1980s were no longer chronically acidic in 2000. These improvements in water chemistry are largely attributed to decreases in S deposition. Throughout the Northeastern US, the concentration of SO_4^{2-} in surface waters has decreased substantially in response to decreased emissions and atmospheric deposition of S. Decreased SO_4^{2-} concentrations of a third or more in lakes and streams have been commonly observed.

- EPA's monitoring programs suggest that the following important changes in lake and stream chemistry occurred during the 1990s in response to S and N emissions reductions: (1) SO_4^{2-} concentration decreased as a percentage of total ion concentration in surface waters; 2) ANC increased modestly in three of the five regions included in surface water efforts; 3) dissolved organic carbon and associated natural organic acidity increased, perhaps toward more natural pre-disturbance concentrations, as surface water acidity contributed from acidifying deposition decreased; and (4) inorganic, and potentially toxic, Al concentrations appear to have decreased slightly in some sensitive aquatic systems.

4.3. N Nutrient Enrichment

The majority of experiments that quantify the effects of N deposition levels on ecosystems (see Table 4-4 and Table 3-25) either evaluate N addition or N gradients. Fertilization experiments often use NH_4NO_3 or $(NH_4)_2SO_4$ additions and assume that these additions would simulate a wide spectra of atmospheric reactive N (N_r) deposition scenarios. Deposition gradient experiments often do not adequately identify all components of N_r deposition. Therefore, publications addressing N additions or deposition gradients often do not include data on all components of N_r.

In terrestrial ecosystems, N_r deposition causes accelerated growth rates in some species, altered competitive interactions among species, and nutrient imbalances, ultimately affecting biodiversity. The onset of these effects may be as low as 3 kg/ha/yr. N utilization is so fundamental to plant growth and nutrient cycling that there are myriad linkages among atmospheric N deposition, other pollutants (e.g., O_3, S, CO_2), environmental stressors (e.g., drought, pests, pathogens), and disturbance regimes (e.g., fire and wind-throw).

In aquatic ecosystems, reactive N that is both leached from the soil and directly deposited can pollute groundwater and surface water. This causes alteration of the diatom community at levels as low as 1.5 kg/ha/yr. Reactive N also promotes eutrophication in coastal ecosystems, ultimately reducing biodiversity, in part due to depletion of O_2 needed for the survival of many species of aquatic plants and animals.

Factors that govern the sensitivity of terrestrial ecosystems to nutrient enrichment from N deposition include the degree of N-limitation, rates and form of N deposition, elevation, climate, species composition, length of growing season, and soil N retention capacity. Critical N loads are described for European ecosystems (see Section 3.3.7.1). Little is known about the extent and distribution of the terrestrial ecosystems in the U.S. that are most sensitive to the effects of nutrient enrichment from atmospheric N deposition.

4.3.1. Terrestrial

The 1993 AQCD concluded that N deposition may cause large effects on terrestrial systems, and the effect of N deposition should consider total N in the system rather than just the oxidized forms. N deposited to an N-deficient ecosystem is generally expected to increase growth. If N is deposited on an ecosystem with adequate N or saturated with N, NO_3^- leaching is expected to occur. Much of the information presented in the 1993 document was based on results from studies of forest systems. N saturation was known to be more common in older forests. Disturbances such as fire and harvesting would push ecosystems to a state of lower N saturation. Fertilization was known to increase growth in N-deficient forests in the short-term, but little was known about long-term effects of N fertilization and the differential growth effects on various tree and herbaceous plant species. It was known that plants do not necessarily benefit from added N. When N increases to the point that it is no longer limiting, deficiencies of other nutrients can occur (Aber, 1989).

A few studies documented the deleterious effects of excessive N on tree growth and grassland biodiversity. Alpine ecosystems were identified as particularly sensitive to N deposition. The studies published since the 1993 assessment generally support its conclusions, provide more information on the long-term effects of N deposition, and expand the knowledge of effects to include more ecosystem and species. A summary of quantified deposition and associated ecological effect is given in Table 4-4.

4.3.1.1. Biogeochemical effects

N cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of N in terrestrial ecosystems (Section 3.3.2.1). The main source of new N_r to ecosystems is atmospheric deposition. N_r deposition disrupts the nutrient balance of ecosystem with numerous biogeochemical effects. The chemical indicators that are typically measured include: nitrate leaching, C:N ratio, N mineralization, nitrification, denitrification, foliar N concentration, and soil water NO_3^- and NH_4^+ levels. Values for these indicators that represent a threshold for the onset of a related biogeochemical or biological effect are also summarized. Note that N saturation does not need to occur to cause adverse effects on terrestrial ecosystems. However, in some regions N saturation is a plausible mechanism of net nitrification and associated NO_3^- leaching in drainage water. Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (see Section 3.2) and deplete soils of nutrient base cations, especially Ca and Mg (Likens, 1998).

- Two of the primary indicators of N enrichment in forested watersheds are the leaching of NO_3 in soil drainage waters and the export of NO_3^- in stream water, especially during the growing season (Stoddard, 1994).

- In general, there is consistency and coherence among experimental evidence from field studies that show NO_3^- leaching can be induced by chronic addition of N (Edwards, 2002; Kahl, 1999; Norton, 1999; Kahl, 1993; Peterjohn, 1996). Several N-exclusion studies in Europe demonstrated that decreases in N deposition produced immediate reductions in NO_3^- leaching from forest stands (Gundersen, 1998; Quist, 1999).

- In upland forested areas in the U.S., most N received in atmospheric deposition is retained in soil, and lesser amounts (7–16%) are retained in plant biomass (Nadelhoffer et al., 1999). Several different data compilations indicate consistent and coherent results that found that 80% to 100% of N deposition is retained or denitrified within terrestrial ecosystems that receive less than about 8–10 kg N/ha/yr (Dise, 1995; Sullivan, 2000; MacDonald, 2002; Aber, 2003; Kristensen, 2004).

- Aber et al. (2003) found that surface water NO_3^- concentrations exceeded 1 μeq/L in watersheds receiving about 9 to 13 kg N/ha/yr of atmospheric N deposition. The lakes and streams found to have high NO_3^- concentration were those receiving N deposition above this range, but responses were variable among those receiving high N deposition. Above this range, mean NO_3^- export increased linearly with increasing deposition at a rate of 0.85 kg NO_3^- kg N/ha/yr for every 1 kg N/ha/yr increase in deposition, although there was considerable variability in N retention among watersheds at higher rates of deposition (Aber, 2003).

- In the west, mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are N-saturated and exhibit the highest stream water NO_3^- concentrations documented within wildlands in North America (Bytnerowicz, 1996) (Fenn, 1998). In the mixed conifer forests of the Sierra Nevada and San Bernardino mountains, the critical load for increased NO_3^- leaching is calculated at 17 kg N/ha/yr.

- Activities or disturbances such as logging or fire that export large quantities of N from the site alter future N availability and site propensity to achieve N saturation (c.f.,, Chanasyk, 2003)

C cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of C in terrestrial ecosystems (Section 3.3.3.1). The most extensive evidence on the interactions between N deposition and C cycling is available for forest ecosystems. Experimental N addition studies show a range of responses in terms of tree mortality and productivity. In general, moderate to high additions of N lead to either no significant change in growth rates or transient growth increases (generally at deposition rates lower than 10 kg N/ha/yr), followed by increased mortality, especially at higher rates of fertilization (see Section 3.3.3.1).

Due to the complexity of interactions between the N and C cycling, the effects of N on C budgets (quantified input and output of C to the ecosystem) are variable. Regional trends in NEP of forests have been documented through models based on gradient studies (Magnani, 2007). There have been critiques of the method and the magnitude of these reported effects (Sutton, 2008). N addition was found to slightly increase ecosystem C in a meta-analysis that examined the effects of N fertilization ranging from 25.5 to 200 kg N/ha/yr on forest ecosystem C content (see Section 3.3.3.1). In the Western U.S., atmospheric N deposition has been shown to cause increased litter accumulation and carbon storage in above-ground woody biomass, which in turn may lead to increased susceptibility to more severe fires (Fenn, 2003).

Less is known regarding the effects of N_r deposition on C budgets of non-forest ecosystem. A meta-analysis, including 16 observations from 9 publications, conducted to evaluate the relationship between N addition ranging from 16 to 320 kg N/ha/yr and C sequestration of non-forest ecosystems showed that N addition has no significant effect on net ecosystem exchange of non-forest ecosystems.

N deposition also affects the patterns of C allocation because most growth occurs above ground. This increases the shoot-to-root ratio, which can be detrimental to the plant because of decreased resistance to environmental stressors, such as drought and windthrow (Minnich, 1995; Fangmeier, 1994; Krupa, 2003; Braun, 2003).

N_2O and CH_4 flux

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical flux of N_2O in terrestrial ecosystems (Section 3.3.4.2). Terrestrial soil is the largest source of N_2O, accounting for 60% of global emission (John, 2002). In a meta-analysis of 80 observations of terrestrial ecosystems with different N forms (NH_4^+, NO_3^-, NH_4NO_3, and urea) and addition rates (10 to 562 kg N/ha/yr), N addition resulted in a two-fold increase in N_2O emission imbalance. There were no quantitative results for other effects. The response of N_2O emission to N addition for coniferous forest, deciduous forest and grasslands was significant (see Section 3.3.4.2).

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical flux of CH_4 in terrestrial ecosystems (Section 3.3.4.1). Non-flooded upland soil is the largest biological sink for atmospheric CH_4, consuming about 6% of the atmospheric CH_4 (Le mer and Roger 2001). A meta-analysis was performed on a data set of 41 observations including four forms of N (NH_4^+, NO_3^-, NH_4NO_3 and urea) and the addition rates ranging from 10 to 560 kg N/ha/yr. The results indicated that N addition reduced CH_4 uptake, but this inhibition was significant only for coniferous and deciduous forests (see Section 3.3.4.1).

4.3.1.2. Species richness, composition and biodiversity

The evidence is sufficient to infer a causal relationship between N_r deposition on the alteration of species richness, species composition and biodiversity in terrestrial ecosystems. The most sensitive terrestrial taxa are lichens. Empirical evidence indicates that lichens in the U.S. are adversely affected by deposition levels as low as 3/ha/yr. Alpine ecosystem are also sensitive to N deposition, changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr and modeling indicates that deposition levels near 10 kg N/ha/yr alter plant community assemblages. A summary of N deposition effects are presented below, organized by ecosystem type.

