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

(Second External Review Draft)

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Table of Contents

List of Tables

List of Figures

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
$CH_3\text{-}S\text{-}CH_3$	dimethylsulfide, DMS
$CH_3\text{-}S\text{-}H$	methyl mercaptan
$(CH_3)_2SO$	dimethyl sulfoxide, DMSO
CH_3SO_3H	methanesulfonic acid
$CH_3\text{-}S\text{-}S\text{-}CH_3$	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
HPVM	
HSO_3^-	bisulfate ion
HSO_4^-	sulfuric acid ion
H_2S	hydrogen sulfide
H_2SO_3	sulfurous acid
H_2SO_4	sulfuric acid
HTC	
hν	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 $\leq$2.5 µm
PM_{10}	particulate matter with aerodynamic diameter $\leq$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 $\geq$ 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

Annex A. Ecosystem Monitoring and Models

A.1. Introduction

A tremendous amount of research has been conducted in the U.S., and elsewhere, over the past three decades on the ways in which atmospheric deposition of sulfur (S) and nitrogen (N) affect the health, condition, and vitality of aquatic, transitional, and terrestrial ecosystems. Much of this work has focused on developing a better understanding of acidification and nutrient enrichment processes. Some of this work has been highly quantitative, allowing researchers to determine key process rates in multiple ecosystem compartments. Nevertheless, quantification of overall ecosystem response requires a higher level of process rate aggregation. It is important to develop quantitative understanding of the extent of past ecosystem effects in response to atmospheric S and N deposition, the extent to which conditions will worsen or recover under continued or reduced deposition levels, and the sustained loads of deposition that would be required to prevent further ecosystem damage and to allow damaged ecosystems to recover. This kind of quantitative understanding cannot evolve directly out of process-based research. It requires development of mathematical models that encode process knowledge and link it in such a way as to produce quantitative estimates of change in resource conditions over time in response to changes in the major forcing functions, including atmospheric deposition, climate, and landscape disturbance. As described in this Annex, many such models have been developed and used to estimate past and future changes in ecosystem condition. Such models cannot be validated, *per se*, because environmental systems are never closed and because important processes yield conflicting, often opposing, results. Therefore, a model can produce the right answer for the wrong reason (cf. Oreskes, 1994). Similarly, a particular process may not be important at a particular site where a model is tested, but assume much greater importance elsewhere. For these reasons, it is critical that environmental models be tested and confirmed at multiple locations that exhibit differing conditions and pollutant loads before they are used as the foundation for public policy (Sullivan, 2000).

Some of the best data with which to test and confirm environmental models are derived from long-term monitoring sites. These are locations where one or more attributes of a natural ecosystem compartment (i.e., surface water, soil, plants) is periodically sampled and analyzed over a long period of time. Such data are often especially valuable for sites which experience rather large changes in one of the forcing functions (often atmospheric deposition). This enables evaluation of the extent to which the model accurately captures the dynamics of ecosystem response(s) that occur. Because many environmental

attributes undergo rather substantial intra- and inter-annual variability in response to climatic variation and other changes, a long period of record is required before a monitoring data set can be used for evaluation of ecosystem response or for model confirmation.

Long-term monitoring data provide not only data with which to test model projections, but also a reality check on scientific understanding of damage and recovery processes. If observed (monitored) changes are not in agreement with process understanding, it is possible or perhaps likely that one or more key processes is not well-understood or well-formulated in the model.

This Annex summarizes the primary long-term monitoring sites and programs in the U.S., and the principal mathematical models used to simulate environmental responses to atmospheric S and N deposition. Quantitative data derived from the model projections and from trends analyses of the monitoring data provide an important part of the foundation for evaluating the past, current, and future effects of S and N deposition, and expected recovery as emissions levels decrease in the future.

A.2. Ecosystem Monitoring

The effects of acidic and N nutrient deposition on ecosystems require long-term study. Changes in ecosystems often occur gradually, and sustained monitoring of key variables provides the principal record of change over time. Monitoring data are also useful for establishing a baseline of resource conditions and determining if short-term events were unusual or extreme (Lovett, 2007). There are limited monitoring programs and data to document ecosystem responses to changes in atmospheric deposition in the past. It is often difficult to sustain funding for ecosystem monitoring, perhaps because results are produced slowly and because results are seldom viewed as novel. Nevertheless, monitoring data provide some of the best means for evaluating the completeness of the scientific knowledge base and for testing how robust our projections of future conditions might be. This section describes some of the more important and useful monitoring programs for evaluating the effects of N and S deposition on ecosystems in the U.S.

There are long-term monitoring sites scattered throughout the U.S. where samples are periodically collected and analyzed to determine the condition of aquatic, transitional, or terrestrial ecosystem elements. Some have been in operation for only a short period of time; others have continued for decades. None extend back far enough to have documented resource conditions prior to the advent of high levels of atmospheric S and N deposition. Some of the monitoring sites exist as an individual entity, or small collection of sites, often established primarily for research purposes. Despite the research focus, many of these long-term research sites include collection of monitoring data. Other long-term monitoring sites exist as part of large regional programs with a specific focus on long-term monitoring. The most significant individual monitoring sites and networks are discussed below.

Lovett et al. (2007) reviewed the characteristics of successful environmental monitoring programs, and argued that monitoring is a fundamental part of environmental science and policy. Their analysis underscored the fact that environmental monitoring costs little relative to the value of the resources that it protects and the policy that it informs. Monitoring data also have substantial added value because they can be used for multiple purposes, including various research objectives.

Ecosystems also require long-term study because most changes occur slowly. When more rapid change does occur, for example in response to an extreme event, a long-term record is needed to put the effects of the extreme event into proper context.

A.2.1. Environmental Monitoring and Assessment Program

The EPA Environmental Monitoring and Assessment Program (EMAP) began regional surveys of the nation's surface waters in 1991 with a survey of Northeastern U.S. lakes. Since then, EMAP and Regional-EMAP (REMAP) surveys have been conducted on lakes and streams throughout the country. The objective of these EMAP surveys is to characterize ecological condition across populations of surface waters. EMAP surveys are probability surveys where sites are picked using a spatially balanced systematic randomized sample so that the results can be used to make estimates of regional extent of condition (e.g., number of lakes, length of stream). EMAP sampling typically consists of measures of aquatic biota (fish, macroinvertebrates, zooplankton, and periphyton), water chemistry, and physical habitat.

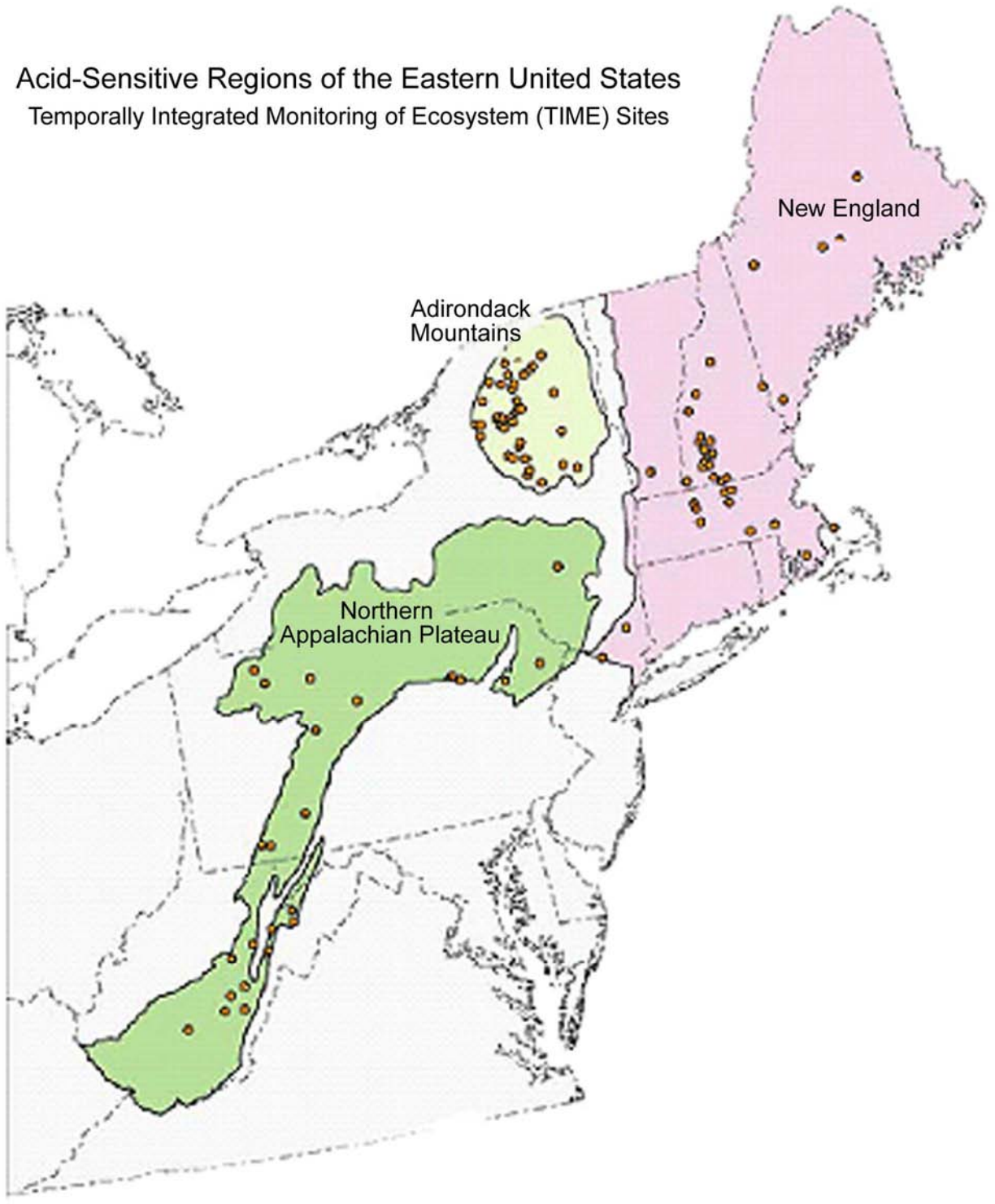
Of particular interest with respect to acidic deposition effects were two EMAP surveys conducted in the 1990s, the Northeastern Lake Survey and the Mid-Atlantic Highlands Assessment of streams (MAHA). The Northeastern Lake Survey was conducted in summer from 1991 to 1994 and consisted of 345 randomly selected lakes in the states of New York, New Jersey, Vermont, New Hampshire, Maine, Rhode Island, Connecticut, and Massachusetts (Whittier, 2002). To make more precise estimates of the effects of acidic deposition, the sampling grid was intensified to increase the sample site density in the Adirondacks and New England Uplands areas known to be susceptible to acidic deposition. The MAHA study was conducted on 503 stream sites from 1993 to 1995 in the states of West Virginia, Virginia, Pennsylvania, Maryland, Delaware, and the Catskill Mountain region of New York (Herlihy, 2000). Sampling was done during spring baseflow. Sample sites were restricted to first through third order streams as depicted on the U.S. Geological Survey (USGS) 1:100,000 digital maps used in site selection. To make more precise estimates of the effects of acidic deposition, the sampling grid was intensified to increase the sample site density in the Blue Ridge, Appalachian Plateau, and Ridge section of the Valley and Ridge ecoregions. Results from both of these surveys were used to develop and select the sampling sites for the Temporally Integrated Monitoring of Ecosystems (TIME) program, which is described below.

A.2.2. Surface Water Chemistry Monitoring

There are two surface water chemistry monitoring programs, administered by EPA, that are especially important to inform the assessment of aquatic ecosystem responses to changes in atmospheric deposition. These are the TIME program (Stoddard, 2003) and the Long-term Monitoring (LTM) program (Ford, 1993; Stoddard, 1998). These efforts focus on portions of the U.S. most affected by the acidifying influence of S and N deposition, including lakes in the Adirondack Mountains of New York and in New England, and streams in the Northern Appalachian Plateau and Blue Ridge in Virginia and West Virginia. Both projects are operated cooperatively with numerous collaborators in state agencies, academic institutions and other federal agencies. The TIME and LTM projects have slightly different objectives and structures, which are outlined below. Stoddard et al. (2003) conducted a thorough trends analysis of the TIME and LTM data.

A.2.2.1. TIME Project

At the core of the TIME project is the concept of probability sampling, whereby each sampling site is chosen statistically from a pre-defined target population. Collectively, the monitoring data collected at the sites are representative of the target population of lakes or streams in each study (Figure A-1). The target populations in these regions include lakes and streams likely to be responsive to changes in acidic deposition, defined in terms of acid neutralizing capacity (ANC), which represents an estimate of the ability of water to buffer acid. It can be either calculated (calculated ANC = sum of base cations – sum of mineral acid anions, where all concentrations are in μeq/L) or titrated in the laboratory (Gran ANC). Measurement of Gran ANC uses the Gran technique to find the inflection point in an acid-base titration of a water sample (Gran, 1952). In the Northeast, the TIME target population consists of lakes with a Gran ANC less than 100 μeq/L. In the Mid-Atlantic, the target population is upland streams with Gran ANC less than 100 μeq/L. In both regions, the sample sites selected for future monitoring were selected from the EMAP survey sites in the region (Section A.2.1) that met the TIME target population definition.



Source: Stoddard et al. (2003).

Figure A-1. Location of acid-sensitive regions of the northern and eastern U.S. These are regions for which statistical survey data are available in the 1990s, and locations of individual TIME sites used in trend analysis.

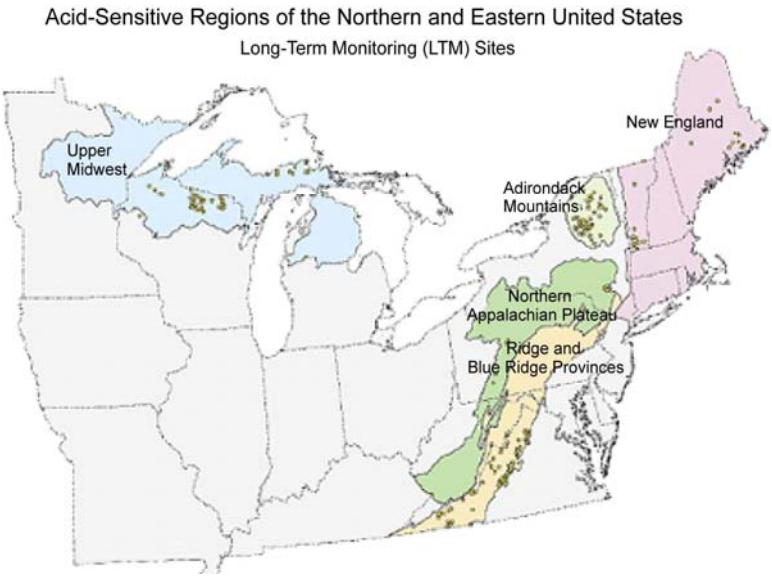
Each lake or stream is sampled annually (in summer for lakes; in spring for streams), and results are extrapolated with known confidence to the target population(s) as a whole using the EMAP site population expansion factors or weights (Larsen, 1993; Larsen, 1994; Stoddard, 1996; Urquhart, 1998). TIME sites were selected using the methods developed by the EMAP (Paulsen, 1991; Herlihy, 2000). The TIME project began sampling northeastern lakes in 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of low-ANC lakes in that region. There are about 1,000 low-ANC Adirondack lakes, out of a total population of 1830 lakes with surface area greater than 1 ha. Data from 30 lakes (representing about 1,500 low-ANC lakes, out of a total population of 6,800) form the basis for TIME monitoring in New England. Probability monitoring of Mid-Atlantic streams began in 1993. Stoddard et al. (2003) analyzed data from 30 low-ANC streams in the Northern Appalachian Plateau (representing about 24,000 km of low-ANC stream length out of a total stream length of 42,000 km).

The initial 1993−1995 EMAP-MAHA sample in the Mid-Atlantic was not dense enough to obtain enough sites in the TIME target population in the Blue Ridge and Valley and Ridge ecoregions. In 1998, another denser random sample was conducted in these ecoregions to identify more TIME sites. After pooling TIME target sites taken from both MAHA and the 1998 survey, there are now 21 TIME sites in the Blue Ridge and Ridge and Valley that can be used for trend detection in this aggregate ecoregion in the Mid-Atlantic in addition to the Northern Appalachian Plateau ecoregion.

A.2.2.2. Long-Term Monitoring Project

As a complement to the statistical lake and stream sampling in TIME, the LTM project samples a subset of generally acid-sensitive lakes and streams that have long-term data, many dating back to the early 1980s (Figure A-2). These sites are sampled 3 to 15 times per year. This information is used to characterize how some of the most sensitive of aquatic systems in each region are responding to changing deposition, as well as giving information on seasonal variation in water chemistry. In most regions, a small number of higher-ANC (e.g., Gran ANC greater than 100 µeq/L) sites are also sampled, and help separate temporal changes due to acidic deposition from those attributable to other disturbances (e.g., climate, land use change). Because of the availability of long-term records (more than two decades) at many LTM sites, their trends can also be placed in a better historical context than those of the TIME sites, where data are only available starting in the 1990s.