Lichens

There is consistent and coherent evidence to support that lichen communities are affected by current levels of N deposition. Sensitive lichens are frequently used as indicators of air pollution and atmospheric deposition levels. In addition to being good subjects for biomonitoring, they constitute important components of the forest ecosystem by contributing to biodiversity, regulating nutrient and hydrological cycles, and providing habitat elements for wildlife (McCune, 1997); see Section 3.3.5).

Lichens that contain a cyanobacterial photobiont appear to be more sensitive to adverse effects from atmospheric N deposition than most other lichens (Hallingbäck, 1991; Hallingback, 1992). The decline of lichens containing cyanobacteria in parts of northern Europe has been associated with N deposition in the range of 5 to 10 kg N/ha/yr (Bobbink, 1998). In the U.S., lichen species are negatively affected by N inputs as low as 3 to 8 kg/ha/yr (Fenn, 2003).

In the San Bernardino Mountains, California, up to 50% of lichen species that occurred in the region in the early 1900s have disappeared (Nash, 1999; Fenn, 2003). The calculated critical load for lichen communities in mixed conifer forests in California is 3.1 kg/ha/yr. (Fenn, 2008).

The Pacific Northwest retains widespread populations of pollution-sensitive lichens (Fenn, 2003). In this area, lichen communities are beginning to show evidence of changes in response to increased N pollution, including decreased distribution of sensitive lichen taxa, and their replacement with nitrophilous species (Geiser, 2007).

Alpine Plant Communities

Consistent and coherent evidence indicates that alpine plant communities are among the most sensitive terrestrial communities to nutrient-enrichment from atmospheric N deposition. Factors that govern the sensitivity of alpine tundra to N deposition include low rates of primary production, short growing season, low temperature, and wide variation in moisture availability in the alpine environment (Bowman, 1994; Bowman, 1993; Fisk, 1998; Bowman, 2001). Alpine herbaceous plants are generally considered N-limited and changes in alpine plant productivity and species composition have been noted in response to increased N inputs (Vitousek, 1997; Bowman, 2006). Alpine plant communities have also developed under conditions of low nutrient supply, in part because soil-forming processes are poorly developed, and this also contributes to their N-sensitivity.

The Western U.S. contains extensive land areas that receive low levels of atmospheric N deposition, interspersed with hot spots of relatively higher N deposition downwind of large metropolitan centers and agricultural areas. Some of these areas of higher N deposition occur at high elevation. Results from several studies suggest that the capacity of Rocky Mountain alpine catchments to sequester N is exceeded at input levels less than 10 kg N/ha/yr (Baron, 1994; Williams, 1999). Changes in an individual species (*Carex rupestris*) were estimated to occur at deposition levels near 4 kg N/ha/yr. Changes in the plant community, based on the first axis of a detrended correspondence analysis, were estimated to occur at deposition levels near 10 kg N/ha/yr. (Bowman, 2006). In comparison, critical loads for alpine plant communities in Europe are between 5-15 kg N/ha/yr (Bobbink, 1998).

Grasslands

Consistent and coherent evidence for reduced biodiversity in response to N deposition is reported for grasslands in the U.S. and Europe. Clark and Tilman (2008) recently evaluated the effects of chronic N addition over 23 years in Minnesota prairie-like successional grasslands and in native savanna grassland and found species numbers declined at the lowest addition level (10 kg N/ha/yr added to 6 kg N/ha/yr of ambient deposition). The authors calculated the critical load as 5.3 kg N/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr.

Change in species composition in response to N deposition has been observed regardless of soil type in European grasslands. Such effects have been found in calcareous, neutral, and acidic environments, species-rich heaths, and montane-subalpine grasslands (Stevens, 2004; Bobbink, 1992; Bobbink, 1998). A transect of 68 acid grasslands across Great Britain, covering the lower range of ambient annual N deposition (5 to 35 kg N/ha/yr), indicates that long-term, chronic N deposition significantly reduced plant species richness. Species richness declined as a linear function of the rate of inorganic N deposition, with a reduction of one species per 4 m^2 quadrat for every 2.5 kg N/ha/yr of chronic N deposition. The empirical critical loads for ten different types of grasslands in Europe ranged between 10 and 30 kg N/ha/yr, above which changes in species composition were documented to occur (Achermann, 2003) (See Section 3.3.7.1).

In the San Francisco Bay area of California, which receives N deposition levels of 10 to 15 kg N/ha/yr, exotic nitrophilous grasses have displaced native grass species, likely due to greater N availability from deposition and from the cessation of grazing, which previously exported N out of the system (Fenn, 2003).

Forests

In this assessment, forests include overstory trees, understory herbaceous plants and mycorrhizae. There is very little information on the effect of N deposition on the biodiversity of overstory trees within forests in the U.S. This is due to the long life span and slow growth of trees which makes such changes difficult to detect. A study of the northern edge of the Great Plains (southern Canada), showed that increasing N deposition over a range of 8 to 22 kg N/ha/yr to aspen-dominated forest and boreal forest caused an increase forest expansion into the grasslands (Kochy, 2001). More is known concerning the effects of N deposition on understory herbs, however most of the evidence is from Europe, where alteration of species composition is known to occur over the gradient of N deposition ranging from 6 to

20 kg N/ha/yr for acid tolerant species and a decline in the cover and abundance of ericaceous shrubs along a gradient from 3 to 12 kg N/ha/yr (Gilliam, 2006). Loss of mycorrhizal diversity was recorded for Alaskan coniferous forest over a gradient of 1 to 20 kg N/ha/yr, and addition studies from oak savanna ecosystems in Minnesota show N addition decreases mycorrhizal diversity (Avis, 2003).

Arid and Semi-arid Grasslands

Alteration to arid and semi-arid plant communities resulting from experimental N fertilization have been reported in the Colorado Plateau, Joshua Tree National Park in California, and the coastal sage scrub community (CSS) of Southern California.

Results from several lines of evidence showed (1) increased biomass of non-native plant species over native species, (2) decreased soil moisture under some conditions, and (3) increased fire risk where dense grasses replaced shrub cover.

In some areas of the CSS of Southern California, dry N deposition may be upwards of 30 kg N/ha/yr (Bytnerowicz, 1996). Native shrub and forb seedlings in this plant community are unable to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses, especially following disturbances such as fire (Eliason, 1997; Yoshida, 2001; Cione, 2002). The coastal sage shrub community in California has been declining in land area and in shrub density for the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Allen, 1998; Padgett, 1999; Padgett, 1999). N deposition is considered a possible cause or contributor to this ecosystem alteration.

Egerton-Warburton and Allen (2000) discerned a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity along a deposition gradient (2 to 57 μg N/g as soil NO_3^-). These shifts in mycorrhizal fungal communities may facilitate replacement of native plant communities by Mediterranean annual grasslands in CSS.

Several lines of evidence suggest that N_r deposition may be contributing to greater fuel loads and thus altering the fire cycle in a variety of ecosystem types (Fenn, 2003). Invasive grasses, which can be favored by high N deposition, promote a rapid fire cycle in many locations (D'Antonio, 1992). The increased productivity of flammable understory grasses increases the spread of fire and has been hypothesized as one mechanism for the recent conversion of CSS to grassland in California (Minnich, 1998).

Deserts

Consistent and coherent evidence that N fertilization alters desert plant communities has been reported in the Chihuahuan Desert, Jordana Basin, Mojave Desert, and the Great Basin. N additions stimulate plant growth and cause the observed invasion of some exotic plant species and associated changes in ecosystem function, especially where water supply is adequate. There is little evidence evaluating the effects of ambient deposition gradients. However there are numerous field experiments that evaluate N addition levels ranging from 10-100 kg N/ha/yr. Deposition rates in the Southwestern U.S. vary from a low of 1–4 kg N/ha/yr to as high as 30–90 kg N/ha/yr downwind of major urban and agricultural areas (Fenn, 2003; Fenn, 2003). For example, parts of the Sonoran desert in and around Phoenix, Arizona, receive between 7.5 and 30 kg N/ha/yr (Nilles, 2001).

Increased grass biomass has also been associated with increased fire frequency in the Mojave Desert (Brooks, 1999; Brooks, 2002; Brooks, 2004). This effect is most pronounced at higher elevation, probably because the increased precipitation at higher elevation contributes to greater grass productivity. In some cases, precipitation may be a more limiting factor than N to plant growth in deserts. Increased N supply at lower elevation in arid lands can only increase productivity to the point at which moisture limitation prevents additional growth. It is observed that fire was relatively rare in the Mojave Desert until the past two decades, but now fire occurs frequently in areas that have experienced invasion of exotic grasses (Brooks, 1999).

4.3.2. Transitional

Anaerobic conditions of water-logged soils in wetlands result in slow decomposition of organic matter and accelerated denitrification. N cycles of two types of wetland, ombrotrophic bogs and coastal salt marshes, were discussed in 1993 AQCD for NO_X. Ombrotrophic bogs are generally considered the most sensitive to atmospheric N deposition because they are nutrient poor, with a closed N cycle in which the predominant source of N is rainfall. The 1993 AQCD found that the three main ecological effects of N deposition on wetland ecosystem are: (1) increasing primary production; 2) modifying microbial processes; and (3) reducing biodiversity and altering ecosystem structure. The studies since 1993 support and extend the conclusions in the 1993 AQCD, especially with regard to the effects of N deposition on species diversity.

4.3.2.1. Biogeochemical Effects

The contribution of N deposition to total N load varies among wetland types. The more N deposition accounts for total N load the more vulnerable the ecosystem is to N deposition For example, in freshwater wetland ecosystems atmospheric deposition is the main source of N to the ecosystem while N deposition is a minor source of N in many saltwater wetlands.

N Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of N (Section 3.3.2.2). N_r deposition contributes to total N load in wetlands. The chemical indicators that are typically measured include: nitrate leaching, N mineralization, and denitrification. N dynamics in wetland ecosystems are variable in time and with type of wetland and environmental factors, especially water availability (Howarth, 1996). A wetland can act as a source, sink, or transformer of atmospherically deposited N (Devito, 1989) and these functions can vary with season and with hydrological conditions. Vegetation type, physiography, local hydrology, and climate all play significant roles in determining source/sink N dynamics in wetlands (Devito, 1989; Koerselman, 1993; Arheimer, 1994; Mitchell, 1996).

N mineralization has been shown to increase with N addition, and this can cause an increase in wetland N export to adjacent surface water (Groffman, 1994). In general, leaching losses of NO_3^- in water derived directly from wetlands are often small because of NO_3^- removal by denitrification. Elevated N inputs to wetlands will often increase the rate of denitrification (Dierberg, 1983) (Broderick, 1988; Cooper, 1990). This process limits environmental effects that are typically associated with increased N supply to soils and drainage waters; however it increases the contribution of greenhouse gasses to the atmosphere. Denitrification appears to be negligible in wetland environments that are typically nutrient (including N) poor, such as some bogs and fens (Morris, 1991).

C Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of C. In numerous freshwater wetland ecosystems atmospheric deposition is the main source of N to the ecosystem. In contrast, N deposition is a minor source of N in many saltwater wetlands.

A meta-analysis that included wetlands with other non-forest ecosystems indicated no effect of N deposition on overall net ecosystem exchange of carbon (See Section 3.3.3). In contrast, above and below ground carbon exchange processes are affected by N deposition. In *Sphagnum*-dominated ombrotrophic bogs, higher N deposition resulted in higher tissue N concentrations and greater NPP (Aldous, 2002; Aldous, 2002), but lower bulk density. A study of 23 ombrotrophic peatlands in Canada with deposition levels ranging from 2.7 to 8.1 kg N/ha/yr showed peat accumulation increases linearly with N deposition, however in recent years this rate has begun to slow indicating limited capacity for N to stimulate accumulation (Moore, 2004). Soil respiration has been studied in European countries under a natural gradient of atmospheric N deposition from 2 to 20 kg/ha/yr. They found enhanced decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher carbon dioxide.

In intertidal wetlands, primary production of plant species typically increases with N addition, however most studies apply fertilizer treatments that are several orders of magnitude larger than atmospheric deposition (Mendelssohn, 1979; Wigand, 2003; Tyler, 2007; Darby, 2008). N fertilization experiments in salt marsh ecosystems show biomass stimulation from 6 to 413% with application rates ranging from 7 to 3120 kg N/ha/yr (EPA, 1993).

Increases in biomass linked to N deposition, have also increased evapotranspiration (Howes, 1986). This changed the soil water balance of water and may influence the direction of plant community succession. Model results suggest 7 kg N/ha/yr is the threshold for an oligotrophic bog to become a mesotrophic bog dominated by trees, as found in the 1993 NO_X AQCD.

N_2O and CH_4 flux

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of N_2O flux in wetland ecosystems. In a meta-analysis, 19 observations, with different N forms (NH_4^+, NO_3^-, NH_4NO_3, and urea) and addition rates (15.4 to 300 kg N/ha/yr), were included to evaluate the effect of N addition on wetland N_2O emission (see Section 3.3.4.2). The results indicated that N addition increased the production of N_2O by about two-fold.

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of CH_4 flux in wetland ecosystems. Wetlands are generally net sources of CH_4, but some wetlands can be net sinks depending on environmental conditions such as drainage and vegetation (Crill, 1994; Saarnio, 2003). A meta-analysis was performed on a data set of 17 observations to assess the effects of N additions on CH_4 fluxes (see Section 3.3.4.1). This data set included four forms of N (NH_4^+, NO_3^-, NH_4NO_3 and urea) and the addition rates ranged from 30 to 240 N kg N/ha/yr (see Section 3.3.4.1). The results indicated that N addition increased CH_4 production from the wetlands, but had no significant effect on CH_4 uptake of wetlands.

4.3.2.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in wetland ecosystems (Section 3.3.5.2). Wetlands contain a high number of rare plant species (Moore, 1989; EPA, 1993; Bedford, 2003). Excess N deposition can cause shifts in wetland community composition by altering competitive relationships among species, which potentially leads to effects such as decreasing biodiversity, increasing non-native species establishment and increasing the risk of extinction for sensitive and rare species.

Changes in plant species composition caused by elevated atmospheric N deposition haven been demonstrated in Europe. (Achermann, 2003) (see Table 3-24) evaluated the empirical evidence linking N deposition to wetland species composition and biodiversity to develop the following critical loads: raised and blanket bogs = 5-10 kg N/ha/yr, poor fens = 10-20 kg N/ha/yr, rich fens 15-35 kg N/ha/yr, mountain rich fens 15-25 kg N/ha/yr, pioneer and low-mid salt marshes 30-40 kg N/ha/yr.

Some wetland species are adapted to low-N environments. High levels of atmospheric N deposition increase the risk of decline and extinction of those sensitive species. In general these include the genus *Isoetes sp*., of which three species are federally endangered; insectivorous plants like the endangered green pitcher *Sarracenia oreophila;* and the genus *Sphagnum*, of which there are 15 species are listed as endangered by Eastern U.S. states. Roundleaf sundew (*Drosera rotundifolia*) is also susceptible to elevated atmospheric N deposition (Redbo-Torstensson, 1994). This plant is native to, and broadly distributed across, the U.S. and is federally listed as endangered in Illinois and Iowa, threatened in Tennessee, and vulnerable in New York (http://plants.usda.gov/). In the U.S., *Sarracenia purpurea* can be used as a biological indicator of local N deposition in some locations (Ellison, 2002). *S. purpurea* is a perennial pitcher plant native to Canada and the Eastern U.S. that grows in nutrient-poor peatlands and is sensitive to changes in N availability. Based on the annual demographic rates, a non stationary matrix model forecasted that the extinction risk within the next 100 years increased substantially if N deposition rate increase (1–4.7%) from the rate of 4.5-6.8 kg N/ha/yr (Gotelli, 2002).

4.3.2.3. Regional vulnerability and sensitivity

- Bogs are among the most sensitive wetland ecosystems to N deposition. In the U.S., peat-forming bogs are most common in areas that were glaciated, especially in portions of the Northeast and Upper Midwest (EPA, 1993).

- N input and output rates of fens are intermediate between bogs and coastal marshes. N deposition could drastically change species composition, increase primary productivity and increase methane emission in fens (Pauli, 2002; Aerts, 1999).

- Atmospheric N inputs contribute to eutrophication problems in coastal marshes at many locations. However marine inputs of N are typically higher than direct atmospheric input. Models of sources of N to wetland ecosystems are not yet available.

- The effect of N deposition on wetland ecosystems depends on the fraction of rainfall in its total water budget and the sensitivity to N deposition was suggested as: bogs (70-100% rainfall) > fens (55-83% rainfall) > intertidal wetlands (10-20% rainfall) (Morris, 1991).

4.3.3. Freshwater Aquatic

General conclusions of the 1993 AQCD for NO_X indicated that productivity of fresh water is usually limited by the availability of phosphorus (P). However, it was noted that high inputs of P from anthropogenic sources could lead to N limitation occurring. The ratio of dissolved organic N to total phosphorous (molar basis) was used as an indicator for nutrient limitation, with values less than 2 indicating N limitation. The proportions of N limited lakes show wide regional variation: Pacific Northwest (27.7%), Upper Midwest (19%), Northeast (5%), Southeast (2.5%). All sub regions of the West contain substantial numbers of N limited lakes.

4.3.3.1. Biogeochemical Effects

N Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of biogeochemical cycling of N in freshwater aquatic ecosystems (Section 3.3.2.3)**.** N_r deposition is the main source of N to headwater streams, lower order streams and high elevation lakes. The predominant chemical indicator is NO_3^- concentration in surface waters. Recent evidence documents examples of lakes and streams that are limited by N and show symptoms of eutrophication in response to N addition. Elevated surface water NO_3^- concentrations occur in both the Eastern and Western U.S.

C Cycling

The evidence is sufficient to infer a causal relationship between Nr deposition and the alteration of biogeochemical cycling of C in freshwater aquatic ecosystems (Section 3.3.3.3). If growth of the autotrophic community of a freshwater stream is N-limited, then N addition will stimulate C-capture via photosynthesis often altering the C cycle. Moreover, a freshwater lake or stream must be N-limited in order to be sensitive to N-mediated eutrophication. There are many examples of fresh waters that are N-limited or N and P co-limited (Elser, 1990; Fenn, 2003; Tank, 2003; Bergström, 2006; Bergström, 2005; e.g.,, Baron, 2006) (See Annex C). (Bergstrom, 2006) concluded that the eutrophication caused by inorganic N deposition indicates that phytoplankton biomass in the majority of lakes in the northern hemisphere is limited by N in their natural state.

Numerous studies investigate the relationship between N concentration of freshwater and primary productivity (reported as chlorophyll *a*, NPP, or an index such as the lake chemistry ratio of DIN:TP) and atmospheric N_r deposition. Typically N addition experiments of lake and stream bioassays in which N was added to waters in field or laboratory in order to measure the response are conducted. A meta-analysis of enrichment bioassays in 62 freshwater lakes of North America found algal growth enhancement from

N amendments to be common in slightly less than half the studies (Elser, 1990). Gradient studies of undisturbed northern temperate, mountain, or boreal lakes that receive low levels of atmospheric N deposition found strong relationships between N-limitation and productivity where N deposition was low, and P and N+P limitations where N deposition was higher (Fenn, 2003; Bergström, 2006; Bergström, 2005). One such study in Sweden found, the lowest productivity occurred at sites where wet N deposition was about 1.3 kg N/ha/yr; increasing productivity occurred at greater than 2.2 kg N/ha/yr (Bergström, 2005).

Overall, productivity of many freshwater ecosystems is currently limited by the availability of N. European and North American lakes may have been N-limited before human-caused disturbance, and remote lakes may have remained N-limited until slight increases in atmospheric N deposition brought about an increase in phytoplankton and periphyton biomass and induced P limitation.

4.3.3.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in freshwater aquatic ecosystems (Section 3.3.5.3). Increased N deposition can cause a shift in community composition and reduce algal biodiversity. Elevated N deposition results in changes in algal species composition, especially in sensitive oligotrophic lakes.

In the West, a hindcasting exercise determined that the change in Rocky Mountain National Park lake algae that occurred between 1850 and 1964 was associated with an increase in wet N deposition that was only about 1.5 kg N/ha (Baron, 2006). Similar changes inferred from lake sediment cores of the Beartooth Mountains of Wyoming also occurred at about 1.5 kg N/ha deposition (Saros, 2003).

Some freshwater algae are particularly sensitive to added nutrient N and experience shifts in community composition and biodiversity with increased N deposition. For example, two species of diatom (a group of algae), *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes and sharp increases have occurred in Lake Tahoe (Interlandi, 1998; Baron, 2000; Wolfe, 2001; Wolfe, 2003; Saros, 2003; Saros, 2005). The timing of this shift has varied, with changes beginning in the 1950s in the southern Rocky Mountains and in the 1970s or later in the central Rocky Mountains. These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world.