Monitored water chemistry variables include pH, ANC, major anions and cations, monomeric aluminum (Al), silicon (Si), specific conductance, dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC). The field protocols, laboratory methods, and quality assurance procedures are specific to each team of investigators. This information is contained in the cited publications of each research group. The EMAP and TIME protocols and quality assurance methods are generally consistent with those of the LTM cooperators. Details of LTM data from each region are given below.



Source: Stoddard et al. (2003).

Figure A-2. Location LTM sites used in the 2003 Surface Water report.

New England Lakes: The LTM project collects quarterly data from lakes in Maine (sampled by the University of Maine; Kahl, 1991; Kahl, 1993) and Vermont (data collected by the Vermont Department of Environmental Conservation`; \Stoddard, 1993; Stoddard, 1998). Data from 24 New England lakes were available for the trend analysis reported by Stoddard et al. (2003) for the time period 1990 to 2000. In addition to quarterly samples, a subset of these lakes have outlet samples collected on a weekly basis during the snowmelt season; these data are used to characterize variation in spring chemistry. The majority of New England LTM lakes have mean Gran ANC values ranging from –20 to 100 µeq/L; two higher ANC lakes (Gran ANC between 100 and 200 µeq/L) are also monitored.

Adirondack Lakes: The trend analysis of Stoddard et al. (2003) included data from 48 Adirondack lakes, sampled monthly by the Adirondack Lake Survey Corporation (Driscoll, 1993; Driscoll, 1995); a subset of these lakes are sampled weekly during spring snowmelt to help characterize spring season variability. Sixteen of the lakes have been monitored since the early 1980s; the others were added to the program in the 1990s. The Adirondack LTM dataset includes seepage and drainage lakes, most with Gran ANC values in the range of –50 to 100 µeq/L; three lakes with Gran ANC between 100 µeq/L and 200 µeq/L are also monitored.

Appalachian Plateau streams: Stream sampling in the Northern Appalachian Plateau is conducted about 15 times per year, with the samples spread evenly between baseflow (e.g., summer and fall) and high flow (e.g., spring) seasons. Data from four streams in the Catskill Mountains (collected by the U.S. Geological Survey; Murdoch, 1993, and five streams in Pennsylvania (collected by Pennsylvania State

University; DeWalle and Swistock, 1994) were analyzed by Stoddard et al. (2003). All of the Northern Appalachian LTM streams have mean Gran ANC values in the range –25 to 50 µeq/L.

Upper Midwest lakes: Forty lakes in the Upper Midwest were originally included in the LTM project, but funding in this region was terminated in 1995. The Wisconsin Department of Natural Resources (funded by the Wisconsin Acid Deposition Research Council, the Wisconsin Utilities Association, the Electric Power Research Institute and the Wisconsin Department of Natural Resources) has continued limited sampling of a subset of these lakes, as well as carrying out additional sampling of an independent subset of seepage lakes in the state. The data reported by Stoddard et al. (2003) included 16 lakes (both drainage and seepage) sampled quarterly (Webster, 1993) and 22 seepage lakes sampled annually in the 1990s. All of the Upper Midwest LTM lakes exhibit mean Gran ANC values from –30 to 80 µeq/L.

Ridge/Blue Ridge streams: Data from the Ridge and Blue Ridge provinces consist of a large number of streams sampled quarterly throughout the 1990s as part of the Virginia Trout Stream Sensitivity Study (Webb, 1989, and a small number of streams sampled more intensively (as in the Northern Appalachian Plateau). A total of 69 streams, all located in the Ridge section of the Ridge and Valley province, or within the Blue Ridge province, and all within the state of Virginia, had sufficient data for the trend analyses by Stoddard et al. (2003). The data are collected cooperatively with the University of Virginia and the National Park Service. Mean Gran ANC values for the Ridge and Blue Ridge data range from –15 to 200 µeq/L, with 7 of the 69 sites exhibiting mean Gran ANC greater than 100 µeq/L.

A.2.3. Forest Inventory and Analysis

The USDA Forest Service's Forest Inventory and Analysis (FIA) program authority is mandated under the Forest and Rangeland Renewable Resources Research Act of 1978 (PL 95–307). Earlier, the program was known as the Forest Survey and has been run continuously since the 1930s. The FIA Program collects, analyzes, and reports information on the status and trends of America's forests: how much forest exists, where it exists, who owns it, and how it is changing, as well as how the trees and other forest vegetation are growing and how much has died or has been removed in recent years. (See http://www.fia.fs.fed.us for more information).

Currently, FIA plots are divided into three phases. Phase 1 establishes approximately three million samples via remote sensing (aerial photographs, digital orthoquads, and satellite imagery). These samples are used to classify land as forest or nonforest. As defined by the U.S. Forest Service, forest land is any land ≥ 1 acre in size that is at least 10% stocked by forest trees of any size. Phase 2 establishes a subset of the Phase 1 plots for ground sampling, approximately one field sample site for every 6,000 acres for a total of about 125,000 plots. The forest characteristics measured include forest type, site attributes, tree

species, tree size, and overall tree condition. Phase 3 plots are the Forest Health Monitoring (FHM) plots, and are a subset of Phase 2 plots. Phase 2 and Phase 3 plots are remeasured every 5 years. Each year, different plots are sampled within defined regions, so that statistical trends for the overall region can be developed on an annual basis.

Phase 2 measurements consist primarily of basic vegetation measurements and general site description. From these measurements information is obtained on tree diameter, tree length, tree quality for use as lumber, tree damage, stocking and seedling and sapling counts.

Approximately one of every 16 Phase 2 plots is measured for forest health attributes in addition to Phase 2 attribute measurements. These plots are known as Phase 3 plots. There is approximately one Phase 3 plot for every 96,000 acres, for a total of roughly 7,800 plots. Measurements for Phase 3 plots include tree crown conditions, lichen community composition, understory vegetation, down woody debris, and soil attributes. O_3 injury to vegetation is also monitored at some Phase 3 plots. Comprehensive reviews of the FIA sampling strategy may be found in Brand et al. (2000) and McRoberts et al. (2004). Goodale et al. (Goodale, 2002) used FIA data to generate estimates of carbon sequestration in forest ecosystems in the U.S. in 1990 and 1991. The home page for the National FIA program can be found at: http://fia.fs.fed.us./

A.2.3.1. Lichens

Lichens are organisms consisting of both fungi and algae. Lichens are very responsive to environmental stressors in forests, including changes in forest structure, air quality, and climate. Many studies have documented the close relationship between lichen communities and air pollution, especially sulfur dioxide (SO_2) and acidifying or fertilizing N- and S-based pollutants. The composition of an epiphytic lichen community is one of the best biological indicators of air pollution in forests, because epiphytic lichens rely totally on atmospheric sources of nutrition.

In several studies (e.g.`, \Muir, 1988), lichens have given much clearer responses to N and S pollutants (in terms of diversity, total abundance, and community composition) than either leaf symptoms or tree growth, and have been one of the few components of terrestrial ecosystems to show a clear relationship to gradients of acidic deposition in the eastern U.S.

Although trees may respond to moderate, chronic levels of air pollution deposition, all of the other influences on tree growth, such as variation in soils, make the responses of trees to pollutants difficult to measure in the field. Epiphytic lichens may be used to assess potential air quality impacts on forest ecosystem health and productivity that are difficult to measure directly. Long-term observation of lichen community change provides early indication of improving or deteriorating air quality. Epiphytic lichens also have important biological roles in many forests, including N fixation, food for animals (deer, caribou,

voles, and flying squirrels), and nesting material for small mammals and birds. Typically, there are 10 to 50 lichen species per FIA plot.

Lichen community information contributes to the investigation of several key forest ecosystem concerns: the contamination of natural resources, biodiversity, and productivity/sustainability. Lichen community data are collected by personnel that receive FIA training on field procedures at the beginning of each field season. They are trained to observe the presence or absence of lichen species, to estimate the abundance of each species, and to collect lichen specimens for identification by a specialist, a lichenologist. Identifications by the lichenologist are part of quality assurance and quality control procedures. Errors are further minimized by audits of the field. The method has two parts that are performed simultaneously. (1) In each standard 0.38 ha FIA plot (see http://www.fia.fs.fed.us/library/field-guides-methods-proc/docs/2006/p3_3_0_sec10_10_2005.pdf for plot design and field methods) the field crew searches for macrolichens on woody plants and collects samples of each lichen believed to be a distinct species. Tree and shrub bases below 0.5 m are excluded from sampling. Lichens on fallen branches and other lichen litter may be included. Given the large plot area, fallen branches typically provide an excellent sample of the canopy lichens. The collection represents the species diversity of macrolichens in the plot as fully as possible, with a maximum time limit of 2 hours. (2) The field crew estimates the abundance of each species using a four-step scale: 1 = rare (<3 individuals in plot); 2 = uncommon (4–10 individuals in plot); 3 = common (>10 individuals in plot but less than half of the boles and branches have that species present); and 4 = abundant (more than half of boles and branches in the plot have the subject species present). As plots are finished, specimens are sent to specialists for identification. Note that the field crew need not accurately assign species names to the lichens, but must be able to distinguish among species, and be able to estimate abundances accurately.

Two procedures are used for constructing plot-level indices: (1) Species richness: A component of diversity, species richness is the total number of epiphytic macrolichen species found in the lichen plot. (2) Community gradients: The dominant gradients across the region are determined using accepted statistical methods. Relationships of these gradients to forest structure, climate and air quality are then analyzed. Scores for air quality and climate are calculated for each plot and are used to answer questions about air quality and forest productivity/sustainability and biodiversity. Data and more information on FIA lichen surveys can be found at: http://fia.fs.fed.us/lichen/.

The lichen community indicator was developed in the Southeast in 1990–93 by Bruce McCune and Jonathan Dey, funded jointly by EPA and the USDA Forest Service (EMAP Program). FHM pilot projects were run in 1994–96 in a variety of eastern states and Colorado, Oregon, Washington and California in the west. The lichen community indicator was included in regular permanent plot surveys starting in 1997 (FHM 1997–1999, FIA after 1999). Regional gradient models have been developed for the southeast (1994), the northeast (1997), and Colorado (1998), and are being developed for the Midatlantic States

(1999–2000) the Pacific Northwest (2001), and California (2003). Lichen communities are now a Phase 3 indicator in the FIA.

A.2.3.2. Soil Quality

Another type of forest health data that the FIA program collects on their Phase 3 plots is the Soil Quality Indicator. The FIA program began consistent sampling related to the Soil Quality Indicator in 2001. The Soil Quality Indicator collects information through field measurements on FIA sample plots and laboratory analyses. Soil condition indicators such as erosion, compaction, and soil chemistry are monitored over time and used to demonstrate trends. Details of the Soil Quality Indicator measurements of FIA can be found here: http://nrs.fs.fed.us/ fia/topics/soils/.

FIA field personnel collect soil data during the Phase 3 field season, which begins in early June and ends in September. Soil samples are sent to the laboratory immediately after collection where they are stabilized by air drying. Laboratory analyses are conducted throughout the fall and winter following the field season. On-plot measurements include soil compaction and bare soil observations. Soil compaction, the percentage of the soil surface exhibiting evidence of soil compaction as well as the type of compaction, is measured by ocular estimation. The relative amount of bare soil is also estimated. Field measurements related to erosion and compaction estimates are made on all four subplots on the Phase 3 field plot. Soil samples are collected on FIA sample plots along soil sampling lines adjacent to subplots 2, 3, and 4. Soils are collected if the soil sampling location is in a forested condition. A total of five samples are collected on each plot (three forest floor, two mineral soil). The entire forest floor layer is sampled from a known area after measuring the thickness of the litter and duff layers at the north, south, east, and west edges of a 12–inch diameter sampling frame. Only organic material that is < one-fourth-inch diameter is collected; rocks and larger woody materials are discarded prior to collection.

Once the forest floor has been removed, mineral and organic soils are sampled volumetrically by collecting cores from two depths: 0 to 4 inches and 4 to 8 inches. The texture of each layer is estimated in the field and characterized as organic, loamy, clayey, sandy, or coarse sandy. Following soil sampling, the depth to any restrictive horizon within the top 20 inches is estimated using a soil probe. Soil samples are mailed to the regional laboratory for physical and chemical analysis.

In the lab, mineral soil samples collected from FIA plots are analyzed for a suite of physical and chemical properties including:

- Bulk density, water content, and coarse fragment (> 2–mm) content
- pH (water and 0.01 M $CaCl_2$)
- Total carbon
- Total inorganic carbon (carbonates) (pH > 7.5 soils only)

- Total N
- Exchangeable cations (Na, K, Mg, Ca, Al, Mn)
- Extractable sulfur and trace metals (Sr, Ba, Mn, Ni, Cu, Zn, Cd, Pb)
- Extractable P (Bray 1 method for pH < 6 soils, Olsen method for pH > 6 soils)

Forest floor and litter samples are analyzed for:

- Bulk density and water content
- Total carbon
- Total N

Soil chemical and physical properties can be highly variable in the field and are expensive to analyze. As a result, interpretation of soil chemical data is confounded by spatial variability within the plot. In addition, depending upon the soil type, both the number of samples and the methods used in collecting these samples may vary between plots, complicating compilation and estimation procedures. Finally, soil samples reflect conditions only in the forest floor and upper 20 cm of the soil. In many systems, the upper portion of the soil profile is likely to be more responsive to disturbance, providing a useful index for monitoring changes in soil properties over time.

A.2.4. USGS Monitoring Programs

A.2.4.1. National Water Quality Assessment Program

The National Water Quality Assessment (NAWQA) Program was created in 1991 by the USGS to assess the nation's water quality in 51 study units defined primarily by major drainage divides. These units comprise approximately 50% of the conterminous U.S. Its major of the program are to determine (1) the condition of the nation's streams, rivers, and ground water, (2) whether these conditions are changing over time, and (3) how these conditions are affected by natural features and human activities.

The major priority of the NAWQA Program since its inception has been on watersheds that have experienced impacts from agriculture and various forms of development. The location of sites, sampling frequency, and types of measurements taken, all reflect this priority. Each study unit runs on a 9–year cycle, with approximately one-third of the study units beginning the cycle every 3 years. Each 9–year cycle is comprised of 3 years of intensive data collection and 6 years of low-level assessment. Three types of sampling sites are established within each study unit: integrator sites, indicator sites, and synoptic sites. Integrator sites are located on major rivers at points that drain much or the entire study unit. Indicator sites drain large fractions of the study unit that are representative of a particular landscape or land use type. Some indicator sites are also located to evaluate point sources of water pollution, and some are located downstream of undisturbed drainages to provide reference, or background conditions. Reference

indicator sites are generally located too low in the drainage basin for assessment of surface water acidification. Sites associated with synoptic studies are chosen for the purpose of improving spatial resolution of data collection within the study unit. The strategies for site selection, sampling, and analysis for synoptic sites are issue-specific and keyed to hydrologic conditions, times, and places of specific interest for the targeted water quality issue.

During the 3-year intensive sampling period, integrator and indicator sites are sampled multiple times, both periodically and in association with high flows. The sampling approach for synoptic studies varies depending on the issue of interest, but is usually done within the second or third year of the intensive sampling period. During the six years of the low-level assessment, sampling usually involves base-flow sampling of high priority integrator sites, and possibly some sampling of indicator sites.

Water quality measurements vary among study units, but usually include pathogens, nutrients (including N and S), trace elements, pesticides, industrial organics, suspended sediment, salinity, temperature, acidity, and dissolved O_2.

NAWQA studies have resulted in over 1000 reports on an extensive list of water quality issues, including freshwater and marine eutrophication associated with N pollution. None deal with acidification, however. Program details and access to publications can be obtained at http://water.usgs.gov/nawqa/.

A.2.4.2. Hydrologic Benchmark Network

The Hydrologic Benchmark Network (HBN) was started in 1963 by the USGS and gradually grew to include 57 river gauging stations and 1 lake-stage station in 39 states by 1990. Most of the stations have been established at the outlet of watersheds that were virtually free of human activities, located in places such as in national parks and forests, wilderness areas, or nature preserves. Streamflow was initially monitored continuously at each station, and samples were collected every month for water-quality analyses that included concentrations of nutrients and all major ions. The frequency of water sampling at HBN stations was decreased to quarterly in 1986 because of budgetary restrictions. Sampling was discontinued in October 1997, except for a small study in the eastern U.S. that focused on the initial response of rivers to decreases in industrial emissions mandated by the Clean Air Act Amendments of 1990 (http://www.epa.gov/oar/oaq_caa.html/).

All HBN watersheds were evaluated in 2002 to determine whether upstream development had made them unsuitable as reference watersheds. The 36 sites that best met the network criteria were selected for continued streamflow monitoring, and water sampling was reinitiated at 15 of those 36 sites. In 2003, 15 of the original HBN stations were equipped with refrigerated, automated samplers and telemetry systems that allow program coordinators to monitor stream conditions and adjust sampling frequency and capture unique stream conditions or special sampling needs. The automated sampling system is designed to collect samples through a wide range of flow conditions and to transmit data by

satellite. About 25 water samples are collected annually at each HBN water quality station and refrigerated on site until retrieved by field personnel who visit the sites regularly. The most recent trends analysis was done by Clow and Mast (1999) to evaluate long-term trends in stream chemistry with respect to the Clean Air Act. The program is further described in a fact sheet that can be found at: http://ny.water.usgs.gov/pubs/fs/fs20053135/.