Extremely high NO_3^- concentrations can have direct adverse effects on fish, invertebrates and amphibians, but the concentrations required to elicit such effects are typically more than 30 times higher than those that would commonly be attributable to atmospheric deposition. For example, mortality of rainbow trout eggs and fry occurred after 30-day incubations in concentrations greater than 79 µg N/L; adverse effects on amphibians and insects occur at even higher concentrations.

4.3.3.3. Regional Vulnerability and Sensitivity

Eutrophication effects on freshwater ecosystems from atmospheric deposition of N are of greatest concern in lakes and streams that have very low productivity and nutrient levels and that are located in the most undisturbed areas.

- In the Western U.S., high-elevation lakes are considered the most sensitive aquatic ecosystems to N deposition. Some examples include the Snowy Range in Wyoming, the Sierra Nevada Mountains, and Lake Tahoe in California, and the Colorado Front Range.
- The most severe eutrophication from N deposition effects are expected downwind of major urban and agricultural centers.

4.3.4. Estuarine Aquatic

The 1993 AQCD for NO_X concluded that the primary N nutrient addition effect on aquatic ecosystems is eutrophication of estuarine and near-coastal marine waters, which results in an increase of algal biomass and changes in community composition. Studies published since 1996 generally support the conclusions of 1993 AQCD. The data for estimating the contribution of N deposition to the nutrient budget of aquatic ecosystems were very sparse and mainly limited to the Chesapeake Bay before 1993. The contribution of N deposition to estuarine eutrophication is now better understood in the Chesapeake Bay and other estuaries.

A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions and generally received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker, 2007). Estuarine and coastal marine ecosystems experience a range of ecological problems associated with nutrient enrichment. Because the productivity of estuarine and near shore marine ecosystems is generally limited by the availability of N_r, excessive contribution of N_r from sources of water and air pollution can contribute to eutrophication.

4.3.4.1. Biogeochemical effects

A recent national assessment of eutrophic conditions in estuaries found that 65% of the assessed systems had moderate to high overall eutrophic conditions and generally received the greatest N loads from all sources, including atmospheric and land-based sources (Bricker, 2007). Estuarine and coastal marine ecosystems experience a range of ecological problems associated with nutrient enrichment. Because the productivity of estuarine and near shore marine ecosystems is generally limited by the availability of N_r, excessive contribution of N_r from sources of water and air pollution can contribute to eutrophication.

N Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and the biogeochemical cycling of N (Section 3.3.2.4). N from atmospheric deposition is estimated to comprise 10% to 40% of the total input of N to many coastal estuaries, and could be higher for some. Atmospheric N loads to great waters and estuaries in the U.S. are estimated to range from 2 to 8% for Guadalupe Bay, TX on the lowest end to ~72% for the Catherines-Sapelo estuary, GA (Castro, 2003) on the highest. At Chesapeake Bay, where N and S deposition and ecological effects have been extensively studied, total atmospheric deposition of atmospheric NO_3 is estimated to contribute from 20% to 30% of total N and 14% of the NH_4 loadings to the Bay.

Estimates of total N loadings to estuaries, or to other large-scale elements in the landscape are computed using measurements of wet and dry N deposition where these are available and interpolated with or without a set of air quality model predictions. Direct atmospheric inputs (directly to the water surface) of reactive N to coastal waters are essentially equal to or greater than those contained in riverine flow in the absence of deposition and may contribute from 20 to > 50% of external N loadings to these systems: 11, 5.6, and 5.6 kg N/ha for the Northeast Atlantic coast of the U.S., the Southeast Atlantic coast of the U.S., and the U.S. Eastern Gulf of Mexico, respectively.

It is unknown if atmospheric deposition alone is sufficient to cause eutrophication. In general, estuaries tend to be N-limited, and many currently receive high levels of N input from human activities to cause eutrophication (Vitousek, 1991; Howarth, 1996). The most widespread chemical indicator of eutrophication is dissolved O_2.

C Cycling

The evidence is sufficient to infer a causal relationship between N_r deposition and alteration to the biogeochemical cycling of C (Section 3.3.3.4). Estuaries and coastal waters tend to be N-limited and are therefore inherently sensitive to increased atmospheric N loading (D'Elia, 1986; Howarth, 2006). This is at least partly because denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek, 1997). However, other limiting factors occur in some locations and during some seasons. Levels of N limitations are affected by seasonal patterns. N-limited conditions are likely to be found during the peak of annual productivity in the summer.

Excess N inputs will affect the Si:N ratio in water. If the Si:N ratio decreases below about 1, the marine food web structure would be expected to change, with decreasing diatom-to-zooplankton-to-higher tropic level ratios and increasing abundance of flagellated algae.

4.3.4.2. Biological Effects

The evidence is sufficient to infer a causal relationship between N_r deposition and the alteration of species richness, species composition and biodiversity in estuarine ecosystems (Section 3.3.5.4). Increased N deposition can cause shifts in community composition, reduced hypolimnetic DO, reduced biodiversity, and mortality of submerged aquatic vegetation. The form of deposited N can significantly affect phytoplankton community composition in estuarine and marine environments. Small diatoms are more efficient in using NO_3^- than NH_4^+. Increasing NH_4^+ deposition relative to NO_3^- in the Eastern U.S. favors small diatoms at the expense of large diatoms. This alters the foundation of the food web. Submerged aquatic vegetation is important to the quality of estuarine ecosystem habitats because it provides habitat for a variety of aquatic organisms, absorbs excess nutrients, and traps sediments. Nutrient enrichment is the major driving factor contributing to declines in submerged aquatic vegetation coverage. The Mid-Atlantic region is the most heavily impacted area in terms of moderate or high loss of submerged aquatic vegetation due to eutrophication. Indicators to assess the eutrophic condition of estuarine and coastal waters are given in the following table:

Table 4-3. Indicators of estuarine eutrophication.

Primary Symptom	Description
Chlorophyll *a*	Excess N input will stimulate primary productivity and chlorophyll a concentration indicates a phytoplankton biomass
Macroalgal Abundance	Macroalgal blooms were moderate or high for half of the nation's assessed estuaries (Bricker, 2007). Macroalgal blooms can cause the loss of important submerged aquatic vegetation by blocking sunlight.
Dissolved O_2	Dissolved O_2 concentration decreases with increasing algal abundance under elevated N, because microbes consume O_2 as they decompose dead algae. Increased atmospheric N deposition could stimulate the development of hypoxic or anoxic zones. The northern Gulf of Mexico is the largest documented zone of hypoxic coastal water in U.S.
Nuisance/Toxic Algal Blooms	Excess N input can cause nuisance or toxic algal blooms, which release toxins in the water that can poison aquatic animals and threaten human health. About one third of the nation's assessed estuary systems exhibited a moderate or high symptom expression for nuisance or toxic algae (Bricker, 2007).

Source: Bricker et al. (2007).

4.3.4.3. Regional Vulnerability and Sensitivity

The most eutrophic estuaries were generally those that had large watershed-to-estuarine surface area, high human population density, high rainfall and runoff, low dilution, and low flushing rates (Bricker, 2007). The national estuary condition assessment conducted by Bricker et al. (2007) found the most impacted estuaries occurred in the mid-Atlantic region and the estuaries with the lowest symptoms of eutrophication were in the North Atlantic. Other regions had mixtures of low, moderate, and high degree of eutrophication. The regional assessment results from the report of Bricker et al. (2007) are summarized in Section 3.3.8.

The Chesapeake Bay is the largest estuary in U.S. Its watershed covers 64,299 square miles and the surface area of the bay and its major tributaries is 4,479 square miles (Pyzik, 1982). The Chesapeake Bay is perhaps the best-documented case study in the U.S. of the effects of human activities on estuarine eutrophication. Recent studies (Boyer, 2002; Howarth, 2007) indicated that atmospheric deposition makes a substantial contribution (about 25%) to the overall N budget of Chesapeake Bay. Human disturbances, such as landscape changes, have exacerbated the negative impacts of N deposition by reducing N removal and retention in the upper watershed region. Anthropogenic N inputs have substantially altered the trophic condition of Chesapeake Bay over the last 50 to 100 years. Symptoms of eutrophication in the bay include high algal production, low biodiversity, and large hypoxia and anoxia zones. Submerged aquatic vegetation was once abundant in Chesapeake Bay, covering about 200,000 acres along the shallows and shorelines. Increased nutrient inputs caused submerged aquatic vegetation declines since the mid-1960s and had fallen to about 38,000 acres by 1984. Eutrophication has been implicated in declines and disappearance of striped bass (*Morone saxatilis*) and blue crab (*Callinectes sapidus*) in Chesapeake Bay.

4.4. Direct Phytotoxic Effects

4.4.1. SO_2

The evidence is sufficient to infer a causal relationship between exposure to SO_2 and injury to vegetation. The current secondary standard for SO_2 is a 3-h avg of 0.50 ppm, which is designed to protect vegetation against acute foliar injury. There has been limited research on acute foliar injury since the last SO_2 AQCD and there is no clear evidence of acute foliar injury below the level of the current standard.

Effects on growth and yield of vegetation are associated with increased SO_2 exposure concentration and time of exposure. The 1982 SO_2 AQCD concluded that more definitive concentration-response studies were needed before useable exposure metrics could be identified. Because of falling ambient SO_2

concentrations and focus on O_3 vegetation effects research, few studies been published that would help develop a metric and define levels of concern for effects of SO_2 on growth and productivity of vegetation. The few new studies published support a causal link between exposure to SO_2 and reduced vegetation growth. However, the majority of these studies have been performed outside the US and at levels well above ambient concentrations observed in the US.

4.4.2. NO, NO_2 and PAN

The evidence is sufficient to infer a causal relationship between exposure to NO, NO_2 and PAN and injury to vegetation. It is well known that in sufficient concentrations NO, NO_2 and PAN can have phytotoxic effects on plants through decreasing photosynthesis and induction of visible foliar injury (EPA, 1993). However, the 1993 NO_X AQCD concluded that concentrations of NO, NO_2 and PAN in the atmosphere are rarely high enough to have phytotoxic effects on vegetation (EPA, 1993). Since the 1993 AQCD, very little new research has been done on these phytotoxic effects at concentrations currently observed in the US.