A.2.4.3. New York City Water Quality Network

The New York District of the U.S. Geological Survey operates a water quality network throughout the water supply watershed for New York City, in the Catskill Mountains region. The purpose of the network is to provide stream flow and water quality data at key locations within the watershed. There are currently 34 sites throughout the network at which stream flow data are collected, and at thirteen of those sites stream water quality data are also collected. The water quality network is composed of paired "nodes" consisting of one or more "upper nodes" that provide water quality of undeveloped, forested watersheds, and "lower nodes" that provide downstream water quality data that may reflect some level of development within the watershed.

Water quality sampling for this program began at the 13 sites in 1998–99. Water samples are collected biweekly and during high flow for approximately 6 storms per year. All water samples are analyzed for concentrations of nutrients and major ions. Because streams in this area are also affected by acidic deposition, acid-neutralizing capacity and 3 forms of Al are also measured. Further details on the program are available at: http://ny.cf.er.usgs.gov/ nyc/unoono.cfm.

A.2.4.4. Catskill Long-Term Monitoring Sites

Within the Catskill Mountains region of New York State, stream samples are collected and stream flow is measured at three locations within the Neversink River basin, and at one site on Rondout Creek. Water samples are collected biweekly and during most storms. These sites are currently part of the EPA LTM program, but also are affiliated with other programs. Sampling at two of the four sites began in the mid 1980s, whereas sampling at the remaining two sites began in 1991. The primary purpose of these sites is to monitor effects of acidic deposition on stream chemistry. The full suite of analytes needed to assess acidic deposition effects are measured on these water samples.

A.2.4.5. Buck Creek, New York

Stream flow and water chemistry are monitored at three locations within Buck Creek watershed, in the western Adirondack Region of New York. Samples are collected biweekly and during most storms at each location. Sampling began in 1998 at two sites and 2001 at the third site. The full suite of analytes

needed to assess acidic deposition effects is measured on these water samples. Measurements of ANC and pH were also collected at one site weekly for the period of 1991 to 2001 (Lawrence, 2004). Recent data from Buck Creek are presented in Lawrence et al. (2007). Buck Creek is the only stream within the acidified region of the Adirondacks where base flow and storm samples are collected in conjunction with flow monitoring.

A.2.5. NSF Long-Term Ecological Research Network

The Long-Term Ecological Research (LTER) program constitutes a loose network of 26 sites (Table A-1), funded by the National Science Foundation (NSF). There is increasing concern over such globally significant problems as loss of biodiversity, climate change, destruction of forests, depletion of stratospheric ozone, regional air and water pollution, and soil erosion. The research conducted at the various LTER sites has examined and continues to examine aspects of these problems and provides scientific information which has been invaluable in the formation of public policy. Site locations and research activities are summarized in (Table A-1). A few of the sites that have been used most extensively for evaluation of long-term effects of N and sulfur deposition are discussed in greater detail below.

Table A-1. LTER site locations and basic site description information.

Site	Landsat WRS	Institutional Affiliations	Principal Biome/ Main Communities	Research Topics
H.J. Andrews Experimental Forest (AND) 44.2, −122.2	Path 46 Row 29; Lat/Long: 44°14'N/ 122°11'W	Oregon State University; USDA Forest Service Pacific Northwest Research Station	Temperate coniferous forest. Douglas-fir/western hemlock/ western red cedar; true fir and mountain hemlock; streams	Successional changes in ecosystems; forest-stream interactions; population dynamics of forest stands; patterns and rates of decomposition; disturbance regimes in forest landscapes
Arctic Tundra (ARC) 68.6, −149.6	Path 73, Row 12; Lat/Long: 68°38'N/ 149°34'W	The Ecosystem Center, Marine Biological Laboratory; Universities of Alaska, Massachusetts, Minnesota, Cincinnati, and Kansas; Clarkson University	Arctic tundra, lakes, streams. Tussock tundra; heath tundra; riverine willows; oligotrophic lakes; headwater streams	Research topics: Movement of nutrients from land to stream to lake; changes due to anthropogenic influences; controls of ecological processes by nutrients and by predation
Baltimore Ecosystem Study (BES) 39.1, −76.3	Path 15, Row 33; Lat/Long 38°54" 04' (N), 76°52" 04' (W)	Institute of Ecosystem Studies; USDA Forest Service, Johns Hopkins University; University of Maryland; Baltimore County and College Park; University of North Carolina; Parks and People Foundation; US Geological Survey; Yale University	Eastern deciduous forest/ Suburban Agriculture fringe, urban parks, residential and commercial patches, riparian and stream habitats	Patch dynamics of built, social, biological, and hydrological components of the metropolitan area; feedback's between social, economic, and ecological components of an urban ecosystem; effect of infrastructure and development on fluxes of nutrients, energy, and water in upland, stream, and coastal regions of metropolitan Baltimore
Bonanza Creek Experimental Forest (BNZ) 64.8, −148.0	Path 69, Row 15; Lat/Long: 64°45'N/ 148°00'W	University of Alaska; Institute of Northern Forestry, USDA Forest Service, Pacific Northwest Research Station	Taiga. Areas of boreal forest including permafrost-free uplands and permafrost-dominated north slopes and lowlands; floodplain seres	Successional processes associated with wildfire and floodplains; facilitative and competitive interactions among plant species throughout succession; plant-mediated changes in resource and energy availability for decomposers; herbivorous control of plant species composition; hydrologic regime and stream ecology

Site	Landsat WRS	Institutional Affiliations	Principal Biome/ Main Communities	Research Topics
Cedar Creek Natural History Area (CDR) 45.4, −93.2	Path 27, Row 28; Lat/Long: 45°24'N/ 93°12'W	University of Minnesota	Eastern deciduous forest and tallgrass prairie. Old fields; oak savanna and forest, conifer bog; lakes; pine forest; wetland marsh and carr	Successional dynamics; primary productivity and disturbance patterns; nutrient budgets and cycles; climatic variation and the wetland/upland boundary; plant-herbivore dynamics
Central Arizona - Phoenix (CAP) 33.5, −11.2	Path 36, Row 37 and Path 36, Row 36° These have been used by CAP although Path 37, Row 37 is centered more closely in the City of Phoenix	Arizona State University (Main and West)	Sonoran Desert scrub. Urban parks, residential, interior remnant desert patches, commercial and industrial patches, urban fringe, regulated river and floodplain (dry), effluent-dominated river	Interactions of ecological and socio-economic systems in an urban environment; influence of land use change on ecological patterns and processes; movement of nutrients through highly manipulated, urban flowpaths; interactions of introduced and native species in urban environment; millennium- and century-scale geomorphic change in landforms and interaction with engineered landscapes
Coweeta Hydrologic Laboratory (CWT) 35.0, −83.5	Path 18, Row 36; Lat/Long: 35°00'N/ 83°30'W	University of Georgia; USDA Forest Service, Southeastern Forest Experiment Station	Eastern deciduous forest. Hardwood forests and white pine plantations	Long-term dynamics of forest ecosystems including forest disturbance and stress along an environmental gradient; stream ecosystems along an environmental gradient; and the riparian zone as a regulator of terrestrial-aquatic linkages
Harvard Forest (HFR) 42.5, −72.2	Path 13, Row 30; Lat/Long: 42°32'N/ 72°10'W	Harvard University; Universities of New Hampshire and Massachusetts; The Ecosystem Center, Marine Biological Laboratory	Eastern deciduous forest. Hardwood-white-pine-hemlock forest; spruce swamp forest; conifer plantations	Long-term climate change, disturbance history and vegetation dynamics; comparison of community, population, and plant architectural responses to human and natural disturbance; forest-atmosphere trace gas fluxes; organic matter accumulation, decomposition and mineralization; element cycling, fine root dynamics and forest microbiology
Hubbard Brook Experimental Forest (HBR) 43.9, −71.8	Path 13, Row 29; Lat/Long: 43°56'N/ 71°45'W	Yale, Cornell, and Syracuse Universities; Institute of Ecosystem Studies; USDA Forest Service, Northeastern Forest Experiment Station	Eastern deciduous forest. Northern hardwood forests in various developmental stages, spruce-fir forests; streams and lakes	Vegetation structure and production; dynamics of detritus in terrestrial and aquatic ecosystems; atmosphere-terrestrial-aquatic ecosystem linkages; heterotroph population dynamics; effects of human activities on ecosystems
Jornada Experimen-tal Range (JRN) 32.5, −106.8	Path 33, Row 37; Lat/Long: 32°30'N/ 106°45'W	New Mexico State University; USDA ARS Jornada Experimental Range; Duke University; NOAA, RTP, NC; University of New Mexico; Dartmouth College, NH; Oregon Gradu-ate Center; Texas Technological University; SUNY Buffalo; University of Keele, UK; Kings College, London, UK; EPA-EMAP, Las Vegas, NV	Hot desert. Playa, piedmont, and swale; bajada, basin, mountain and swale shrubland; mesquite dunes	Desertification; factors affecting primary production; animal-induced soil disturbances; direct and indirect consumer effects; vertebrate and invertebrate population dynamics; grazing effects on ecosystem structure and function; biodiversity and ecosystem function; small mammal effects on soil and vegetation heterogeneity; soil microbial processes; surface hydrology; trace gas emissions from soils; eolian processes
W.K. Kellogg Biological Station (KBS) 42.4, −5.4	Path 21, Row 31; Lat/Long: 85°24'W/ 42°24'N	Michigan State University, Michigan Agricultural Experiment Station	Row-crop agriculture. Conventional and organic-based corn-soybean-wheat cultivation; perennial biomass cultivation; native successional communities	Ecological interactions underlying the productivity and environmental impact of production-level cropping systems; patterns, causes, and consequences of microbial, plant, and insect diversity in agricultural landscapes; gene transfer, community dynamics, biogeochemical fluxes
Konza Prairie Research Natural Area(KNZ) 39.1, −94.6	Path 28, Row 33; Lat/Long: 39°05'N/ 96°35'W	Kansas State University	Tallgrass prairie. Tallgrass prairie; gallery forest; prairie stream	Effects of fire, grazing and climatic variability on ecological patterns and processes in tallgrass prairie ecosystems, use of remotely sensed data and geographic information systems to evaluate grassland structure and dynamics

Site	Landsat WRS	Institutional Affiliations	Principal Biome/ Main Communities	Research Topics
Luquillo Experimental Forest (LUQ) 18.3, −65.8	Path 4, Row 47 and 48; Lat/Long: 18°18'N/ 65°47'W	Center for Energy and Environment Research, University of Puerto Rico; Institute of Tropical Forestry, USDA Forest Service, Southern Experiment Station	Tropical rainforest. Tabonuco forest; palo Colorado forest; palm brake; dwarf forest and montane streams	Patterns of and ecosystem response to different patterns of disturbance; land-stream interactions; effect of management on ecosystem properties; integration of ecosystem models and geographic information systems
McMurdo Dry Valleys - Antarctica (MCM) −78.0, +165.0	Path 56, Row 116	Desert Research Institute, Reno, Nevada; U.S. Geological Survey, Boulder, Colorado	Polar desert oases	Microbial ecosystem dynamics in arid soils, ephemeral streams, and closed basin lakes; resource and environmental controls on terrestrial, stream and lake ecosystems; material transport between aquatic and terrestrial ecosystems; ecosystem response to greater hydrologic flux driven by warming climate
Niwot Ridge/ Green Lakes Valley (NWT) 40.1, −105.6	Path 34, Row 32; Lat/Long: 40°03'N/ 105°37'W	Institute of Arctic and Alpine Research, University of Colorado	Alpine tundra; Fellfield; meadow; herbaceous and shrub tundras; cliffs and talus; glacial lakes; streams and wetlands	Patterns and controls of nutrient cycling; trace gas dynamics, plant primary productivity and species composition; geomorphology, and paleoecology
North Temperate Lakes (NTL) 46.0, −89.7 and 43.1, 89.4	Path 25, Row 28 and Path 24, Row 30 Lat/Long: 46°00'N/ 89°40'W and 89°24/ 43°06	Center for Limnology, University of Wisconsin-Madison, Wisconsin	Northern temperate lakes in glacial landscapes in urban, agricultural and forested watersheds. Oligotrophic, dystrophic and eutrophic lakes; temporary forest ponds; warm and cold streams; sphagnum-leatherleaf bog; conifer swamp; mixed deciduous and coniferous forests	Physical, chemical and biological limnology; hydrology and geochemistry; climate forcing; producer and consumer ecology; ecology of invasions; ecosystem variability; lakescape and landscape ecology
Palmer Station (PAL) Antarctica −64.7, −64.0	Path 219 , Row 105; Lat/Long: 64°40'S/ 64°W	University of California, Santa Barbara; Old Dominion University	Polar marine. Coastal and open ocean pelagic communities; seabird nesting areas	Oceanic-ice circulation and models; sea-ice dynamics; biological/physical interactions; effect of sea ice on primary production, consumer populations and apex predators; bio-optical models of primary production; spatial distribution and recruitment in consumer populations; seabird population dynamics and reproductive ecology
Plum Island Sound (PIE) 42.67, −70.99	Path 12, Row 30; Lat/ Long: 42°40'/ 70°59' Site has the following X and Y bounds in decimal coordinates: X min = −71.22 X max = −70.75. Y min = 42.50 Y max = 42.83. The total area is approximately 37 km x 37 km or 1369 km^2	The Ecosystems Center, Marine Biological Laboratory; Universities of South Carolina and New Hampshire; Massachusetts Audubon; Wells, Maine, NERRS	Coastal estuary	Linkages between land and coastal waters involving organic carbon and organic N inputs to estuarine ecosystems from watersheds with various land covers and uses
Sevilleta National Wildlife Refuge (SEV) 34.3, −106.8	Path 33, Row 36; To acquire entire site area, Path 32, Row 36, Path 32, Row 37 and Path 33, Row 37 are also needed. Lat/ Long: 34°19'/ 106°62'W	University of New Mexico; U.S. Fish and Wildlife Service	Multiple: intersection of subalpine mixed-conifer forest/meadow, riparian cottonwood forest, dry mountainland, grassland, cold desert, hot desert. Conifer savanna; creosote bush; desert grassland; mesquite and sand dunes; Great Basin shrub and shortgrass steppes; tallgrass swales; riparian communities	Landscape and organism population dynamics in a biome tension zone; semiarid watershed ecology; climate change; biospheric/atmospheric interactions; paleobotany/ archaeology; microbial role in gas flux; and control of landscape heterogeneity; scale effects on spatial and temporal variability
Shortgrass Steppe (SGS) 40.8, −104.8	Path 33, Row 32; Lat/Long: 40°49'N/ 104°46'W	Colorado State University; USDA Forest Service; USDA Agricultural Research Service	Floodplain; shrubland; saltmeadow	Soil water; above- and belowground net primary production; plant population and community dynamics; effects of livestock grazing; soil organic matter accumulation and losses, soil nutrient dynamics; and ecosystem recovery from cultivation

Site	Landsat WRS	Institutional Affiliations	Principal Biome/ Main Communities	Research Topics
Virginia Coast Reserve (VCR) 37.5, −74.8	Path 14, Row 34; Lat/Long: 37°30'N 75°40'W	University of Virginia	Coastal barrier islands. Sandy intertidal; open beach; shrubthicket; mature pine forest; salt marsh; estuary	Holocene barrier island geology; salt marsh ecology, geology, and hydrology; ecology/ evolution of insular vertebrates; primary/ secondary succession; life-form modeling of succession

A.2.5.1. Hubbard Brook Experimental Forest

The Hubbard Brook Ecosystem Study (HBES) at Hubbard Brook Experimental Forest (HBEF) is the longest-running precipitation and stream chemistry (1963 to present) monitoring program in the U.S. (see http://www.hubbardbrook.org). HBEF was established in 1955 as a major center for hydrologic research in New England. The site is located within the boundaries of the White Mountain National Forest in central New Hampshire. The 3138–ha, bowl-shaped valley has hilly terrain, ranging from 222 to 1015 m elevation. The HBES originated in 1960 with the intention of applying the small watershed approach to the study of element fluxes and cycles. The goal of the study is to develop a better understanding of ecological patterns and processes that characterize the northern forest in eastern North America, and its response to both natural and human disturbances. In 1987, HBEF joined the NSF's LTER network (http://www.lternet.edu). Hubbard Brook is renowned for its long-term record of measurements, landscape-scale experiments of whole watersheds, and the involvement of scientists from diverse disciplines and institutions.

The HBEF is entirely forested, mainly with deciduous northern hardwoods: sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), and yellow birch (*Betula allegheniensis*), and some white ash (*Fraxinus americana*) on the lower and middle slopes. Other less abundant species include mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), and trembling aspen (*Populus tremuloides*). Red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), and white birch (*Betula papyrifera* var. *cordifolia*) are abundant at higher elevations and on rock outcrops. Hemlock (*Tsuga canadensis*) is found along the main Hubbard Brook. Pin cherry (*Prunus pensylvanica*), a shade intolerant species, dominates all sites for the first decade following a major forest disturbance. Logging operations ending around 1915–1917 removed large portions of the conifers and better quality, accessible hardwoods. The present second-growth forest is even-aged and composed of about 80 to 90% hardwoods and 10 to 20% conifers.

The HBEF is an oblong basin about 8 km long by 5 km wide. Hubbard Brook is the single major stream draining the basin. Numerous smaller tributary streams of varying size drain into Hubbard Brook including Watershed 6 (WS-6), which is the biogeochemical reference watershed.

One of the strengths of the HBES is the long-term monitoring program. Section A.3.3.1 lists the major parameters included in the HBES long-term monitoring study. The monitoring data illustrate that short-term observations can be misleading and that decades of monitoring may be required to detect real

changes in complex ecosystems. The long-term record at the HBEF provides: (1) insight into ecosystem function; 2) empirical data for testing models and generating hypotheses; 3) a record of extreme or unusual events; and (4) information that is relevant to regional national and global environmental issues.

Some of the monitoring is done on experimentally manipulated watersheds. There are nine gaged watersheds at the HBEF, four of which have been treated experimentally. A tenth ungauged watershed was also treated. Table A-2 includes summary data on the various watersheds. Datasets for long-term monitoring can be found at http://www.hubbardbrook.org/ data/dataset_search.php. The datasets most often used to examine ecosystem response to ambient deposition of N and S are from WS-6 and Mirror Lake, since they have not been experimentally manipulated. Watershed 6 is the biogeochemical reference catchment at HBEF where monitoring began in June 1963. Measured stream chemistry parameters include major anions and cations, pH, silica, dissolved organic and inorganic carbon, specific conductance, dissolved O_2, ANC, and PO_4. Stream chemistry data can be accessed at http://www.hubbardbrook.org/ data/dataset.php?id=8. The normal sampling interval for WS-6 is weekly, with more frequent samples taken at times of increased discharge.

Table A-2. Study watersheds at HBEF

WS	Area (ha)	Slope (°)	Aspect	Elevation (m)	Gauge Type	Initial Yr.
1	11.8	18.6	S22°E	488–747	V-notch weir	1956
2	15.6	18.5	S31°E	503–716	V-notch weir	1957
3	42.4	12.1	S23°W	527–732	V-notch wir	1957
4	36.1	15.6	S40°E	442–747	V-notch weir	1960
5	21.9	15.4	S24°E	488–762	V-notch weir, San Dimas flume	1962
6	13.2	15.8	S32°E	549–792	V-notch weir, San Dimas flume	1963
7	77.4	12.4	N16°W	619–899	V-notch weir, San Dimas flume	1965
8	59.4	14.0	N12°W	610–905	V-notch weir, San Dimas flume	1968
9	68.4		NE	685–910	V-notch weir	1995
10	12.1		SE	470–595	None	1970

Monitoring of streamflow and water chemistry has shown that the study watersheds have similar characteristics. Within each watershed there are a variety of soils, vegetation, microtopographical features, and micro-climate. Nevertheless, the composition of these variables seems to be similar from watershed-to-watershed. Thus, the effects of experimental manipulations of watersheds can be adequately evaluated by comparison with neighboring unmanipulated watersheds.

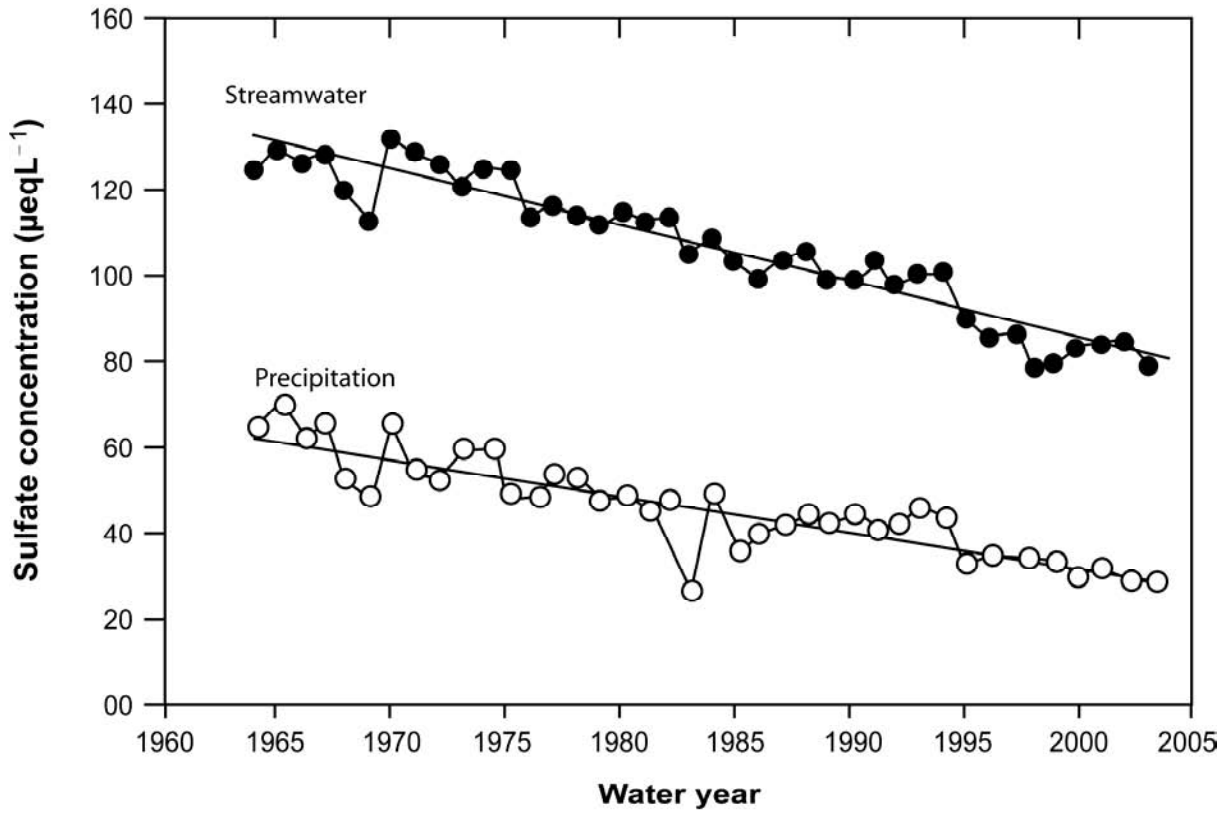
The most conspicuous streamflow characteristic is the seasonal shift from large volume of flow in spring to very low flow in late summer and early autumn. These yearly highs and lows reflect seasonal

spring snowmelt that often occurs over a few days or weeks and the slow progressive decrease in flow from the transpirational draft in summer, respectively. The numerous streams in the HBEF range from small ephemeral channels that often dry up during summer to a large perennial 5th-order stream (Hubbard Brook).

Mirror Lake is a 15–ha oligotrophic clearwater lake adjacent to HBEF. The lake normally mixes in spring and fall, and is ice-covered from about December 1st to April 15th each year. Part of the drainage to the lake originates in the Experimental Forest. The lake water is dilute, slightly acidic, and quite clear, with low productivity and low concentrations of nutrients in the water. Numerous studies have been conducted on Mirror Lake since the mid-1960s, including extensive physical, chemical, biological, and paleoecological research (cf. Likens, 1985). Data are available since 1967 for lakewater concentrations at discrete depths for base cations, pH, and dissolved O_2. Ammonium, major anions, phosphate, and dissolved silica have been measured routinely since 1970, although some data are available prior to these dates for each solute. Other standard monitoring data include temperature and specific conductance at each depth. Prior to 1990, not all records had complete solute arrays. Since 1990, DIC and ANC have also been measured on a routine basis, although some prior data do exist for those parameters. The usual sampling interval for Mirror Lake is four to six times each year, especially at times of maximum and minimum thermal stratification. Data for Mirror Lake and inlet and outlet streams can be found at: http://www.hubbardbrook.org/data/ dataset_search.php.

The soils, vegetation, and climate at the HBEF are characteristic of the northern hardwood forest complex, which spans much of the north-central and northeastern U.S. and southeastern Canada. Streamflow and stream chemistry reflect the landscape characteristics of the drainage area. Consequently, results from the relatively small watersheds at the HBEF are to a first approximation representative of a much larger regional area. During the scientific debate that occurred prior to passage of the Clean Air Act Amendments of 1990, the trends in sulfate (SO_4^{2-}) concentrations in streamwater and precipitation at HBEF were very influential in convincing scientists and policy makers that decreasing S emissions would yield large decreases in the concentration of SO_4^{2-} in precipitation and streamwater in the northeastern U.S. (Lovett, 2007). Monitoring data collected since 1963 (Figure A-3) played a major role in development of the watershed-ecosystem concept and methods for analyzing and understanding watershed biogeochemical cycles (Bormann, 1967; Likens, 1978; Likens, 1995; Lovett, 2007).

An extensive effort has been made to bring together some of the results of research that had been done at Hubbard Brook over the last several decades. Over the duration of the HBES there have been six books and more than 1,000 papers published. In addition, more than 500 abstracts were published and more than 100 graduate theses completed. A complete list of titles is available at http://www.hubbardbrook.org/pubs/pub_search.php. To date, four synthesis volumes have been completed (Likens, 1977; Bormann, 1979; Likens, 1985; Likens, 1992).



Source: Lovett et al. (2007) ; updated from Likens et al. (2002).

Figure A-3. Long-term record of SO_4^{2-} concentration in streamwater and precipitation at Watershed 6 of HBEF.

A.2.5.2. Coweeta

The Coweeta LTER research program (http://coweeta.ecology.uga.edu/) in North Carolina is based in the eastern deciduous forest of the Blue Ridge Physiographic Province of the southern Appalachian Mountains. The program entails long-term cooperation between the University of Georgia and the U.S. Department of Agriculture (USDA) Forest Service Coweeta Hydrologic Laboratory. The research program centers on the effects of disturbance and environmental gradients on biogeochemical cycling, and the underlying watershed ecosystem processes that regulate and respond to those cycles. Coweeta represents one of the longest continuous environmental studies of any North American landscape.

The research at Coweeta focuses largely on how water, soil, and forest resources respond to management practices, natural disturbances, and the atmospheric environment. It also aims to identify practices that mitigate impacts on these watershed resources. Current topics of emphasis include (1) analyses of long-term changes in hydrology, nutrient cycling, and productivity in response to management practices and natural disturbances; 2) assessment of prescribed burning effects on the forest environment; 3) interdisciplinary implementation of ecosystem management on the national forests; 4) effects of

climatic change on productivity; 5) impacts of atmospheric deposition on forest processes and ecosystems; 6) cumulative effects of land use practices on water quality; 7) physiological studies of forest carbon balance and competition; and (8) biodiversity.

Investigators at the Coweeta Hydrologic Laboratory have recorded N dynamics of streams and precipitation in mature mixed hardwood-covered watersheds since 1972. Research has been conducted on responses to management practices such as clearcutting, selective cutting, conversion of native hardwood to coniferous forest, and old-field succession. Reference watersheds were characterized as in a transition phase between stage 0 and stage 1 of watershed N saturation. Evidence for stage 3 of N saturation, where the watershed is a net source of N rather than a N sink, was found for the most disturbed watershed at Coweeta.

The Coweeta Basin comprises 2185 hectares within the Blue Ridge geologic province in North Carolina. The laboratory has been dedicated to forest hydrology research since its establishment in 1933. Elevations range from 679 to 1592 m. More than 50 km of streams drain the area.

Coweeta is the first major mountain range contacted by air masses moving over the industrialized Piedmont region to the south. Analyses of precipitation chemistry have shown the influence of both local and regional activities on nutrient inputs to forest ecosystems.

Since Coweeta was established, 32 weirs have been installed on streams. Seventeen of these weirs are currently operational. Stream gauging was initiated on most watersheds between 1934 and 1938, and stream chemistry measurements date back to 1968.

Research has been conducted on eight mixed hardwood control areas and 13 catchments where forest management prescriptions have been applied. Past treatments have included varying intensities of cutting, ranging from light selection through clear-cutting; conversion of hardwoods to grass and subsequent succession to hardwoods; multiple-use management; mountain farming; and the application of herbicides and fertilizers.

Research and monitoring data from Coweeta has been extensively analyzed and reported in the scientific literature. Example recent publications include Swank and Vose (1997, Grossman et al. (1998, Schofield et al. (2001, and Scott and Helfman (2001).

Long-term changes in soils have been identified in reference and managed watersheds over two decades (Knoepp, 1994). For example, changes in exchangeable soil cation content varied with aspect: concentrations decreased on a north-facing slope but were stable on a south-facing slope. The demonstrated impacts of forest management practices have varied considerably. Soils in a white pine plantation showed stable C levels, but cations declined.

Commercial sawlog harvest resulted in large increases in soil C and cation concentrations, which remained elevated for 17 years. Whole-tree harvest resulted in decreased soil C for the next 14 years.

Clearly soil response to harvest varies with type of harvest and site. Long-term studies like these have proven useful in guiding ecosystem management projects in the southern Appalachians (Meyer, 1996).

A.2.5.3. Walker Branch

Walker Branch Watershed is located on the U.S. Department of Energy's Oak Ridge Reservation in Tennessee. The 97.5 ha Walker Branch watershed has been the site of long-term, intensive environmental studies since the late-1960s (see http://walkerbranch.ornl.gov/).

The forest soils are acidic, very cherty, infertile, and permeable. They are formed over dolomitic bedrock, but retain little evidence of their carbonate parent material. The forest vegetation is primarily oak-hickory with scattered pine on the ridges and mesophytic hardwoods in the valleys.

Initially, the research and monitoring of Walker Branch centered primarily on the geologic and hydrologic processes that control the amounts and chemistry of water moving through the watershed. Past projects have included:

- watershed hydrology and forest nutrient dynamics,
- forest micrometeorology,
- atmospheric deposition,
- International Biological Program Eastern Deciduous Forest Biome Project,
- trace element cycling and stream nutrient spiraling, and
- effects of acidic deposition on canopy processes and soil chemistry.

These projects have all contributed to a more complete understanding of how forest watersheds function and have provided insights into the solution of energy-related problems associated with air pollution, contaminant transport, and forest nutrient dynamics. Available long-term data at this site include:

- Daily climate data
- Monthly climate data
- Precipitation
- Atmospheric deposition

- Stream discharge and annual runoff
- Stream chemistry
- Vegetation

A.2.6. Water, Energy, and Biogeochemical Budgets Program

The Water, Energy, and Biogeochemical Budgets (WEBB) Program was started in 1991 at five small watersheds in the U.S. to examine water, energy, and biogeochemical fluxes and to determine the effects of atmospheric deposition, climatic variables, and human influences on watershed processes. The five sites are at Loch Vale, Colorado; Luquillo Experimental Forest, Puerto Rico; Panola Mountain, Georgia; Sleepers River, Vermont; and Trout Lake, Wisconsin. These sites are supported, in part, by other programs in the USGS, other Federal and State Agencies, and Universities. Two of these sites, Loch Vale and Sleepers River, have been used extensively to evaluate the effects of atmospheric sulfur and N deposition, and are described here. Each of those sites is also part of the LTER network.

A.2.6.1. Sleepers River

The Sleepers River Research Watershed in northeastern Vermont was established by the Agricultural Research Service (ARS) of the USDA in 1959 and is now operated jointly by the USGSand the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL), with collaboration from several other Federal agencies and universities (see http://nh.water.usgs.gov/ projects/sleepers/index.htm). The USGS uses hydrologic measurements and chemical and isotopic tracing techniques to determine how water moves from the hillslope to the stream, and what processes cause chemical changes, including the neutralization of acid rain. Research results provide insights on how pollutants move through ecosystems, and how ecosystems may respond to climatic change.

The watershed is covered by 1 to 4 m of glacial till, a compacted fine silty material that formed underneath glacial ice as it moved overland. The till was formed primarily from local bedrock, which is a calcareous granulite/quartz-mica phyllite. About 60 to 80 cm of soil has developed in the till. Weathering of calcite in the till and bedrock causes highly buffered streamflow, compared to most streams in New England, and a nutrient-rich biological environment. Sleepers River is, therefore, an end member in regional biogeochemical cycling studies (Hornbeck, 1997).

The Sleepers River area has reverted from a predominately cleared, agricultural landscape to a mostly forested one. A Northern Hardwood forest, dominated by sugar maple, white ash, yellow birch, and beech, with lesser amounts of red spruce and balsam fir, now covers two-thirds of the area; the

remaining open land is primarily pasture and hayfields. Dairy farming and logging are the primary human enterprises in the watershed. The average annual temperature is 6 °C and the average annual precipitation is 1.1 m, 20% to 30% of which falls as snow.

Sleepers River has one of the longest historical hydrologic and climatologic data bases for a cold-region area in the U.S., featuring measurements of precipitation and streamflow since 1959, snow depth and corresponding water content since 1960, soil frost depth since 1984 (Shanley, 1999, and ground-water levels since 1991. These and other measurements constitute a valuable resource for hydrologic modeling and for the evaluation of climatic changes. Sampling site locations are shown in Figure A-4.