4.4.3. HNO_3

The evidence is sufficient to infer a causal relationship between exposure to HNO_3 and changes to vegetation. Experimental exposure of HNO_3 resulted in damage to the leaf cuticle of pine and oak seedlings which may predispose those plants to other stressors such as drought, pathogens and other air pollutants (Bytnerowicz, 1998; Bytnerowicz, 1998b). Several lines of evidence, including transplant and controlled exposure studies, indicate that HNO_3 is likely contributing to the decline in lichen species in the Los Angles basin (Boonpragob, 1991; Riddell, 2008; Nash, 1999). Current deposition of HNO_3 is contributing to N saturation of some ecosystems close to sources of photochemical smog (Fenn, 1998) such as the mixed conifer forests of the Los Angeles basin mountain (Bytnerowicz, 1999b; Bytnerowicz, 1999a).

4.5. Mercury Methylation

The evidence is sufficient to infer a causal relationship between S deposition and increased methylation of Hg, in aquatic environments where the value of other factors is within adequate range for methylation (Section 3.4.1.4). The main agent of Hg methylation is SO_4^{2-}-reducing-bacteria, and experimental evidence from laboratory to mesocosm scales has established that only inconsequential amounts of MeHg can be produced in the absence of SO_4^{2-}. These experimental results are highly coherent with one another, and with observational studies at larger scales. Mechanistic links have been established between changes in SO_4^{2-} and methylation of Hg, and changes in the amount of SO_4^{2-} present have been shown to be followed by commensurate changes in MeHg. Quantification of this response in natural settings has proved difficult because of the presence of multiple interacting factors: in aquatic environments where SO_4^{2-} and Hg are present, the amount of MeHg produced has been shown to vary with O_2 content, temperature, pH, and supply of labile organic carbon. In watersheds where no effect of changes in SO_4^{2-} deposition have been recorded on methylation of Hg, one or several of those interacting factors were not present in the amounts required for methylation to occur. Watersheds with conditions known to be conducive to Hg methylation can be found in the Northeastern U.S. and Southeastern Canada, but studies in other regions with significant Hg accumulation in biota have not been as extensive.

Mercury is a highly neurotoxic contaminant, and enters the food web in the methylated form. MeHg is then concentrated in higher trophic levels, including fish eaten by humans, with undesirable consequences for affected species, and for populations that consume large amounts of fish. Once MeHg is present, other variables influence how much of it accumulates in fish. Current evidence indicates that increased S deposition very likely results in MeHg accumulation in fish.

Table 4-4. Summary of N deposition levels and corresponding ecological effects.

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
U.S.						
Coastal sage scrub	Level = 9.8 to 35 kg N/ha/yr Species = nitrate as (HNO_3/NO_3) Measure = referred to Padgett et al. (1999)	60 kg N/ha/yr; as NH_4NO_3 between Jan. and March 1994, 1995, 1996 in two 30 kg N/ha/yr applications	N addition caused a shift in arbuscular mycorrhizal community composition with decreased species richness and diversity promoting a shift from shrub to grasslands	California		Egerton-Warburton and Allen (2000)
Coastal sage scrub	Level = not reported Species = not reported Measure = not reported	10 µg/g NH_4NO_3; Or 50 µg/g NO_3^-; Or 50 µg/g NH_4+	No evidence. that decline in native coastal sage scrub and increase in exotic grass is due to mycorrhizal response to increased NO_3^-	Southern California	*Artemisia californica* (native); *Bromus madritenis spp*. Rubens (exotic)	Yoshida and Allen (2001)
Coastal sage scrub	Level = Up to 30 kg N/ha/yr Species = not reported Measure = referred to Bytnerowicz et al. 1987; Fenn et al. 2003b	60 kg N/ha/yr; as NH_4NO_3	Soil inoculum from high N deposition site caused native shrub growth depression likely due to mycorrhizal fungi response. Growth of exotic grass may be promoted by soil inoculum from high N deposition site.	Western Riverside County Multispecies Reserve; University of California Riverside Botanical Gardens	*Artemisia californica* (native); *Bromus madritenis* spp. Rubens (exotic)	Siguenza et al.(2006)
Desert	Level = 30 kg N/ha/yr Species = not reported Measure = referred to Bytnerowicz et al. 1987	Two additions of 16 kg N/ha/yr, one as NH_4NO_3 and one as an NPK treatment	N addition increased biomass of non-native plants by ~54% , decreased native species biomass by about ~39%	Mojave desert	Creosote bush (Larrea *tridentate*), invasive grasses *Bromus madritensis* spp. Rubens, and Schismus spp.; and the forb *Erodium cicutarium*	Brooks (2003)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Desert	Level = 1.71 to 2.45 kg N/ha/yr Species = NH_4NO_3; Measure = field study for 16 yrs with network of six funnel precipitation collectors	Long term experiment: 100 kg N/ha/yr as granular NH_4NO_3 to 10 plots 2x/yr since Dec. 1995; Single season experiment: 20 kg N/ha/yr to 40 plots once	Long term: increased the cover of warm season grasses and decreased the cover of legumes; Short term: increased N lead to significant plant community structure change, especially in blue and black grama grassland patch types	Chihuahuan Desert	Blue and black grama (*Bouteloua gracilis* and *Bouteloua eropoda*, respectively)	Baez et al.(2007)
Forest	Level = 3.6 and 3.5 kg N/ha/yr on east slope; 1.1 kg N/ha/yr on west slope Species = not reported Measure = referred to Williams et al 1998; NADP 1999; Stottlemyer et al 1997)	No addition	East side: low C:N, lignin:N, and high N:Mg and N:P Increased foliar [N], soil % N, N mineralization rates, Mg depletion, and P enriched on East side stands; East side lakes higher [NO_3];	Eastern vs. Western slope of Continental Divied in Rocky Mtns.		Baron et al., (2000)
Forest	Level = 1–2 kg N/ha/yr on west slope; 3–5 kg N/ha/yr on east slope Species = not reported Measure = unspecified	No addition	East side had decreased soil organic horizon C/N and foliar C/N, and increased foliar N concentration, foliar N/Mg, foliar N/P and potential net mineralization; Englemann spruce forest biogeochemistry altered	Eastern vs. Western slope of Continental Divied in Rocky Mtns.	Englemann spruce	Rueth and Baron (2002)
Forest	Level = 1.2 to 23 kg N/ha/yr dry dep and 0.8 to 45 kg N/ha/yrwet dep Species = (for both) = NO_3^- and NH_4+ Measure = various citations	No addition	N saturation observed at 25–45 kg N/ha/yr of total inorganic N deposition. Where N saturation occurred, high NO_3^- concentrations in streamwater, soil, leaves; high NO emissions; high foliar N:P.	California – Los Angeles Air Basin		Bytnerowicz and Fenn (1996)
Forest (coniferous)	Level = 2 study sites: CP = 18.8 kg N/ha/yr BF= 2.9 kg N/ha/yr Species = NO_3^- and NH_4+ Measure = ion concentrations via liq. ion chromatography and colorimetrically via Technicon TRAACS 800 autoanalyzer	No addition	Site nearest to urban area (Los Angeles) received much more N deposition, as well as other pollutants (i.e. S deposition), and received much more fog, coinciding with much more wet deposition of N in that site Ecosystem was N saturated, as evidenced by high streamwater NO_3^- concentration, 151 and 65 µeq/L at upper and lower ends, respectively, of Devil Canyon West Fork	San Bernardino Mountains, California	Voniferous forest	Fenn et al.(2000)
Forest (mixed-chaparral, hardwood, coniferous)	Level = 11 to 40 kg N/ha/yr Species = NO_3^- and NH_4+ Measure = ion exchange resin column throughfall collectors (Fenn et al. 2002)	No addition	DIN export was scale dependent, with highest export occurring in watersheds of ~ 150–ha. Differences attributed to temporal asynchrony between N availability and biological demand	San Bernardino Mountains, CA	Mixed forest- chaparral, hardwood, coniferous	Meixner and Fenn (2004)
Forest (coniferous)	Level = 8 kg N/ha/yr and 82 kg N/ha/yr Species = not reported Measure = referred to Fenn et al., 2002	0, 50, 150 kg N/ha/yr annually from 1996 to 2002	Tree mortality was 9% higher and beetle activity 50 % higher for unfertilized trees at the high deposition site compared to the low pollution site. Tree mortality and beetle activity increased 8% and 20%, respectively under highest N fertilization rates at the low deposition site	San Bernardino Mountains, CA	Ponderosa pine	Jones et al. (2004)
Forest (chaparral)	Level = 35 kg N/ha/yr Species = not reported Measure = taking mean of two methods (estimation methods using data in situ and published data; NADP)	No addition	Continued high export (~3 kg N/ha/yr) of NO_3^- in stream water (15 yr) after prescribed burn indicates that chaparral ecosystem did not recover N-retention capabilities after disturbance	San Dimas Experimental Forest (40 km NW of LA), San Gabriel Mountains, CA	Chamise (*Adenostoma fasiculatum*), *Ceanothus spp*., live oak (*Quercus agrifolia*)	Meixner et al. (2006)
Forest (conifer)	Level = 1.2 to 71.1 kg N/ha/yr Species = NO_3^- and NH_4+ Measure = Throughfall measurements; ion exchange resin columns (Fenn & Poth 2004)	No addition	Empirical critical load for adverse impacts on lichen at 3.1 kg N/ha/yr. Enhanced NO_3^- leaching calculated with N deposition above 17 kg N/ha/yr. Lowered litter C:N and increases foliar N also observed at highly polluted sites.	California mixed conifer forests	Lichens, Ponderosa pine	Fenn et al. (2008)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest	Level = 20 to 35 kg N/ha/yr Species = NO_3^- Measure = field studies and NuCM, a nutrient cycling model (Fenn et al. 1996)	No addition	Areas with higher deposition had increased NO_3^- leaching, increased soil acidity, and decreased base cation saturation.	Southern California		Fenn et al.(2003)
Forest	Level = 3.2 to 5.5 kg N/ha/yr Species = not reported Measure = data from Loch Vale, a NADP/NTN monitoring station and Campbell et al. 2000	25 kg N/ha/yr of NH_4NO_3	N addition increased N concentration in foliar and organic soil horizon	Fraser Experimental Forest, Colorado	Spruce	Rueth et al. (2003)
Forest	Level = 1.7 kg N/ha/yr Species = not reported Measure = referred to Stottlemyer and Troendle 1992, Stottlemyer et al. 1997	25 kg N/ha/yr of NH_4NO_3	N addition doubled N mineralization rates and stimulated nitrification	Loch Vale watershed , Colorado	Old-growth spruce	Rueth et al.(2003)
Forest (alpine)	Level = 50 kg N/ha/yr Measure = referred to Sievering et al. 1995; Theodose and Bowman 1997 and Fisk et al. (1998)	200 kg N/ha/yr in 1993 and 1994; No fertilizer in 1995; 100 kg N/ha/yr as $(NH_4)_2SO_4$ in 1996 and 1997 Nutrient amendments consisted of a mixture a mixture of $(NH_4)_2)NO_3$ and $(NH_4)_2SO_4$ for the N plots	N deposition increased plant foliage productivity but reduced species richness. The reduction of species is best explained by changes in soil chemistry that resulted directly or indirectly from N additions	Niwot Ridge, Colorado	Alpine tundra: sedge *Kobresia myosuroides*. *Acomastylis rossii*, *Polygonum viviparurn Trifolium*. More mesic tundra-A. rossii and *Deschumnpsia caespitosa*. Snow bed- *D.caespitosa*, *Sibbaldia rocurnbens*, *Rifolium parryi*	Seastedt and Vaccaro (2001)
Forest	Level = 11.5 to 25.4 kg N/ha/yr Species = NO_3^- and NH_4+ Measure = both the TRAACS 800 Autoanalyzer and vai 16 IMPROVE monitoring sites and 11 NADP/NTN wet dep. sites	No addition	Concentrations of N in lichen thallus were highest at eastern and westernmost sites where N deposition was highest, implicating both agricultural (east) and urban (west) sources;	Columbia River Gorge, OR/WA	Lichens	Fenn at al.(2007)
Forest (maple-dominated hardwood)	Level = 5 to 8 kg N/ha/yr Species = not reported Measure = NADP 2006	30 kg N/ha/yr as $NaNO_3$	Arbuscular micorrhizal fungal biomass, storage structures and lipid storage declined in response to N addition	Northern Michigan	Maple-dominated hardwood- Sugar maple (*Acer saccharum*)	van Diepen et al. (2007)
Forest	Level = 3.3 to 12.7 kg N/ha/yr Species = not reported Measure = at NERC, 29 Jan 2003, compiled data sets and used them in stats model by Ollinger et al 1993, or used published values	No addition	At deposition levels above approximately 7–10 kg N/ha/yr, stream NO_3^- concentration increase with increasing deposition Soil C:N and nitrification flux increased with N deposition N dep not significantly important with foliar chemistry	Northeastern U.S.		Aber et al. (2003)
Forest	Level = 5.4 kg N/ha/yr Species = not reported Measure = McNulty and Aber, 1993	15.7 to 31.4 kg N/ha/yr as NH_4Cl-N or $NaNO_3^-$N	Forest trees in plots receiving < 20 kg N/ha/yr had high rate of growth initially followed by a decline, and forests trees in plots receiving > 25 kg N/ha/yr showed moderate rates of decline.	Vermont	Red spruce	McNulty et al.(1996)
Forest (herbaceous layer)	Level = 7 kg N/ha/yr Species = not reported Measure = Shepard et al. 1989	14 and 28 kg N/ha/yr as crystalline $(NH_4)_2SO_4$	N addition decreased herbaceous cover under hardwoods	Adirondack Park, New York	Hardwood	Hurd et al.(1998)
Forest (ectomycorrhiza)	Level = 3.5–7.8 kg/ha/yr N in wet deposition Species = not reported Measure = NADP data	Greenhouse study: 3 rates of N applications (0, 35, 140 kg/ha).	Ectomycorrhizal abundance and richness declined along increasing N deposition transect under pitch pine. The decline in richness was significantly correlated with the N deposition rate. In greenhouse study, pine seedling biomass was inversely related to N addition.	New Jersey Pine Barrens	Pitch pine	Dighton et al.(2004)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest	Level = Wet plus dry deposition 600 eq ha/yr for N and 900 equiv./ha/yr for S Species: not reported Measure =Kahl et al. 1999	1800 equiv.·ha–1·yr–1 for 10 yrs (bimonthly additions of dry $(NH_4)_2SO_4$ at the rate of 300 equiv. NH_4 and SO_4^{2-}/ha per application)	After 10 yrs of treatment, basal area increment of sugar maple was enhanced 13 to 104%, whereas red spruce was not significantly affected. The increase in sugar maple radial growth was attributed to a fertilization effect from the $(NH_4)_2SO_4$ treatment	Bear Brook, Maine	Sugar maple; red spruce	Elvir et al. (2003)
Forest	Level = 17 kg N/ha/yr Species: not reported Measure = referred to Adams et al. 1993	35.5 kg N/ha/yrand 40.5 kg S/ha/yr fertilized annually $(NH_4)_2SO_4$ (17 yrs)	N addition enhanced growth of black cherry and yellow poplar during the first 7 yrs, but reduced growth of these species in yrs 9 to 12, with no change in red maple or sweet birch	Fernow Experimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	DeWalle et al.(2006)
Forest (mixed hardwood)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. 1993	35 kg N/ha/yr $(NH_4)_2SO_4$ (16 yrs)	Possible declining growth vigor in red maple, and to lesser extent black cherry and tulip poplar. Observed interspecific differences in growth and plant nutrition responses suggest eventual changes in species composition under increasing N saturation.	Fernow Experimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	May et al. (2005)
Forest (mixedhardwood)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. 1993	35 kg N/ha/yr $(NH_4)_2SO_4$ (12 yrs)	N addition altered response of N-processing microbes to environmental factors, becoming less sensitive to seasonal changes in soil moisture and temperature	Fernow Experimental Forest, West Virginia	Mixed hardwood- red oak, red maple, tulip poplar, black cherry, sweet birch	Gilliam et al.(2001)
Forest (herbaceous layer)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. 1993	35 kg N/ha/yr $(NH_4)_2SO_4$ (4 yrs)	Increased foliar N in overstory tree species and Viola rotundifolia and decreased foliar Ca_2^+ and Mg_2^+, in response to 4 yrs of treatment. Nitrification rates were equally high in soils of all watersheds; Results support earlier studies that high amounts of ambient N deposition brought about N saturation on untreated watersheds at the Fernow Experimental Forest	Fernow Experimental Forest, West Virginia	*Viola rotundifolia Michx*	Gilliam et al.(1996)
Forest (herbaceous layer)	Level = 17 kg N/ha/yr Species = not reported Measure = referred to Adams et al. 1993)	35 kg N/ha/yr $(NH_4)_2SO_4$ (6 yrs)	no significant impact on the herbaceous layer under hardwoods	Fernow Experimental Forest, West Virginia	Mixed hardwood	Gilliam et al. (2006)
Forest	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites (Ollinger et al., 1993) and estimates from Munger et al. (1996).	50 and 150kg N/ha/yr for 15 yrs	Mortality of red pine reached 56% in 15 yrs in the pine high N plot, and biomass accumulation has stopped altogether. The high N hardwood stand shows increased aboveground NPP, but excess N availability and a severe drought in 1995 contributed to mortality of 72% of red maple trees by 2002. Species importance and litterfall patterns were altered in several plots after 1995. Roots, foliage and wood have diminished as net sinks for added N, re-emphasizing the role of soils in N retention concentrations of NH_4+ plus NO_3were not detected in soil water until the 15th yea r. Losses of inorganic N remain high in the high N plots (higher in pines than hardwoods) and low N plots in the pine stand also have measurable DIN losses. Foliar and fine root N concentrations are elevated significantly	Harvard Forest	Red pine (*Pinus resinosa Ait*.), black and red oak (*Quercus velutina Q. rubra*) black birch (*Betula lenta*), red maple (*Acer rubrum*), American beech (*Fagus grandifolia*) and black cherry (*Prunus serotina*)	Magill et al.(2004)
Forest (herbaceous layer)	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites (Ollinger et al., 1993) and estimates from Munger et al. 1996.	50 and 150kg N/ha/yr	Following 7 yrs of N additions, density and biomass of herb layer species had declined by 80% and 90%	Harvard Forest	Understory of red pine	Rainey et al. (Rainey, 1999)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Forest (mixed hardwood and coniferous)	Level = 6.6 to 8 kg N/ha/yr Measure = regional extrapolation from NADP sites (Ollinger et al., 1993) and estimates from Munger et al. 1996.	50 and 150kg N/ha/yr.	Wood production increased (hardwood) and decreased (coniferous) Calculated N budgets for the first 6 yr showed extremely high N retention (85–99%). Of the retained N, 50–83% appears to be in the long-term, recalcitrant soil pool. Foliar N increased 25% (hardwood) and 67% (coniferous); NO_3 leaching increased continuously over 6–yr study in coniferous forest, but was unchanged in hardwood forest, most (85–99%) of added N was retained, primarily in recalcitrant soil pool	Harvard Forest	Red pine (*Pinus resinosa Ait.*) stand and mixed hardwood stand	Magill et al. (1997)
Oak savanna	Level = 5.3 kg N/ha/yr Species = not reported Measure = NADP 2003	54 , and 170 kg N/ha/yr 16–yr addition of NH_4NO_3	N addition decreased total ectomycorrhizal fungal diversity by 50% and changed species composition.	Minnesota	Native oak savannah: bur oak (*Quercus macrocarpa Michaux*) and pin oak (*Q.ellipsoidalis E.J. Hill*), ectomycorrhizal fungi	Avis et al. (2003)
Grassland	Level = 6 kg N/ha/yr Species = 58% NH_4, 42% NO_3 Measure = CASTN35 for total inorganic (wet plus dry) N deposition; local wet deposition from the on-site NADP monitoring station	10, 20, 34, 54 or 95 kg N/ha/yr at three, five, five, seven and nine yrs, respectively from 1982 to 2004	Reduced relative number of species at every deposition level. Species numbers were reduced more per unit of added N at lower addition rates, suggesting that chronic but low-level N deposition may have a greater impact on diversity than previously thought. Chronic (23 yr) N addition (10 kg N/ha/yr) reduced plant species numbers by 17% relative to controls receiving ambient. Critical load calculated at 5.3 kg/ha/yr with an inverse prediction interval of 1.3–9.8 kg N/ha/yr	Cedar Creek Biological Station, Minnesota	Species=rich mixture of native C4 grasses and forbs (full list at http://www.cedarcreek.umn.edu/)	Clark and Tilman (2008)
Grassland	Level = not reported Species = not reported Measure = not reported	0, 54.4, and 272 kg N/ha/yr NH_4NO_3 added twice a yr for 18 yrs	Most of the forbs were lost from the high N plots, and two grass species, P. pratensis and A. repens, dominated. Loss of plant diversity in areas of high N. Change in composition of soil microbial community; increased bacterial and decreased fungal fatty acid methyl ester activity	Cedar Ck, LTER, Minnesota	ornamental grasses (Schizachyrium scoparium- Little Bluestem)	Bradley et al(2006)
Grassland	Level = 10–15 kg N/ha/yr in San Jose grasslands; 4–6 kg N/ha/yr at peninsula sites Species = not reported Measure = referred to Blanchard et al, 1996	No addition	Dry N deposition from smog contributes to grass invasion. Soil N limits grass invasion on serpentinitic solids. Grazing cattle select grasses over forbs, and grazing lead to a net export of N as cattle are removed for slaughter. Decreased populations of the bay checkerspot butterfly due to invasion of grasses after cattle grazing.	San Francisco Bay area, California	Bay checkerspot butterfly/ serpentinitic grasslands	Weiss (1999)
Grassland	Level = 10–15 kg N/ha/yr Species = not reported Measure =referred to Weiss 1999	No addition	N deposition displaced native grass species by exotic nitrophilous grasses. Low levels of soil N normally limit grass invasion in serpentinitic soils, but in ungrazed areas with experimental N fertilization or high N deposition, the introduced grasses crowd out many native species.	San Francisco Bay area, California	Serpentinitic grasslands	Fenn et al.(2003)
Grassland	Level = not reported Species = not reported Measure = not reported	70 kg N/ha/yr divided into a liquid $Ca(NO_3)_2$ pulse with the first autumn rains and a time-release pellet application (Osmocote) in January of each yr for 3 yrs.	After three yrs, N deposition suppressed plant diversity, forb production, and forb abundance in association with enhanced grass production	Jasper Ridge Biological Preserve, California	*Avena barbata*, *Bromushordeaceus*, *Lolium multiflorum*, *Avena fatua*, and *Bromus diandrus*, *Anagallis arvensis*, *Geranium dissectum*, Erodium botrys, Vicia sativa, Crepis vesicaria	Zavaleta et al.(2003)
Grassland (alpine)	Level =5 kg N/ha/yr Species = not reported Measure = not reported	20, 40, 60 kg N/ha/yr for 8 yrs	N deposition caused changes of plant species composition within 3 yrs of the initiation of the experiment and were significant at all levels of N addition. Changes in net nitrification were detectable at levels above 20 kg N/ha/yr. N addition increased NO_3^- leaching and NO_3^- concentration in soil water	Colorado Front Range	Alpine dry meadows	Bowman et al.(2006)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Grassland	Level = 5 kg N/ha/yr Measure =referred to Sievering et al. 1995; Theodose and Bowman 1997 and Fisk et al. (1998)	200 kg N/ha/yr In 1993 and 1994; No fertilizer in 1995; 100 kg N/ha/yr as $(NH_4)_2SO_4$ in 1996 and 1997; As a mixture of ammonium nitrate ((NH,)'NO,) and ammonium SO_4^{2-} ((NH,)'SO,)	Increased plant biomass and tissue N concentration	Niwot Ridge, Colorado	Alpine tundra: sedge *Kobresia myosuroides*. *Acomastylis rossii*, *Polygonum viviparurn Trifolium*. More mesic tundra-A. Rossii and *Deschumnpsia caespitosa*. Snow bed- D.caespitosa, *Sibbaldia procurnbens*, *Trifolium parryi*	Seastedt and Vaccaro (2001)
Grassland	Level = not reported Species = not reported Measure = not reported	0, 10, 40, 70, and 100 kg N/ha/yr for 75 days	N addition increased growth. Native species gained more height at every level of N availability compared to exotics	Greenhouse study	Two N. American natives, Blue grama, western wheatgrass, and Four exotics, cheatgrass, leafy spurge, Canada thistle, Russian knapweed	(Lowe, 2002)
Grassland	Level = 5 kg N/ha/yr Measure =referred to Sievering et al. 1995; Theodose and Bowman 1997 and Fisk et al. (1998)	25 kg N/ha/yr with biweekly additions of 2 g of NH_4NO_3 dissolved in deionized water for two yrs	N addition caused a community shift towards greater dominance of hairgrass in wet alpine meadows.	Niwot Ridge, Colorado	Alpine tundra: sedge Kobresia myosuroides. *Acomastylis rossii*, *Polygonum viviparurn Trifolium*. More mesic tundra-A. Rossii and Deschumnpsia caespitosa. Snow bed- D.caespitosa, *Sibbaldia procurnbens*, Trifolium	Bowman et al.(1995) Burns,(2004).
Lake	Estimated background N deposition value of 0.5 kg N/ha/yr in 1900, from a 19–yr record of measured values from Loch Vale (Colorado, USA; NADP site CO98) the mean wet N-deposition values was estimated at 1.5 kg N/ha/yr	No addition	Increasing N deposition caused a shift in algae community composition	Loch Vale, Colorado Baron (2006)and Beartooth Lake, Minnesota (Saros et al. (2003)	Algae	(2006) Saros et al.(2003)
Lake	Level = 2 kg N/ha/yr Measure = NAPD site from 1981 through 1996	N additions in semi-continuous laboratory bioassays of mixed diatom assemblages,	Increasing N shifted diatom species in alpine lakes.	Rocky Mountain , Colorado	*Diatoms-Stephanodiscus minutulus*, *Stephunodiscus niugarue*, and *Cyclotella bodanica*.	Interlandi and Kilham (1998)
Surface waters	Level = 8–10 kg N/ha/yr Measure = NADP from 1982 to 1994	No addition	Chronic N deposition resulted in increased N leaching.	Eastern U.S./ New England and Adirondack lakes		Stoddard et al. (1994)
Surface waters	Level = 4.71 kg N/ha/yr –200% increase in NO_3^- loading from wet deposition over the prior decade, increasing from 8 kg N/ha/yr for 1985–1987 to 16.5 kg N/ha/yr 1990–1992 Species= not reported Measure = NADP	No addition	A shift in from an N-limited system to an N-saturated system. Many lakes having (NO_3^-) concentrations greater than 10 íequiv/L. Increasing atmospheric deposition of N with elevation is causing a change from N limitation to P limitation in the highest-elevation bristlecone pines	Niwot Ridge/Green Lakes, Colorado Front Range		Williams et al.(1996)
Wetland (freshwater)	Level = 10 to14 kg N/ha/yr	Hawley Bog: 2 treatments of 0.1 or 1.0 mg NH_4 N/L every 2 weeks between June 1 and Sept 30 for 1998, 1999, and 2000	Negative population growth rate of pitcher plant	Hawley Bog (MA) Molly Bog (VA)	*Sarracenia purpurea*	Gotelli and Ellison (2002) Gotelli and Ellison (2006)
Coastal-Marine		Discontinuously diluted N limited cultures, which were pulsed with NO_3^-every 3 days;	Large diatoms became dominant when nitrate was supplied as the only N source once in 3 days sinking rate of the nitrate grown population was higher (0.12 m/day) than that of the ammonium grown population (0 m/day). For natural systems, this implies nitrate-controlled systems production by larger algae is relatively high. This may be an explanation for the higher sedimentation rates of organic material in coastal or oceanic upwelling areas as compared to ammonium-controlled (regenerative) systems. Specific nitrate uptake was related to cell volume		Marine phytoplankton (Stolte study)	Stolte et al. (1994)