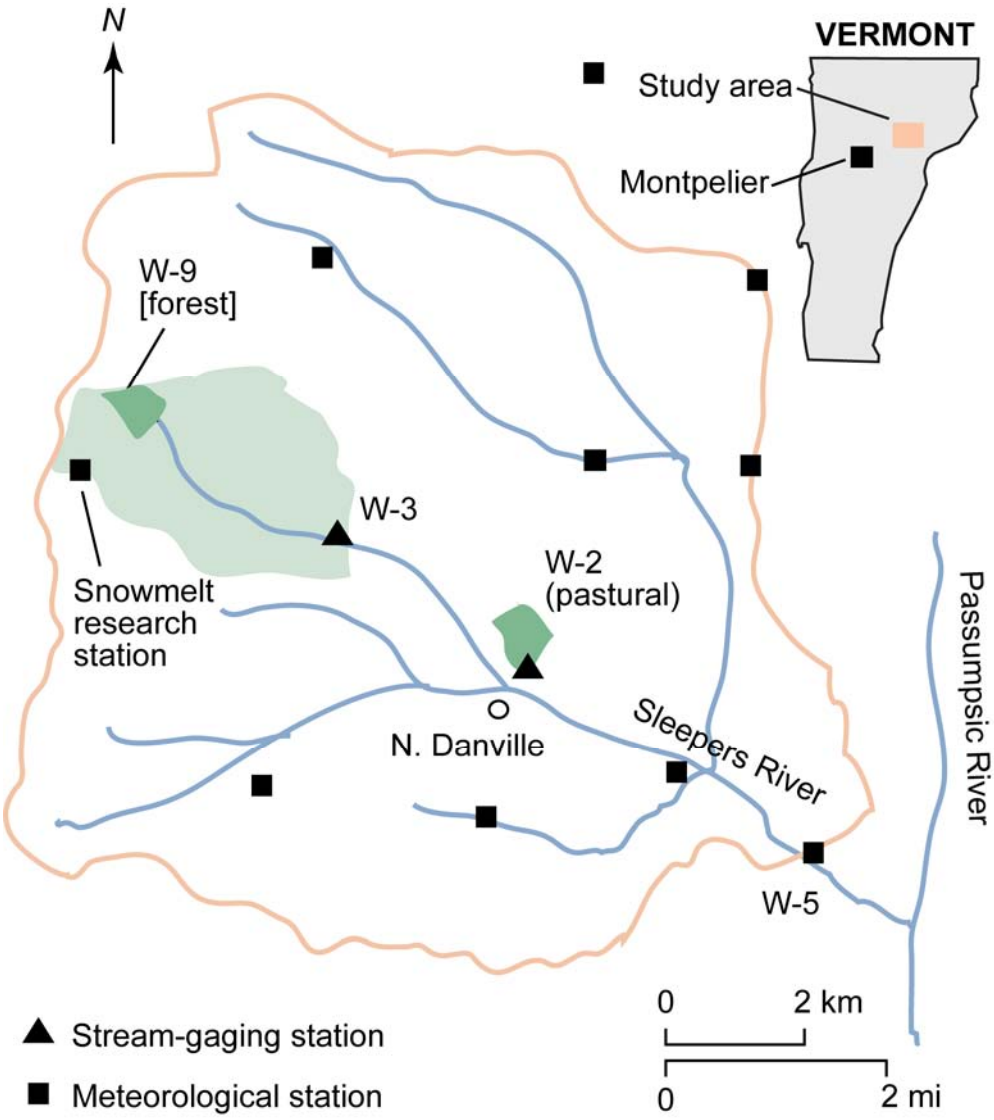


Figure A-4. Location of sampling stations in Sleepers River watershed, Vermont.

Recent research findings include the following:

- Precipitation is acidic, but streamflow is well-buffered from calcite weathering in till and bedrock.
- Infiltrating snowmelt causes ground water to rise into the permeable soil zone, where it moves rapidly downslope.
- Naturally occurring isotopic and chemical tracers indicate that "old" water dominates streamflow, and that water acquires solutes from weathering and biogeochemical processes along both deep and shallow flowpaths.
- Nitrate (NO_3^-) in streamflow is supplied primarily by mineralization and nitrification in the soil, rather than directly by the N content of precipitation.

The fate of NO_3^- in the forest ecosystem is being investigated by analysis of both the N and O isotopes of the NO_3^- ion. The isotopic composition of NO_3^- in streamflow matches that of NO_3^- produced by mineralization and nitrification in the soil, indicating that streamflow NO_3^- is derived from the soil and not from the rain or snowmelt that causes the high flow (Kendall, 1995). This finding suggests that most incoming atmospheric N is incorporated at least temporarily in the soil where it is utilized by the biota.

A.2.6.2. Loch Vale

The Loch Vale Watershed is a 661–ha alpine/subalpine basin located in the south-central Rocky Mountains, about 100 km northwest of Denver, Colorado. The basin is in a roadless area in Rocky Mountain National Park and is accessed by a 5–km hike or ski from the trailhead near Bear Lake. The western boundary of the basin is the Continental Divide; streams drain to the northeast. Basin elevations range from 4192 m (13,153 ft) at Taylor Peak to 3110 m (10,200 ft) at the outlet. There are two main subbasins in Loch Vale: Andrews Creek drains the northern subbasin, and Icy Brook drains the southern subbasin. These two creeks join above The Loch, which is the lowest of three lakes in the basin. Stream gauges are operated on Andrews Creek, Icy Brook, and at The Loch outlet. Water chemistry monitoring occurs at The Loch and on both inlet streams (see http://nh.water.usgs.gov/projects/sleepers/index.htm).

Large glaciers that covered much of Rocky Mountain National Park during the late Pleistocene sculpted the basin into characteristic glacial landforms, including steep U-shaped valleys, cirques, and arêtes. When the glaciers retreated about 12,500 years ago, they deposited till of varying thickness, which is confined mostly to the forested, lower part of the basin. Smaller, more recent glacial advances left younger till, talus, and rock deposits in the upper parts of the basin. The younger glacial and periglacial deposits are largely unvegetated.

Available water chemistry data include major ions, nutrients, DIC, DOC, and, for selected samples, a range of isotopes including $^{2}H/H$, $^{18}O/^{16}O$, $^{15}N/^{14}N$ and $^{18}O/^{16}O$ in nitrate ion, ^{35}S, $^{34}S/^{32}S$, $^{87}Sr/^{86}Sr$, ^{13}C, ^{12}C). Monitoring of precipitation and hydrology include the following elements:

- Precipitation: quantity — 3 sites continuous; chemistry, 1 site, biweekly.
- Stream discharge, 2 sites (Andrews Creek-Loch Vale, Icy Brook-Loch Vale).
- Stream chemistry, (Andrews Creek, Icy Brook-Loch Vale).
- Spring discharge, conductance, and temperature, 3 sites continuous.
- Spring water chemistry, 3 sites biweekly, 20–30 sites once during low-flow season.
- Soil lysimeters, 5 sites, biweekly to monthly during summer and fall.
- Snowpack amount and chemistry (depth, snow-water equivalent) basin-wide survey at maximum accumulation, index sites biweekly to monthly.
- Selected microenvironment runoff, e.g., rock outcrop, talus fields, weekly to monthly.
- Meteorology: 3 sites (wind speed, wind direction, air temperature, incoming and outgoing radiation, relative humidity), continuous.
- Gas flux (CO_2 and CH_4) in wetland, forest, and talus soils, weekly to monthly; CO_2 concentrations in surface waters at 10–15 sites several times annually.
- Snowmelt lysimeter discharge and chemistry, monitored for three years, currently inactive.

Atmospheric deposition of N to Loch Vale is high compared to most other sites in the Rockies, although considerably lower than most impacted sites in eastern North America and Europe. The alpine/subalpine ecosystem at Loch Vale exhibits symptoms of advanced watershed N saturation, indicating sensitivity to N deposition. Talus landscapes contribute substantially to N export in streamflow, and soil microbial processes are important in cycling N, even in areas such as talus that have little soil development. Research at this site indicates that N export is a function of both deposition and internal N-cycling processes that are affected by variability in climate.

A.2.7. Other Monitoring Programs

A.2.7.1. Bear Brook

The Bear Brook Watershed (BBW) is located in eastern Maine (44°52'15" latitude, 68°06'25" longitude), approximately 60 km from the Atlantic coastline. The BBW is a paired watershed study funded by EPA since 1987 as part of The Watershed Manipulation Project (WMP) within the National Acid Precipitation Assessment Program (NAPAP) (see http://hydromodel.com/bbwm.htm; http://www.umaine.edu/DrSoils/bbwm/bbwm.html). As a long-term research watershed, the BBW includes bench-scale, micro-site, plot, and whole watershed investigations. The major purposes of the BBW project are to:

- Identify and quantify the major processes that control surface water acidity, with a major emphasis on (1) the role of excess SO_4^{2-} and nitrate provided via atmospheric deposition and experimental application, and (2) the rate of cation supply from chemical weathering and cation desorption.

- Assess the quantitative and qualitative responses at the watershed level to different (both increased and decreased) levels of acidic deposition.

- Evaluate the ability of existing models of water acidification to predict short- and long-term chemical variations in surface water chemistry and to predict watershed soil responses to increased and decreased loading of strong acids.

The watershed includes two first order streams: East Bear Brook (EBB) and West Bear Brook (WBB). On each stream, a catchment outlet was selected and gauged so that both streams have about the same catchment area (EBB = 10.7 ha and WBB = 10.2 ha). Since streams are close and face the same slope direction, the watersheds are geographically similar and are appropriate for a paired watershed zintervals. Both watersheds have a maximum discharge of about 0.01 mm/ha/sec or 0.15 m^3/s. Annual water yield relative to incoming precipitation for WBB ranges from 68 to 77% and EBB ranges from 62–68%.

Stream channels in each watershed are well defined. Each stream bed is approximately 1 m wide at the weir and water flows over exposed bedrock in places. Elsewhere, the streambeds are comprised of boulders and gravel. Both streams have undergone intermittent dry periods during summer over the course of the study. One V-notch weir was constructed on each of the streams during winter 1987–1988. Mean discharge in each stream is about 0.13 cfs.

Sampling frequency at the weirs was every three weeks during the winter of 1986–1987 and at least weekly thereafter. On the basis of sampling conducted prior to beginning the manipulation experiment (1987–1989), the streams had the following characteristics: ANC, −5 to 90 µeq/L; air-equilibrated pH, 4.7 to 7.2; specific conductance of approximately 26 µS/cm; and DOC of 1 to 4 mg C/l.

Soils in the Bear Brook watersheds are primarily Spodosols. The average depth of the overburden in the watersheds is 0.5 m, with a range of 0 to 5.2 m. Soil pH (0.01M $CaCl_2$) values ranged from 2.9 in the O horizon, to 3.9 in the B horizon, to 4.4 in the C horizon. The bedrock is primarily metamorphosed and folded politic graded beds and quartzites, with granitic dikes. The surficial material is till.

The forest is comprised primarily of deciduous species with areas of conifers. Tree species include American beech (*Fagus grandifolia*), birch (*Betula* sp.), maple (*Acer* sp.), red spruce (*Picea rubens*), balsam fir (*Abies balsamea*), white pine (*Pinus strobus*), and hemlock (*Tsuga canadensis*). Coniferous stands, which occupy approximately 17% of the total watershed area, occur more commonly in the upper, steeper portions of the watersheds.

Although the Bear Brook project was intended as an experimental manipulation of West Bear Brook, there is also great value in the long-term monitoring data collected at East Bear Brook, the non-manipulated reference watershed. This two-decade long monitoring record provides information on the response of an acid-sensitive low-order stream in Maine to changes that have occurred in atmospheric deposition since 1986.

Results of the Bear Brook project have been widely published (Norton, 1994; cf. Kahl, 1993; Norton, 1999; Norton, 1999).

A.2.7.2. Shenandoah Watershed Study

The Shenandoah Watershed Study (SWAS) program is a monitoring and research network focused on low-order, high-gradient streams associated with public lands in western Virginia (see http://swas.evsc.virginia.edu/). The objectives of the program are to increase understanding of factors that govern biogeochemical conditions and stressor-response relationships in forested mountain watersheds of the central Appalachian region. Success in addressing these scientific and problem-oriented objectives has been achieved through development of a data collection network that accounts for spatial gradients, as well as temporal variation, in the chemical composition of the region's relatively undisturbed headwater streams.

The program is notable for the length of the continuous data record that has been obtained, including the longest-running record (28 years) of stream water composition and discharge in the National Park System. The SWAS component of the program, which now includes 14 streams in Shenandoah National Park, was initiated in 1979. The Virginia Trout Stream Sensitivity Study (VTSSS) component,

which now includes 51 streams in National Forests and other conservation lands, was initiated in 1987. The distribution of SWAS-VTSSS study sites in relation to public lands is shown in Figure A-5.

The SWAS-VTSSS program has been maintained as a cooperative effort involving the Department of Environmental Sciences at the University of Virginia, the National Park Service, the EPA, the USDA Forest Service, the U.S. Geological Survey, the Virginia Department of Game and Inland Fisheries, and Trout Unlimited. The monitoring sites account for ecological variation among the region's forested mountain watersheds with a data-collection strategy that represents: (1) spatial variation through the distribution of hydrochemical monitoring within a lithologic classification system; and (2) temporal variation through long-term data collection at fixed locations sampled at different frequencies.

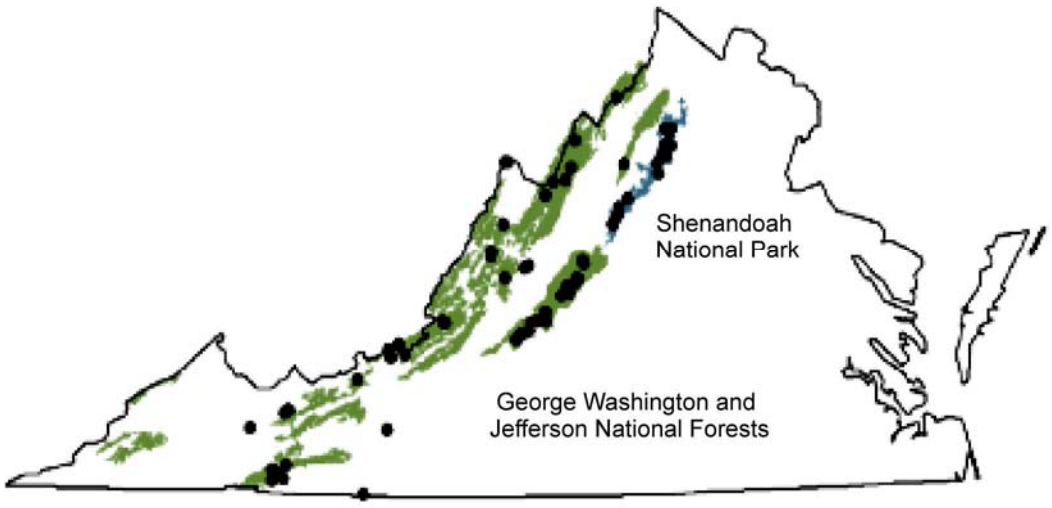


Figure A-5. SWAS-VTSS Program Study Sites. The length of the stream water chemical composition record for SWAS-VTSSS study watersheds is 20 to 28 years. SWAS sites are located in Shenandoah National Park (shaded blue). VTSSS sites are mainly located in Virginia's National Forests (shaded green).

The lithologic classification system includes 6 classes based on the physical and chemical properties of bedrock formations in the region. ANC and concentrations of related acid-base constituents in stream waters, as well as other biotic and abiotic properties of watersheds, differ among the lithologic classes.

The SWAS-VTSSS data collection framework is most-well developed in the Blue Ridge Mountains Province within Shenandoah National Park, where stream water composition data are collected seasonally at 14 sites, weekly at 6 sites, and every four hours during episodic high-flow conditions at 3 sites with continuous discharge gauging. Stream water composition data are collected on a seasonal basis at an

additional 51 sites located outside of the Park, in both the Blue Ridge Mountains and Ridge and Valley Provinces.

Stream water samples collected through the SWAS and VTSSS programs are analyzed for ANC, pH, and the major anions (SO_4^{2-}, nitrate, and chloride) and cations (calcium, magnesium, potassium, and sodium) by methods appropriate for low-ionic strength natural waters. Both the SWAS and VTSSS sample streams were selected based on geographic distribution, representation of the major bedrock types underlying the mountain ridges in the region, and minimization of recent watershed disturbance. All but a few of the sample streams currently support reproducing populations of native brook trout. All of the sample streams supported brook trout populations historically.

Sustained data collection in a network constructed of intensively studied sites nested within a geographically extensive set of less intensively studied sites has allowed detection and interpretation of change that has occurred in a context of multiple time scales and stressors. Responses to multi-year changes in acidic deposition have been reflected in long-term trends in quarterly concentrations of SO_4^{2-}, ANC, and other acid-base constituents of streams in the network. Expectations for southeastern watersheds with soils that retain sulfur, for example, have been confirmed by the lack of regional improvement in stream water quality following reductions in acidic deposition mandated by the Clean Air Act. The acid-base chemistry of streams in the network also varies seasonally and on shorter time scales. Weekly and higher-frequency automated stream water sampling during periods of high runoff have supported the study of episodically more-acidic conditions, including the study of fish sensitivity with in-stream bioassays and development of models to predict severity and recurrence intervals.

By accounting for significant spatial gradients and temporal patterns in the region, the SWAS-VTSSS hydrochemical data collection program provides a basis for both observing and interpreting watershed-scale change, as well as an informed foundation for process-oriented research. Monitoring data and research findings obtained through the SWAS-VTSSS program have contributed to increased scientific understanding, as well as to policy formulation and implementation.