Type of Ecosystem	Ambient N Deposition[1] (kg N/ha/yr)	N Additions (kg N/ha/yr)	Biological and Chemical Effects	Study Site	Study Species	Reference
Variable	Variable	60–120 kg N/ha/yr (variable range across 23 different experiments)	Soil CEC and temperature were the strongest contributors to multivariable explanation of species richness response to experimental N addition in 23 studies throughout the U.S. Greater plant species loss was associated with lower soil CEC, colder temperature and larger production increases	Variable	Variable	Clark et al. (2007)
China and Europe						
Forest	Level = 3 kg N/ha/yr Species = not reported Measure = not reported	30 yrs of annual additions of NH_4NO_3 in 3 treatments: N1 and N2 (34 and 68 kg N/ha/yr) and 20 yrs of N3 (108 kg N/ha/yr), plus a control	Stimulate stemwood production in all levels of N addition until 7 yrs into experiment; thereafter the second and third treatments (with medium and high N addition) decreased stemwood production and the first treatment (the lowest amount of N addition) continued to increase stemwood production throughout experiment	Northern Sweden	Scots pine	Högberg et al.(2006)
Forest (boreal)	Level = 3–12 kg N/ha/yr Species = not reported Measure = MATCH model of N-deposition for 1996; surveys in permanent plots in the National Forest Inventory	No addition	N deposition decreased the abundance and cover of ericaceous shrubs	Sweden	Vaccinium species (*Ericaceae*)	Strengbom et al.(2003)
Lake	Level = Wet DIN = 1.3–11 kg N/ha/yr Total N = 1–4 and 9–18 kg N/ha/yr Species = wet DIN and total N Measure = SEPAs use of MATCH model	No addition	Increased lake concentrations of inorganic N caused P limitation in summer and increased eutrophication with increased lake algal productivity	Sweden		Bergström et al.(2005)
Wetland	Level = 0.2 – 0.3 g $N/m^2/a$ (2 – 3 kg N/ha/yr) Species = NH_4+ and NO_3^- Measure = refers to Ruoho-Airola et al. 1998	Cumulative addition of 3 g $N/m^2/a$ (30 kg N/ha/yr) as NH_4NO_3 on six occasions during growing season	Increased NH_4NO_3 affected comp. of moss layer, specifically decreasing *Sphagnum balticum*, and caused decrease in litter and an increase of a Vaccinium species	Eastern Finland	*Sphagnum sp.*, *Eriophorum vaginatum*, *Carex pauciflora*, *Vaccinium oxycoccos*, Scheuchzeria palustris	Saarnio et al.(2003)
Wetland	Level = not reported Species = not reported Measure = not reported	240 kg N/ha/yr as NH_4NO_3 applied in field experiment where 3 of 6 plots received treatment every 2 weeks for 2 yrs	N addition increased above ground biomass and abundance of *Deyeucia angustifolia*, stimulated CO_2 and CH_4, and N_2O emissions from *D. angustifolia* wetlands. N_2O emissions significantly influenced by N addition.	Northeast China	*Deyeucia angustifolia*	Zhang et al. (2007)
Wetland	Level = 2 to 20 kg N/ha/yr Species = not reported Measure = national precipitation monitoring programs of each country and refer to the 3 yrs prior to peat sampling in experiment	No addition	N deposition increased N increased microbial activity, CO_2 emissions, and dissolved organic carbon release. Decomposition rates for material accumulated under higher atmospheric N supplies resulted in higher carbon dioxide (CO_2) emissions and dissolved organic carbon release	Nine European countries	Species like Sphagnum	Bragazza et al.(2006)

[1] Ambient N deposition information is divided into three categories:
Level = deposition rate
Species = chemical species of N that were measured
Measure = source of the deposition data reported (i.e. a monitoring network, reference to another publication, etc.)