The mathematical model, Model of Acidification of Groundwater in Catchments (MAGIC), was first calibrated using data obtained for White Oak Run, a SWAS-VTSSS study stream in Shenandoah National Park. MAGIC is the most widely used acid-base chemistry model in the U.S. and Europe and the principal model used by the National Acid Precipitation Assessment Program in the 1980s to estimate future damage to lakes and streams in the eastern U.S. The MAGIC model has since been applied in a number of regional assessments that relied extensively on stream water and soils data obtained through the SWAS-VTSSS program. Among these are:

- The Southern Appalachian Mountain Initiative, a multi-state effort to evaluate alternative approaches to solving regional air-pollution problems. MAGIC projections indicated that even ambitious emission control strategies would not result in near-term recovery of the region's most acidified surface waters – a consequence of base-cation depletion in soils exposed to decades of acidic deposition.

- The Shenandoah Assessment, an assessment of acidification effects on aquatic systems in Shenandoah National Park. MAGIC reconstructions indicated that Park streams associated with base-poor bedrock lost about 70 µeq/L between 1900 and 1990. MAGIC projections indicated that some streams may recover given prospective reductions in acidic deposition, but others will not.

Data and findings provided through the SWAS-VTSSS program have also proven relevant to the evaluation and implementation of national air pollution control policies. The SWAS-VTSSS program provides data for the EPA's long-term monitoring of surface water response to legislated reductions in sulfur emissions. Whereas SO_4^{2-} concentrations in surface water declined during the 1990–2000 period for four northeastern regions with sensitive surface waters, the SWAS-VTSSS study region, in contrast, experienced increasing stream-water SO_4^{2-} concentrations and continuing acidification.

Recent publications that were based on analyses of SWAS-VTSSS data include Cosby et al. (1991, Stoddard et al. (1993, Sullivan et al. (Sullivan, 2003), 2004), and Webb et al. (2004).

A.2.7.3. Fernow

The Fernow Experimental Forest, established in 1934, is located just south of the city of Parsons in the most mountainous region of West Virginia. It is surrounded by the Monongahela National Forest, which comprises about 900,000 acres of rugged, hilly terrain. Most research at Fernow is focused on improvement of forest management (see http://www.fs.fed.us/ne/parsons/fefhome.htm).

Scientists at Fernow are developing information and techniques for sustainably managing hardwood forests in the central Appalachians. The mixed hardwood forest covers about 78% of West Virginia and supplies important timber products, provides recreational opportunities, and supports a diverse assemblage of wildlife and plant species.

The Fernow Experimental Forest was heavily logged between 1905 and 1911. The forest now contains about 1900 ha of second- and third-growth Appalachian hardwood stands, which are representative of average to better than average sites found on approximately 4 million ha of the forest type in West Virginia and surrounding states. At the lowest elevations, the original forests consisted mainly of hardwoods, with eastern hemlock (*Tsuga canadensis* [L.] Carr.) along stream bottoms and on

north slopes. Forests at the higher elevations were dominated by red spruce (*Picea rubens* Sarg.) and hemlock. Small patches of pure spruce occurred on the tops of the mountains.

Elevations in the Fernow range from 533 to 1112 m, with slopes of 10% to 60%. A rock layer composed of fractured hard sandstone and shale underlies most of the Fernow. A majority of the soils are of the Calvin and Dekalb series, which originated from these rocky materials (loamy-skeletal mixed mesic Typic Dystrochrepts). On the southeastern part of the forest, Greenbrier limestone outcrops to produce a midslope zone of limestone soil of the Belmont series (fine-loamy mixed mesic Typic Hapludalfs). Almost all Fernow soils, including the sandstone, shale, and limestone soils, are well-drained, medium textured loams and silt loams. Average soil depth is about 1 m, and average soil pH is about 4.5.

A rainy, cool climate is typical on the Experimental Forest. Precipitation, which averages about 145 cm per year, is evenly distributed throughout the year. Mean annual temperature is about 9 °C, and the length of the growing season is approximately 145 days.

The forest types and conditions today reflect the site qualities and past history of the area. Oaks (*Quercus* spp.) are most common and are found on all sites along with American beech (*Fagus grandifolia* Ehrh.) and sweet birth (*Betula lenta* L.). Excellent sites in coves and on north slopes support primarily northern red oak (*Quercus rubra* L.), sugar maple (*Acer saccharum* Marsh.), yellow-poplar (*Liriodendron tulipifera* L.), black cherry (*Prunus serotina* Ehrh.), white ash (*Fraxinus americana* L.), basswood (*Tilia americana* L.), cucumbertree (*Magnolia acuminata* L.), and beech. Fair sites on south and east slopes usually support oak stands composed of red oak, white oak (*Quercus alba* L.), chestnut oak (*Quercus prinus* L.), and scarlet oak (*Quercus coccinea* Muenchh.). Other fair site species include red maple (*Acer rubrum* L.), sweet birch, black gum (*Nyssa sylvatica* Marsh.), sassafras (*Sassafras albidum* Nutt.), and sourwood (*Oxydendrum arboreum* [L.] DC.). Good sites commonly support a mixture of excellent and fair site species. Black locust (*Robinia pseudoacacia* L.), sweet birch, and Fraser magnolia (*Magnolia fraseri* Walt.) are consistent but generally minor components of the forest on all sites. American chestnut was a major forest component until it was eliminated by the chestnut blight.

The Fernow Experimental Forest encompasses practically the entire Elk Lick Run drainage, which is about 5.8 km long and 3.5 km across at the widest point. Elk Lick Run has seven major tributaries including Big Spring, which drains a headwater limestone formation. Headwater areas on two of these tributaries have been gauged to show how forest management influences streamflow.

Research on the Fernow Experimental Forest by the Timber and Watershed Project scientists is done in cooperation with the Monongahela National Forest, West Virginia University, Marshall University, Pennsylvania State University, Virginia Tech, and the West Virginia Division of Natural Resources.

Scientific studies on the Fernow have followed two lines of research, with considerable overlap. Silvicultural research, focused mostly on mixed hardwood stands, addresses questions relating to regenerating, growing, tending, and harvesting trees and stands. Watershed research has addressed some of the more basic questions about water use by forests and forest hydrology, as well as critical issues affecting roads, best management practices, and forest management effects on water and soil resources. The Fernow also has been in the forefront of research on acidic deposition and N saturation. A whole-watershed acidification study has been conducted since 1989. Recently, research on threatened and endangered species has assumed a more prominent role, due to the presence of Indiana bat and running buffalo clover on the Fernow.

A.2.7.4. National Ecological Observatory Network

The National Ecological Observatory Network (NEON) is a continental-scale research platform that is primarily focused on discovering and understanding the impacts of climate change, land-use change, and invasive species on ecology. It will also generate data that will be useful for assessing effects of NO_X and SO_X deposition on ecosystems. NEON has not yet been implemented; it is described here because it represents an ambitious monitoring program that is expected to be very useful in the near future. NEON will gather long-term data on ecological responses of the biosphere to changes in land use and climate, and on feedbacks with the geosphere, hydrosphere, and atmosphere. NEON is proposed as a national observatory, consisting of distributed sensor networks and experiments, linked by advanced cyber infrastructure to record and archive ecological data for at least 30 years. Using standardized protocols and an open data policy, NEON is intended to gather essential data for developing scientific understanding and theory required to manage the nation's ecological challenges. The program description is found at www.neoninc.org/.

A.3. Modeling

A.3.1. Principal Ecosystem Models Used in the U.S.

It is particularly difficult to study endpoints at the larger levels of biological organization (e.g., at the population, community, biogeochemical, and ecosystem-level) with monitoring studies. Geographic areas are larger, and timeframes are longer, rendering it difficult to obtain data in sufficient quantity to detect impacts unless they are exceptionally severe. Therefore, the most common approach to study endpoints at these scales is to develop and apply a model. Models may be calibrated using data from monitoring, survey, or laboratory or field experiments and are useful tools in predicting larger-scale,

longer-term impacts. However, verifying the predictions and assessing the overall validity of the model can be challenging.

Some of the most frequently used ecosystem models designed to quantify effects of atmospheric N and S deposition are discussed below. It is important to note that the ecosystem models are parameterized for specific areas and may not be readily applicable to other locations without significant re-parameterization.

There are four principal models that are currently being used in the U.S. to assess the effects of S and N deposition on terrestrial and freshwater aquatic ecosystems: MAGIC, NuCM, PnET/BGC, and DayCent-Chem. Two models, SPARROW and WATERSN, are commonly used to evaluate N loading to large river systems and to estuaries. These six models are briefly reviewed in the following sections. Each review begins with a summary of the provenance and conceptual basis of the model and contains references to some of the published applications. This is followed by a more detailed description of the processes included in the model, the inputs required, and the output variables simulated by the model.

The ranges of process complexity, temporal resolution and spatial discretization represented in these models are considerable. These ranges make comparative summaries of inputs, outputs, and processes across the models problematic. The models are all currently in use because they are, in a sense, complementary to each other, with each providing an approach or satisfying requirements unique to their own structure and intended applications. As a result, there is no good way to develop satisfying comparative equivalences among the components of the various structures. It is also beyond the scope of this document to present the level of detail necessary to run any of the models. The descriptions below must of necessity be brief. References to appropriate texts designed to provide more detail are given for each model.

Following the discussion of the four models most frequently used in the U.S., there are brief descriptions of the most important models of S and N deposition effects that are being used in Europe and elsewhere.

A.3.1.1. MAGIC

The MAGIC model (Cosby, 1985; Cosby, 1985; Cosby, 1985) is a mathematical model of soil and surface water acidification in response to atmospheric deposition based on process-level information about acidification. MAGIC has been applied extensively in North America and Europe to both individual sites and regional networks of sites, and has also been used in Asia, Africa and South America. The utility of MAGIC for simulating a variety of water and soil acidification responses at the laboratory, plot, hillslope, and catchment scales has been tested using long-term monitoring and experimental manipulation data.

MAGIC has been widely used in policy and assessment activities in the U.S. and in several countries in Europe (Cosby, 1985; Cosby, 1990; Cosby, 1995; Cosby, 1996; Ferrier, 2001; Jenkins, 1990; Clair, 2004; Sullivan, 1998; Moldan, 1998; Hornberger, 1989; Whitehead, 1997; Whitehead, 1988; Wright, 1994; Wright, 1998; e.g.`, \Beier, 1995; Sullivan, 2006).

MAGIC Model Structure

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (see Figure A-6). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: (1) a section in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving SO_4^{2-} adsorption, cation exchange, dissolution-precipitation- speciation of aluminum, and dissolution-speciation of inorganic carbon; and (2) a mass balance section in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils.

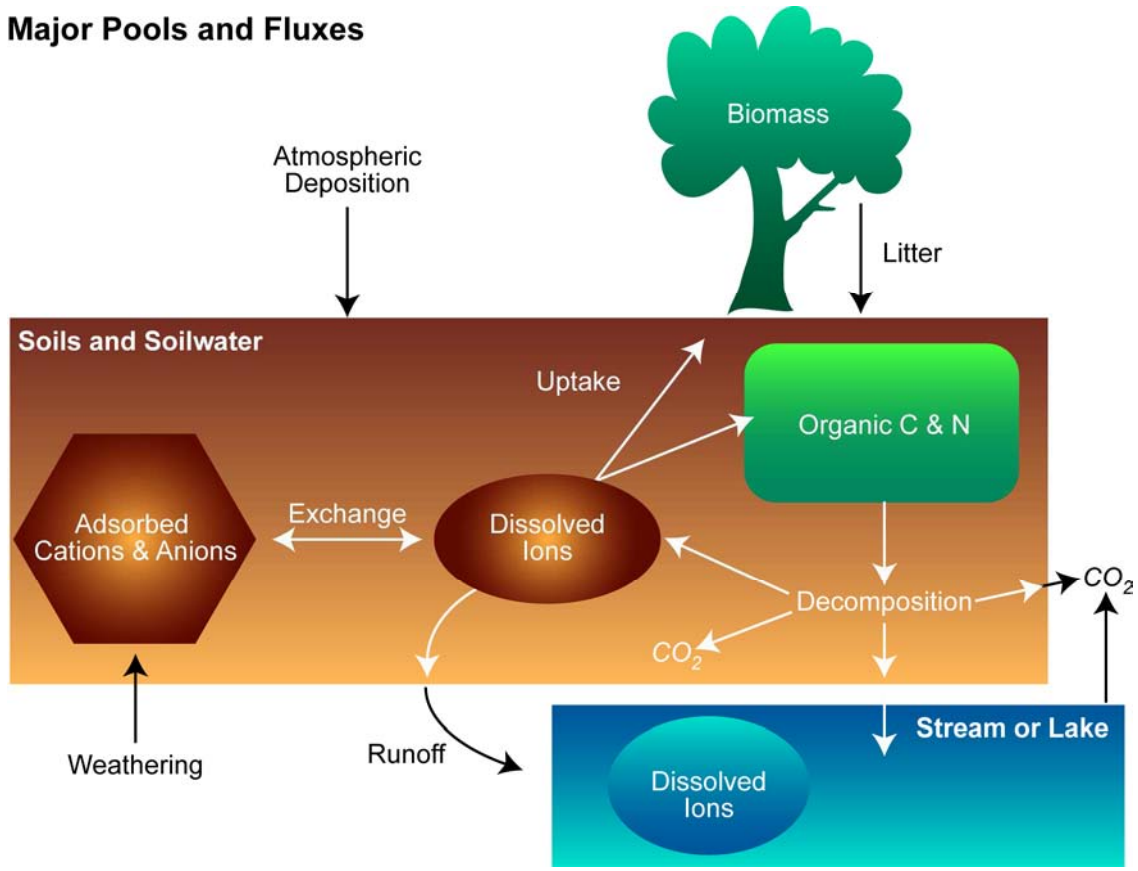


Figure A-6. Conceptual structure of the MAGIC model showing major pools and fluxes included in simulation of effects of S and N deposition.

Cation exchange is modeled using equilibrium (Gaines-Thomas) equations with selectivity coefficients for each base cation and aluminum. SO_4^{2-} adsorption is represented by a Langmuir isotherm. Aluminum dissolution and precipitation are assumed to be controlled by equilibrium with a solid phase of aluminum trihydroxide. Aluminum speciation is calculated by considering hydrolysis reactions as well as complexation with SO_4^{2-}, fluoride and dissolved organic compounds. Effects of carbon dioxide on pH and on the speciation of inorganic carbon are computed from equilibrium equations. Organic acids are represented in the model as tri-protic analogues. Weathering rates are assumed to be constant. Two alternate mechanisms are offered for simulation of nitrate and ammonium in soils and water: (1) first order equations representing net uptake and retention; or (2) a set of equations and compartments describing process-based N dynamics controlled by C and N pools and fluxes in the compartments.

Atmospheric deposition fluxes for the base cations and strong acid anions are required as inputs to the model. These inputs are generally assumed to be uniform over the catchment. Atmospheric fluxes are calculated from concentrations of the ions in precipitation and the rainfall volume into the catchment. The atmospheric fluxes of the ions must be corrected for dry deposition of gas, particulates and aerosols and for inputs in cloud/fog water. The volume discharge for the catchment must also be provided to the model.

In general, the model is implemented using average hydrologic conditions and meteorological conditions in annual or seasonal simulations, i.e., mean annual or mean monthly deposition, precipitation and lake discharge are used to drive the model. Values for soil and surface water temperature, partial pressure of carbon dioxide and organic acid concentrations must also be provided at the appropriate temporal resolution.

The MAGIC model can be implemented as a one- or two-soil representation of a catchment with or without wetlands. Atmospheric deposition enters the soil compartment(s) and the equilibrium equations are used to calculate soil water chemistry. The water is then routed to the stream compartment, and the appropriate equilibrium equations are reapplied to calculate runoff chemistry. Input-output mass balance equations are provided for base cations and strong acid anions, and charge balance is required for all ions in each compartment (for complete details of the model see \Cosby, 1985; Cosby, 1985; Cosby, 1985; Cosby, 2001).

For most applications, model outputs for 15 stream water variables are used. These variables consist of the concentrations of 10 ions (H; Ca; Mg; Na; K; NH_4; SO_4^{2-}; NO_3; Cl; and total inorganic Al), the stream discharge (Q), stream pH, sum of base cation (SBC) concentrations (SBC = Ca + Mg + Na + K + NH_4), sum of mineral acid anion (SAA) concentrations (SAA = Cl + SO_4^{2-} + NO_3) and the charge balance acid neutralizing capacity (ANC = SBC – SAA). These variables are expressed in units of m/yr (or m/mo) for Q, µmol/L for inorganic Al, and µeq/L for all other variables. In addition, model output for 7 soil and soilwater variables are frequently used, the total base saturation and individual cation saturations for Ca, Mg, Na, and K, the soilwater pH and the Ca/Al ratio in soil water.

The aggregated nature of the model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibrations are based on volume weighted mean annual or seasonal fluxes for a given period of observation. The length of the period of observation used for calibration is not arbitrary. Model output will be more reliable if the annual flux estimates used in calibration are based on a number of years rather than just one year. There is a lot of year-to-year variability in atmospheric deposition and catchment runoff. Averaging over a number of years reduces the likelihood that an “outlier” year (very dry, etc.) is used to specify the primary data on which model forecasts are based. On the other hand, averaging over too long a period may remove important trends in the data that need to be simulated by the model.

The calibration procedure requires that stream water quality, soil chemical and physical characteristics, and atmospheric deposition data be available for each catchment. The water quality data needed for calibration are the concentrations of the individual base cations (Ca, Mg, Na, and K) and acid anions (Cl, SO_4^{2-}, and NO_3) and the pH. The soil data used in the model include soil depth and bulk density, soil pH, soil cation-exchange capacity, and exchangeable bases in the soil (Ca, Mg, Na, and K). The atmospheric deposition inputs to the model must be estimates of total deposition, not just wet

deposition. In some instances, direct measurements of either atmospheric deposition or soil properties may not be available for a given site with stream water data. In these cases, the required data can often be estimated by: (a) assigning soil properties based on some landscape classification of the catchment; and (b) assigning deposition using model extrapolations from some national or regional atmospheric deposition monitoring network.

Soil data for model calibration are usually derived as aerially averaged values of soil parameters within a catchment. If soils data for a given location are vertically stratified, the soils data for the individual soil horizons at that sampling site can be aggregated based on horizon, depth, and bulk density to obtain single vertically aggregated values for the site, or the stratified data can be used directly in the model.

Calibration of the model (and estimation of historical changes at the modeled sites) requires a temporal sequence of historical anthropogenic deposition. Current understanding of ecosystem responses to acidic deposition suggests that future ecosystem responses can be strongly conditioned by historical acid loadings. Thus, as part of the model calibration process, the model should be constrained by some measure of historical deposition to the site. However, such long-term, continuous historical deposition data may not exist. The usual approach is to use historical emissions data as a surrogate for deposition. The emissions for each year in the historical period can be normalized to emissions in a reference year (a year for which observed deposition data are available). Using this scaled sequence of emissions, historical deposition can be estimated by multiplying the total deposition estimated for each site in reference year by the emissions scale factor for any year in the past to obtain deposition for that year.

A.3.1.2. NuCM Model

The current NuCM model is based on the original Integrated Lake Watershed Acidification Study (ILWAS) model of the 1980s (cf. Chen, 1984; Goldstein, 1984; Gherini, 1985). NuCM was developed as an extension to the ILWAS model by investigators in the Integrated Forest Study see (Johnson, 1992), and the model code was written by Tetra-Tech, Inc. (Liu, 1991). NuCM was developed to explore potential effects of atmospheric deposition, fertilization and harvesting in forest ecosystems. Because NuCM was designed primarily for simulating the effects of atmospheric deposition on nutrient cycling processes, its construction emphasizes soil and soil solution chemistry (Liu, 1991). As a stand-level model, NuCM incorporates all major nutrient cycling processes (uptake, translocation, leaching, weathering, organic matter decay, and accumulation). Vegetation is divided into leaf, bole and root compartments for under- and overstory vegetation. NuCM simulates the cycling of N, P, K, Ca, Mg, Na, and S based on expected optimal growth rates (input by the user and reduced in the event of nutrient limitation), user-defined litterfall, weathering, N and S mineralization rates, soil minerals composition, initial litter, soil organic matter pools, and C/N ratios.

The model has been calibrated for different vegetation types, including a loblolly pine (*Pinus taeda* L.) stand at Duke University (Johnson, 1995), a mixed deciduous stand at Walker Branch (Johnson, 1993) and a red spruce (*Picea rubens Sarg.*) stand in the Great Smoky Mountains (Johnson, 1996). The NuCM model was used as part of the Southern Appalachian Mountain Assessment (Sullivan, 2002).

NuCM Model Structure

In NuCM, the ecosystem is represented as a series of vegetation and soil components. The overstory consists of one generic conifer and one generic deciduous species of specified biomass and nutrient concentration (foliage, branch, bole, roots). For mixed species stands, average values for biomass and nutrient concentration by component must be used. NuCM also includes an understory, which can be divided into canopy, bole, and roots. Maximum potential vegetative growth in the model is defined by the user and is constrained in the model by the availability of nutrients and moisture. The forest floor is simulated from litterfall inputs and litter decay. Litterfall mass inputs are defined by the user, and litter decay is represented as a four stage process where: (1) coarse litter decays to fine litter; 2) fine litter decays to humus and cations; 3) humus decays to organic acids, NH_4^+, SO_4^{2-}, H^+, and CO_2; and (4) organic acids decay to NH_4^+, SO_4^{2-}, H^+, and CO_2. Each stage is represented as a first-order equation.

The soil includes multiple layers (up to 10), and each layer can have different physical and chemical characteristics. The user defines bulk density, cation exchange capacity, exchangeable cations, adsorbed phosphate and SO_4^{2-}, and four soil minerals and their composition. These inputs define the initial soil exchangeable/adsorbed pools and total pools. Initial total soil N pools are simulated from litterfall and decay, as described above, and user-defined C/N ratios. Vegetation, litter, and soil pools change over a simulation in response to growth, litterfall and decomposition, and nutrient fluxes via deposition, leaching and weathering.

The processes that govern interactions among these pools include translocation, uptake, foliar exudation and leaching, organic matter decay, nitrification, anion adsorption, cation exchange and mineral weathering. Translocation, defined as the removal of nutrients from foliage prior to litterfall, is user-specified. Maximum uptake is calculated from biomass and nutrient concentrations; actual uptake is equal to this maximum value when sufficient nutrients are available and reduced when nutrients become limiting. Reduced uptake first allows reduced nutrient concentrations in plant tissues, then causes a reduction in growth. Foliar exudation and leaching rates are simulated as proportional to foliar concentrations using user-defined coefficients.

Mineral weathering reactions are described in the model using rate expressions with dependencies on the mass of mineral present and solution-phase hydrogen-ion concentration taken to a fractional power. Cation exchange is represented by the Gapon equation. The model simulates a tri-protic organic acid with a fixed charge density. Nitrification is represented in the form of a Michaelis–Menton rate expression.

Phosphate adsorption is represented by a linear isotherm, and SO_4^{2-} adsorption is represented by a Langmuir adsorption isotherm.

Climate inputs to the NuCM model are through input meteorological files (typically 1 to 5 years long), which are repeated in order to generate long-term simulations. The meteorological files contain daily values for precipitation quantity, maximum and minimum air temperature, cloud cover, dewpoint, atmospheric pressure, and wind speed. Monthly soil temperature data are also required.

Precipitation is routed through the canopy and soil layers and evapotranspiration, deep seepage, and lateral flow are simulated. The movement of water through the system is simulated using the continuity equation, Darcy's equation for permeable media flow, and Manning's equation for free surface flow. Percolation occurs between layers as a function of layer permeability's and differences in moisture content. Nutrient pools associated with soil solution, the ion exchange complex, minerals, and soil organic matter are all tracked explicitly by NuCM.

Wet deposition is calculated from precipitation amounts and user-input air quality files which define precipitation concentrations on a monthly basis. Dry deposition is calculated from air concentrations in the air quality files combined with user-defined deposition velocities and simulated leaf areas. Leaching is calculated from soilwater percolation and simulated soil solution concentrations using the soil chemical and biological algorithms defined above for each soil horizon.

The only processes in the NuCM model that are explicitly temperature-dependent are evaporation, occurrence of precipitation as rainfall versus snowfall, snowpack melting, litter decay, and nitrification. Temperature affects processes such as cation exchange, mineral weathering, and uptake only indirectly. Precipitation effects are manifested strictly through the hydrologic simulations; none of the nutrient processes are dependent explicitly upon moisture.

A.3.1.3. PnET-BGC

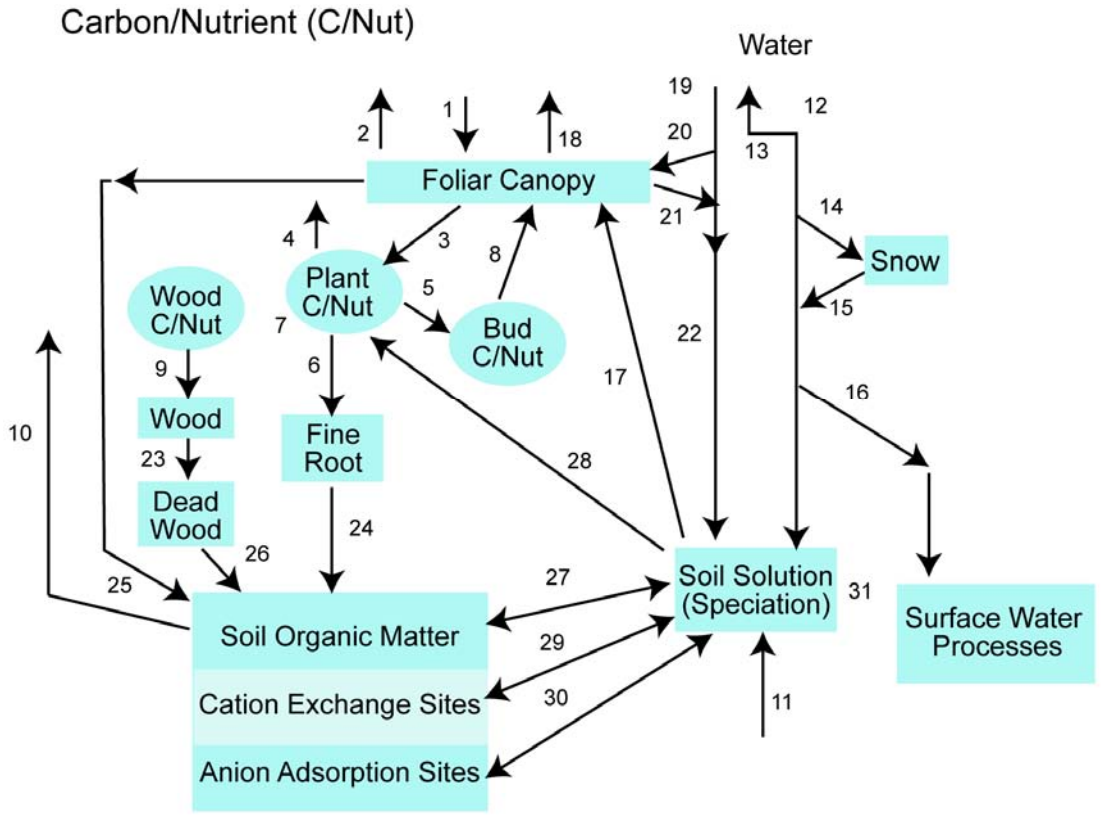
PnET-BGC is an integrated dynamic biogeochemical model that simulates chemical transformations of vegetation, soil and drainage water. The PnET-BGC model was formulated by linking two submodels (vegetation and biogeochemical) to allow for the simultaneous simulation of major element cycles in forest and interconnected aquatic ecosystems. The vegetation submodel is based on PnET-CN (Aber, 1992; Aber, 1997; Aber, 1997), a simple generalized model of monthly carbon, water, and N balances that provides estimates of net primary productivity, N uptake, and water balances. The biogeochemical submodel BGC (Gbondo-Tugbawa, 2001, expands PnET to include vegetation and organic matter interactions of other elements (Ca^{2+}, Mg^{2+}, K^+, Na^+, Si, S, P, Al^{3+}, Cl^-, and F^-), abiotic soil processes, solution speciation, and surface water process.

PnET-BGC was initially developed for and applied to the northern hardwood forest ecosystem. The model has been tested using vegetation, soil and water chemistry data from the Hubbard Brook

Experiment Forest (HBEF) (Gbondo-Tugbawa, 2001). The model has subsequently been applied to intensively studied watersheds in the Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen, 2005) and northern New England (Chen, 2005; Chen, 2005). PnET-BGC has also been used to evaluate the effects of current and future atmospheric deposition scenarios (Gbondo-Tugbawa, 2002; Sullivan, 2006).

PnET-BGC Model Structure

PnET/BGC simulates major biogeochemical processes, such as forest canopy element transformations, hydrology, soil organic matter dynamics, N cycling, geochemical weathering, and chemical equilibrium reactions in solid and solution phases, and allows for simulations of land disturbance (Gbondo-Tugbawa, 2001) (see Figure A-7). The model uses mass transfer relationships to describe weathering, canopy interactions and surface water processes. Chemical equilibrium relationships describe anion adsorption, cation exchange and soil solution and surface water speciation. Soil solution equilibrium reactions are described using the tableau approach (Morel, 1993). A more detailed description of the model can be found in Gbondo-Tugbawa et al., 2001a.



Processes Depicted:

1. Gross Photosynthesis
2. Foliar Respiration
3. Transfer to Mobil C
4. Growth and Maintenance Respiration
5. Allocation to Buds
6. Allocation to Fine Roots
7. Allocation to Wood
8. Foliar Production
9. Wood Production
10. Soil Respiration
11. Weathering Supply
12. Precipitation
13. Interception
14. Snow-Rain Partition
15. Snowmelt
16. Shallow Flow
17. Water Uptake
18. Transpiration
19. Deposition (Wet + Dry)
20. Foliar Nutrient Uptake
21. Foliar Exudation
22. Throughfall & Stemflow
23. Wood Litter
24. Root Litter
25. Foliar Litter
26. Wood Decay
27. Mineralization/Immobilization
28. Nutrient Uptake
29. Cation Exchange Reactions
30. Anion Adsorption Reactions
31. Drainage

Source: Gbondo-Tugbawa et al. (2001).

Figure A-7. Structure of the PnET-BGC model illustrating the compartments and flow paths of carbon and nutrients (C/Nut) within the model.

The model operates on a monthly time step and is applied at the stand to small-watershed scale. The process of photosynthesis, growth and productivity, litter production and decay, mineralization of organic matter, immobilization, and nitrification in PnET have been described in Aber and Federer (Aber, 1992) and Aber et al. (1997). The BGC submodel uses the Gaines–Thomas formulation (White, 1986) to describe cation exchange reactions within the soil. The exchangeable cations considered in the model include Ca^{2+}, Mg^{2+}, Na^{+}, H^{+}, Al^{3+}, K^{+}, and NH_4^{+}. A pH-dependent adsorption isotherm is used to describe the SO_4^{2-} adsorption process. The speciation of monomeric aluminum is calculated in the model,

including both organic and inorganic forms. Organic acids are described using a triprotic analogue (Driscoll, 1994, and the total amount of organic acids is estimated as a certain fraction (based on the charge density) of DOC. The model simulates ANC in surface waters as an analogue to ANC measured by Gran plot analysis, by considering the contributions of DIC, organic anions and Al complexes (Driscoll, 1994).

The PnET/BGC model requires inputs of climate, wet and dry deposition chemistry, and weathering data. Climate inputs consist of minimum and maximum air temperature, solar radiation, and precipitation. The model uses a constant dry-to-wet deposition ratio by default, but a variable ratio can also be applied (Chen, 2004). The model inputs utilize canopy enhancement factors to depict the increased dry deposition observed in coniferous and mixed forest stands compared to hardwood forests. Deposition and weathering fluxes for all major elements are required as model inputs. Weathering rates are assumed to remain constant over time.

Calibration of PnET-BGC is based on empirical relationships and observations. The model uses historical reconstructions of climate, atmospheric deposition, and land disturbance in order to construct hindcasts of the response of forests to past acidic deposition. The model can also be used to predict the response of acid-sensitive forest ecosystems to future changes in acidic deposition, for example in response to controls on atmospheric emissions. A detailed description of the model, including a detailed uncertainty analysis of parameter values, is available in Gbondo-Tugbawa et al. (2001).

A.3.1.4. DayCent-Chem

DayCent-Chem links two widely accepted and tested models, one of daily biogeochemistry for forest, grassland, cropland, and savanna systems, DayCent (Parton, 1998), and the other of soil and water geochemical equilibrium, PHREEQC (Parkhurst, 1999). The linked DayCent/PHREEQC model was created to capture the biogeochemical responses to atmospheric deposition and to explicitly consider those biogeochemical influences on soil and surface water chemistry. The linked model expands on DayCent's ability to simulate N, P, S, and C ecosystem dynamics by incorporating the reactions of many other chemical species in surface water.

Hartman et al. (2007) used DayCent-Chem to investigate how wet and dry deposition affect biological assimilation, soil organic matter composition, ANC and pH of surface waters, and also Al mobilization, soil base cation depletion, and base cation flux. Model results were tested against a long-term data set available from Andrews Creek in Loch Vale Watershed, Rocky Mountain National Park, Colorado.

DayCent-Chem Model Structure

DayCent is the daily time-step version of CENTURY, a non-spatial, lumped parameter model that simulates C, N, P, S, and water dynamics in the soil-plant system at a monthly timestep over time scales

of centuries and millennia (Parton, 1994). CENTURY can represent a grassland, crop, forest, or savanna system with parameters that describe the site-specific plant community and soil properties. DayCent, the daily timestep version of CENTURY, adds layered soil temperature, a trace gas submodel, a more detailed soil hydrology submodel, and explicitly represents inorganic N as either NO_3^- or NH_4^+ (Kelly, 2000) Del Grosso, 2001; Parton, 1998). DayCent 5 is an object-oriented model written in the C++ programming language that implements a layered soil structure and algorithms to manage soil layers. The model is initialized with an organic soil depth and up to 10 soil layers, where each layer has a specified thickness, texture, bulk density, field capacity, wilting point, and saturated hydraulic conductivity.