Glossary

Acid Neutralizing Capacity (ANC)

A key indicator of the ability of water to neutralize acidifying inputs. This ability depends largely on associated biogeochemical characteristics.

Acidification

The process of decreasing the pH of a system. Systems that can be acidified by atmospheric deposition of acidic or acidifying compounds include lakes, streams, and forest soils.

Algae

Photosynthetic, often microscopic and planktonic, organisms occurring in aquatic ecosystems.

Algal bloom

A rapid and extreme increase of an algae population in a lake, river, or ocean.

Alpine

The biogeographic zone made up of slopes above the *tree line*, and characterized by the presence of rosette-forming herbaceous plants and low, shrubby, slow-growing woody plants.

Anthropogenic

Resulting from human activity or produced by human beings.

Arid region

An area receiving < 250 mm precipitation per year.

Atmosphere

The gaseous envelope surrounding the Earth. The dry atmosphere consists almost entirely of nitrogen and O_2, together with trace gases including carbon dioxide and ozone.

Base cation saturation

The degree to which soil cation exchange sites are occupied with base cations (e.g. Ca^{2+}, Mg^{2+}, K+) as opposed to Al3+ and H+. Base cation saturation is a measure of soil acidification, with lower values being more acidic. A marked increase in the sensitivity of soils to changes in base saturation occurs at a threshold of approximately 20%.

Bioaccumulation

The gradual increase in accumulation of some compounds in organisms with increasingly higher trophic levels.

Biodiversity

The total diversity of all organisms and ecosystems at various spatial scales (from genes to biomes).

Buffering capacity

The ability of a body of water and its watershed to resist changes in pH.

Carbon sequestration

The process of increasing the carbon content of a reservoir other than the atmosphere.

Catchment

An area that collects and drains rainwater.

Climate

Climate in a narrow sense is usually defined as the ‘average weather’, or more rigorously, as the statistical description in terms of the mean and variability of relevant quantities over a period of time ranging from months to thousands or millions of years. These quantities are most often surface variables such as temperature, precipitation, and wind. Climate in a wider sense is the state, including a statistical description, of the *climate system*. The generally accepted period of time is 30 years, as defined by the World Meteorological Organization (WMO).

Critical load

A quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge.

Denitrification

The anaerobic reduction of oxidized nitrogen (e.g., nitrate or nitrite) to gaseous nitrogen (e.g., N_2ON_2O or N_2N_2), normally accomplished by denitrifying bacteria.

Dry deposition

The movement of gases and particles from the atmosphere to surfaces in the absence of precipitation (e.g., rain or snow) or occult deposition.

Ecological community

An assemblage of populations of different species, interacting with one another

Ecosystem services

Ecological processes or functions having monetary or non-monetary value to individuals or society at large. They may be classified as (i) supporting services such as productivity or biodiversity maintenance; ii) provisioning services such as food, fibre, or fish; iii) regulating services such as climate regulation or carbon sequestration; and (iv) cultural services such as tourism or spiritual and aesthetic appreciation.

Ecosystem

The interactive system formed from all living organisms and their abiotic (physical and chemical) environment within a given area. Ecosystems cover a hierarchy of spatial scales and can comprise the entire globe, *biomes* at the continental scale, or small, well-circumscribed systems such as a small pond.

Eutrophication

The enrichment of a waterbody with nutrients, resulting in increased productivity (of algae or aquatic plants), and sometimes also decreased dissolved O_2 levels.

Eutrophy

Eutrophy generally refers to a state of nutrient enrichment, but it is commonly used to refer to condition of increased algal biomass and productivity, presence of nuisance algal populations, and a decrease in dissolved O_2 concentrations.

Evapotranspiration

The combined process of water evaporation from the Earth's surface and transpiration from vegetation.

Fen

A phase in the development of the natural succession from open lake, through reedbed, fen and carr, to woodland as the peat develops and its surface rises.

Freshet

A great rise or overflowing of a stream caused by heavy rains or melted snow.

Greenhouse gas

Those atmospheric gasses that absorb and emit radiation emitted by the Earth's surface, the atmosphere, and clouds within the infrared portion of the spectrum. This property causes the greenhouse effect. Water vapor (H_2OH_2O), carbon dioxide (CO_2), nitrous oxide (N_2ON_2O), methane (CH_4), and ozone (O_3O_3) are the primary greenhouse gases in the Earth's atmosphere. Besides these, the *Kyoto Protocol* also deals with the greenhouse gases sulfur hexafluoride (SF_6), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

Gross primary production

The total carbon fixed by plants through photosynthesis.

Heathland

A wide-open landscape dominated by low-growing woody vegetations such as heathers and heathland grasses. Heathlands generally occur on acidic, nutrient-poor, and often sandy and well-draining soils.

Hypoxic

Events that lead to a deficiency of O_2.

Invasive species and invasive alien species

A species aggressively expanding its range and population density into a region in which it is not native, often through outcompeting or otherwise dominating native species.

Leaching

The removal of soil elements or chemicals by water movement through the soil.

Lowland

In physical geography, lowland is any relatively flat area in the lower levels of regional elevation. The term can be applied to the landward portion of the upward slope from oceanic depths to continental highlands, to a region of depression in the interior of a mountainous region, to a plain of denudation, or to any region in contrast to a highland.

Net ecosystem exchange (NEE)

The net flux of carbon between the land and the atmosphere, typically measured using eddy covariance techniques. Positive values of NEE usually refer to carbon released to the atmosphere (i.e., a source), and negative values refer to carbon uptake (i.e., a sink)

Net ecosystem production (NEP)

The difference between net primary production (NPP) and heterotrophic respiration (mostly decomposition of dead organic matter) of that ecosystem over the same area. NEP = -NEE, with positive values indicating a sequestration of atmospheric carbon in to biosphere.

Net primary production (NPP)

The *gross primary production* minus autotrophic *respiration*, i.e., the sum of metabolic processes for plant growth and maintenance, over the same area.

Nitrification

The biological oxidation of ammonia to nitrite and then to nitrate. This process is primarily accomplished by autotrophic nitrifying bacteria that obtain energy by reducing ammonium and/or nitrite to nitrate.

Nitrogen mineralization

The conversion of organic nitrogen into plant-available inorganic forms (e.g. NH_3 or $NH_4^+NH_4^+$) by microorganisms.

Nitrogen-retention capacity

The length of time that an ecosystem can retain nitrogen in (?) organisms (e.g., plant or microbe) and soil-organic matter. Nitrogen-retention capacity is highly affected by soil, vegetative, topographic, and land-use factors.

Nitrogen saturation

The condition in which nitrogen inputs from atmospheric deposition and other sources exceed the biological requirements of the ecosystem.

Occult deposition

The transmission of gases and particles from the atmosphere to surfaces by fog or mist.

Ombrotrophic bog

An acidic peat-accumulating wetland that is fed by rainwater (instead of groundwater) and, thus, especially poor in nutrients.

pH

A measure of the relative concentration of hydrogen ions in a solution. The formula for calculating pH is: $pH = {}^{-}\text{-}\log_{10}[H^+]$, where $[H^+]$ represents the hydrogen ion concentration in moles per liter. The pH scale ranges from 0 to 14. A pH of 7 is neutral. A pH less than 7 is acidic and a pH greater than 7 is basic.

Phytoplankton

The plant forms of *plankton*. Phytoplankton are the dominant plants in the sea and are the basis of the entire marine food web. These single-celled organisms are the principal agents of photosynthetic carbon fixation in the ocean.

Primary Production

All forms of production accomplished by plants, also called primary producers. See *GPP, NPP,* and *NEP*.

Semi-arid regions

Regions of moderately low rainfall (100– and 250–mm precipitation per year), which are not highly productive and are usually classified as *rangelands.*

Sensitivity

The degree to which a system responds to pollution (e.g. acidification, n-nutrient enrichment, etc.). The response may be direct (e.g., a change in growth following a change in the mean, range, or variability of N deposition) or indirect (e.g., changes in growth due to alterations in competitive dynamics between species or decreased biodiversity , themselves following N deposition).

Streamflow

Water flow within a river channel. A synonym for *river discharge*.

Surface runoff

The water that travels over the land surface to the nearest surface stream; *runoff* of a drainage *basin* that has not passed beneath the surface since precipitation.

Throughfall

The precipitation falling through the canopy of a forest and reaching the forest floor.

Trophic level

The position that an organism occupies in a food web.

Tundra

A treeless, level, or gently undulating plain characteristic of the Arctic, sub-Arctic regions and some alpine regions characterized by low temperatures and short growing seasons.

Upland terrestrial ecosystem

Generally considered to be the ecosystems located at higher elevations directly above riparian zones and wetlands. Vegetation in an upland ecosystem is not in contact with groundwater or other permanent water sources.

Valuation

The economic or non-economic process of determining either the value of maintaining a given ecosystem type, state, or condition or the value of a change in an ecosystem, its components, or the services it provides.

Vulnerability

Susceptibility to degradation or damage from adverse factors or influences. Vulnerability is a function the exposure and its sensitivity.

Welfare effects

Effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and on personal comfort and well-being, whether caused by transformation, conversion, or combination with other air pollutants (CAA 302(h)).

Wet deposition

The transmission of gases and particles from the atmosphere to surfaces by rain or other precipitation.

Wetland

Those areas that are inundated or saturated by surface or ground water at a frequency and duration sufficient to support a prevalence of vegetation adapted to water-saturated soil conditions. Wetlands include swamps, marshes, bogs, and similar areas.

Zooplankton

The animal forms of plankton. They consume phytoplankton or other zooplankton.

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