PHREEQC is a model based on equilibrium chemistry of aqueous solutions interacting with minerals, gases, exchangers, and sorption surfaces. The model is written in the C programming language and has an extensible chemical database. Version 2.7 of PHREEQC is used in the linked DayCent-Chem model to compute aqueous speciation, ion-exchange equilibria, fixed-pressure gas-phase equilibria, dissolution and precipitation of mineral phases to achieve equilibrium, and irreversible aqueous mineral phase reactions. The aqueous model uses ion-association and Debye Huckel expressions. Ion-exchange reactions are modeled with the Gaines-Thomas convention and equilibrium constants are derived from Appelo and Postma (1993).

The DayCent-Chem model inputs are climate drivers consisting of daily precipitation, and minimum and maximum air temperatures. The model also requires daily atmospheric wet deposition concentrations for precipitation species Ca^{2+}, Cl^-, K^+, Mg^{2+}, Na^+, NH_4^+, NO_3^-, SO_4^{2-}, and H^+ and daily dry deposition amounts or dry/wet ratios for all precipitation species. Initial conditions for model simulations include: (1) initial snowpack water content and chemical composition; 2) initial soil solution concentrations; and (3) initial exchangeable cations in each soil layer. Potential annual denudation rates for each mineral phase that could be dissolved in the soil, groundwater, or stream solutions must also be provided.

DayCent-Chem implements a geochemical submodel of layered pools and properties that provides information exchange, such as of water fluxes and solute concentrations, between the coupled models, and calculates daily geochemical outputs. The geochemical submodel defines soil layers and a groundwater pool that correspond to those in Day-Cent 5's original soil class. Surface water concentrations are computed in a two-step process where solutes are first transported, and then PHREEQC undertakes solution reactions. At each timestep, the model updates exchangeable base cation pools and soil solutions in each soil layer, along with groundwater and stream solutions.

DayCent 5 output includes daily evapotranspiration; soilwater content; outflow; inorganic and organic C, N, P, and S stream fluxes; C, N, P, and S contents in soil and plant pools; net primary production (NPP); nutrient uptake; trace gas flux; and heterotrophic respiration. In addition to standard DayCent 5 outputs, at each daily timestep the model writes the solution chemistry for soil layers, groundwater, and stream.

A.3.1.5. SPARROW

SPAtially Referenced Regressions on Watersheds (SPARROW) is a hybrid statistical/deterministic model used to estimate pollutant sources and contaminant transport in surface waters. SPARROW can be used to estimate pollutant loading to downstream receiving waters for a number of water quality constituents. The model as constructed for evaluating N export to estuaries will be presented here.

SPARROW was first described by Smith et al. (1997) as a water quality model designed to reduce problems with interpreting watershed data as a result of sparse sampling, network bias, and basin heterogeneity. SPARROW combines regression techniques and process information regarding contaminant transport and retention in watershed and riverine systems. Literature values for watershed retention rates are used; in-stream retention of N is estimated by a first-order decay function (Smith, 1997).

$$L_i = \sum_{n=1}^{N} \sum_{j \varepsilon J(i)} \beta_n S_{n,j} e^{(-a' Z_j)} e^{(-\delta' Z_{i,j})}$$

where

L_i = load in reach i;

n, N = source index where N is the total number of considered sources;

$J(i)$ = the set of all reaches upstream and including reach i, except those containing or upstream of monitoring stations upstream of reach i;

β_n = estimated source parameter;

Sn,j = contaminant mass from source n in drainage to reach j;

α = estimated vector of land-to-water delivery parameters;

Z_j = land-surface characteristics associated with drainage to reach j;

δ = estimated vector of instream-loss parameters; and

$T_{i,j}$ = channel transport characteristics.

Source: Preston and Brakebill (1999).

Figure A-8. Mathematical form of the SPARROW model.

Others have developed similar regression models relating in-stream water quality measurements to watershed nutrient sources and basin attributes (Howarth, 1996; Mueller, 1997; Jaworski, 1997). These simple correlative models assume that contaminate sources and sinks are homogenously distributed and do not make a distinction between watershed and in-stream loss processes. SPARROW is distinct from these methods by incorporating spatial representation of basin attributes in the model. Model correlations between basin attributes and water quality measurements are strengthened by incorporating these spatial

references (Alexander, 2001; Smith, 1997). Spatially referenced basin attributes include land use, point and non-point N sources, temperature, soil permeability, and stream density, among others (Figure A-8). (Preston, 1999) shows the mathematical form of the SPARROW model (Figure A-8). Smith et al. (1997) provided an example of SPARROW model development for application to the conterminous U.S. Their exploratory model included five N sources and eight land surface characteristics as potential factors that deliver N from land to water. In-stream decay coefficients for three stream size classes were also tested for significance (Table A-3).

The final model resulted in the inclusion of each of the five N sources and three (temperature, soil permeability, and stream density) of the eight land to water delivery factors. Parameter selection was primarily based on statistical significance. Further discussion regarding the exclusion of precipitation and irrigated land, both of which were determined to be significant, can be found in Smith et al. (1997). Parameter estimates are evaluated for robustness through the use of bootstrap analysis.

The bootstrap procedure involves randomly selecting, with replacement, *M* monitored loads and associated predictor variables from among the observations in the data set (*M* is the number of monitored reaches in the reach network). Where a sampled observation has an upstream monitored load as one of its predictors, the monitored value is used, regardless of whether the upstream station appears in the bootstrap sample. Coefficient values are estimated from the bootstrap sample. The bootstrap process is repeated 200 times, resulting in 200 estimates of each coefficient. From these estimates, the mean coefficient value (called the bootstrap estimate), minimum confidence interval, and probability that the estimated coefficient has the wrong sign are determined (Smith, 1997).

Spatial referencing in the model occurs in two ways: (1) land surface polygons are mapped in conjunction with nonpoint contaminant sources and the land-water delivery variables (temperature, soil permeability, stream density, etc.) and (2) the stream reach network is mapped along with point sources, channel transport characteristics, and measured transport rates. The positive impacts of this spatial referencing can be quantified by eliminating the channel decay coefficients from the model and creating a new model with only the contaminant sources and land-water delivery variables in the original model (Smith, 1997). Removing this spatial reference provided by the reach network results in a model with significantly higher mean squared error and lower predictive capacity (Table A-4).

Table A-3. Parameter Estimates, Probability Levels, and Regression Results for the Chesapeake Bay Total Nitrogen Sparrow Model

Explanatory Variables	Parameter Estimates	Probability Level
Nitrogen sources	β	
Point Sources	1.496	<0.005
Urban area (acres)	7.008	0.010

Explanatory Variables	Parameter Estimates	Probability Level
Fertilizer application (lb/yr)	0.2790	<0.005
Livestock waste production (lb/yr)	0.3361	<0.005
Atmospheric deposition (lb/yr)	1.024	<0.005
Land-to-water delivery	α	
Temperature (°F)	–	–
Precipitation (in)	–	–
Avg slope (%)	–	–
Soil permeability (in/h)	0.0754	0.095
Stream density (l/mi)	–	–
Wetland (%)	–	–
Instream loss (days)[a]	δ	
T1 (Q ≤200 ft^3/s)	0.7595	<0.005
T2 (200 ft^3/s < Q ≤1,000 ft^3/s)	0.3021	<0.005
T3 (Q > 1,000 ft^3/s)	0.0669	<0.005
Tu (reservoir retention)	0.4145	<0.005
R-squared	0.961	
Mean square error	0.1669	
Number of observations	79	

[a]T, travel time
Q, stream discharge
lb/yr, pounds per yr
°F, degrees Fahrenheit
in/h, inches per hour
mi, mile;
in, inches
%, percent
ft^3/s, cubic feet per second
–, value not statistically significant

SPARROW has also been applied to spatially identify N sources at the scale of the Chesapeake Bay watershed (Preston, 1999). A similar set of N sources, land-to-water delivery parameters, and in-stream loss rates to those used in Smith et al. (1997) were considered for this model (Preston, 1999). Only estimates for parameters that were used in the final model are given in Table A-5.

The final model included five N sources, one land-to-water deliver parameter (soil permeability), and four in-stream loss rates (including reservoir retention). Comparisons between predicted and observed N loading provided an r^2 value of 0.961 (Preston, 1999). Because the data that are used in SPARROW are spatially referenced, model results can be mapped.

Table A-4. Effect of spatial referencing on measures of regression model performance for predicting total N flux using the sparrow model.

Model Components	Mean Square Error	R2
Includes full spatial referencing (SPARROW)a	0.4544	0.8743
Excludes in-stream decay and reservoir retention	0.9659b	0.7307

A.3.1.6. WATERSN

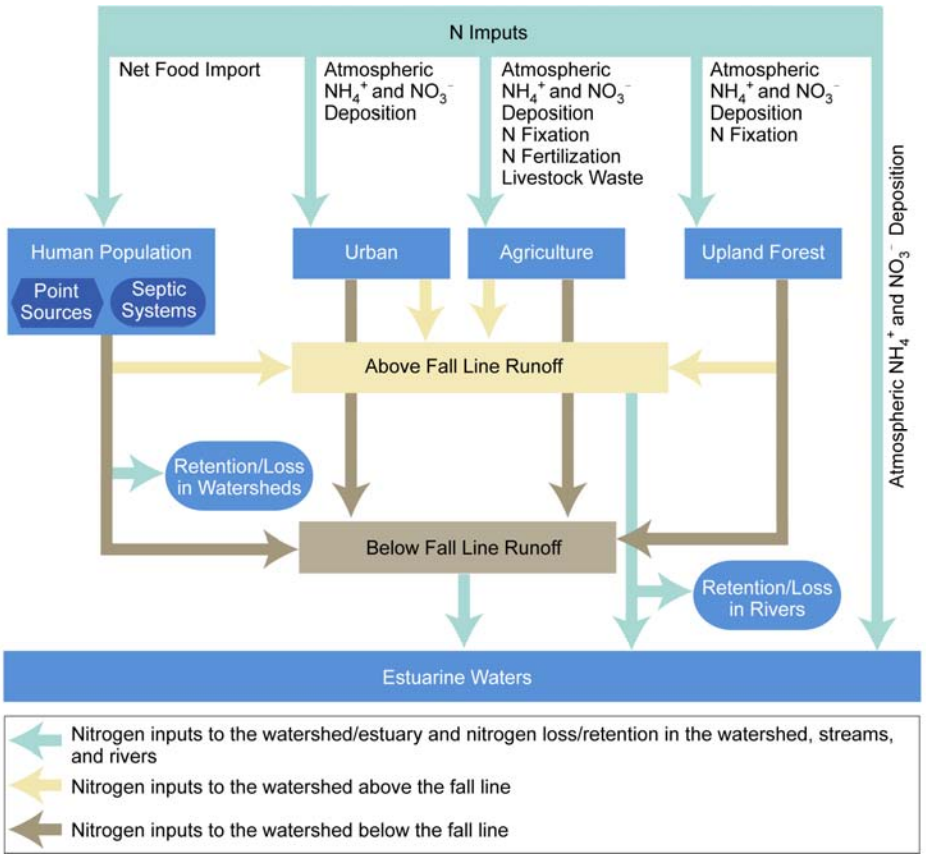
The Watershed Assessment Tool for Evaluating Reduction Strategies for Nitrogen (WATERSN) model is a steady-state numerical N budgeting model that estimates the amount of N exported to rivers and estuaries from forest, agricultural and urban land uses. The model is intended to provide an understanding of the relative contribution of N export from these land uses to estuaries, and to evaluate N export reduction strategies that are specific to each land use type (Driscoll, 2007).

Figure A-9 shows a conceptual diagram of the N budgeting system used in WATERSN. A detailed description of the original model calculations is provided in Castro et al. (2001). Subsequent model applications (2003; Castro, 2002) Driscoll, 2003; Whitall, 2004) have developed modifications to the approach originally described in Castro et al. (2001).

WATERSN uses calculations described in Jordan and Weller (1996) to estimate N inputs to the watershed/estuary system. Estimated anthropogenic sources of N inputs to the modeled watershed/estuary system include: (1) crop and lawn fertilizer application, (2) biotic N fixation by leguminous crops and pastures, (3) atmospheric deposition of wet and dry inorganic N (NH_4^+, NO_3^-), (4) net N import of food for human consumption, and (5) net N import of feed for livestock (Castro, 2002).

Agricultural Areas

N available for water-borne export to estuaries from agricultural lands is determined as the difference between N inputs and outputs (Castro, 2001). Modeled N inputs to agricultural lands consist of wet and dry atmospheric NH_4^+ and NO_3^- deposition, N fertilization, biotic N fixation, and livestock waste (Castro, 2002). Wet and dry deposition are derived from NADP and CASTNET data. Average annual wet deposition rates of NH_4^+ and NO_3^- are taken from NADP sites in or near the study watersheds. Dry deposition of NH_4^+ and NO_3^- is calculated as an average of all CASTNET sites nearest to the study watersheds. WATERSN assumes that dry deposition of both NH_4^+ and NO_3^- to the estuary surface is 25% less than dry deposition to the watershed (Castro, 2002). Meyers et al. (2000) described the uncertainty of estimates of wet and dry deposition and considered it to be no less than a factor of 2. Estimates of N fertilization are taken from agricultural census data. WATERSN assumes that all fertilizer sold in a county



Source: Castro et al. (2003).

Figure A-9. Schematic diagram of the WATERSN approach to estimate the contribution made by different N sources to the total N inputs an estuary.

is applied in that county. This is considered to be the most certain N input to the model (±25%) (Castro, 2002). WATERSN estimates both non-symbiotic and symbiotic N fixation for crops, pastures, hay fields and upland forests. Non-symbiotic rates were taken from literature values for crops, orchards, upland forests, and non-wooded pastures (Hendrickson, 1990; Stevenson, 1982; Woodmansee, 1978). Symbiotic rates of N fixation are based on type of legume, crop N harvest, N in unharvested portions of crops, soil N availability, and fertilization rate. These estimates are less certain than for N fertilization, but are noted as being a relatively minor N source in most of the study watersheds. Livestock waste was calculated as the difference between livestock consumption of N in feed and production of N in meat, milk, and eggs for human consumption (Jordan, 1996).

N outputs from agricultural land include crop harvest, pasture grazing, volatilization of NH_3 and denitrification. Data regarding crop harvest are obtained from agricultural census. N removed through crop harvest is estimated by multiplying the crop harvest by the percent N in each crop. Estimates for grazing are based on sheep, cattle, and horse populations (USDA online database in \Castro, 2002, their dietary N requirements, and proportion of dietary N obtained from grazing (Jordan, 1996). NH_3

volatilization is assumed to be 10% of the N input from fertilizer and atmospheric deposition, and 20% of livestock manure inputs (Schlesinger, 1992). Denitrification rates were originally estimated as 10 to 30% of the N inputs from fertilizer and atmospheric deposition and 20% of livestock N waste. Subsequent applications of WATERSN (Castro, 2003) modified denitrification rates from agricultural lands to vary with the mean watershed temperature and are based on a denitrification activity Q_{10} value of 2 (Maag, 1997; Stanford, 1975). A Q_{10} value of 2 suggests that the denitrification rate used by the model will change by a factor of 2 for every 10 degree change in temperature based on a direct relationship between temperature and denitrification.

Urban Areas

N inputs to urban areas include atmospheric and non-atmospheric sources. The total atmospheric N deposition input to urban areas is taken as the total (wet + dry) inorganic (NO_3^- and NH_4^+) N deposition rate to the watershed multiplied by the total urban area in the watershed. Non-atmospheric sources include point sources (primarily waste water treatment plants) and non-point sources (septic systems and pervious/impervious surface runoff) of N in urban areas (Castro, 2002).

N outputs from urban areas include waste water treatment plant effluent, septic system leachate, and total N runoff from pervious and impervious lands. Measured total N data are used to calculate N export for wastewater treatment plants that have available data. A strong regression relationship between measured total N discharged from wastewater treatment plants and human populations that use wastewater treatment facilities is used to estimate total N discharges from wastewater treatment plants that do not have total N monitoring data available. Septic system output is determined by multiplying watershed specific human per capita N excretion rates by the human population of the watershed. WASTERSN assumes that 75% of this N is exported to the estuary (Castro, 2002). The soil water assessment tool (SWAT) is used to estimate non-point source non-atmospheric total N runoff from pervious and impervious urban lands. SWAT is a distributed parameter, continuous time model applicable at the watershed scale. Required inputs to SWAT include climatic variables, soil properties, elevation, vegetation information, and land use. SWAT is designed to predict land use and land management impacts on water, sediment, and agricultural yields in large watersheds (Castro, 2002). The model assumes that 75% of atmospheric N inputs to urban areas is exported to the estuary (Fisher, 1991). Alternatively, this N export term can be modified.

Upland Forests

N inputs to forests are assumed to be in the form of atmospheric deposition and non-symbiotic N fixation. Outputs from forests are estimated with a non-linear regression relationship between wet deposition of inorganic N and stream water export of dissolved inorganic nitrogen (DIN) developed using

results from a multitude of forest watershed studies. Exported dissolved organic nitrogen (DON) was assumed to be equal to 50% of the inorganic N export (Castro, 2002).

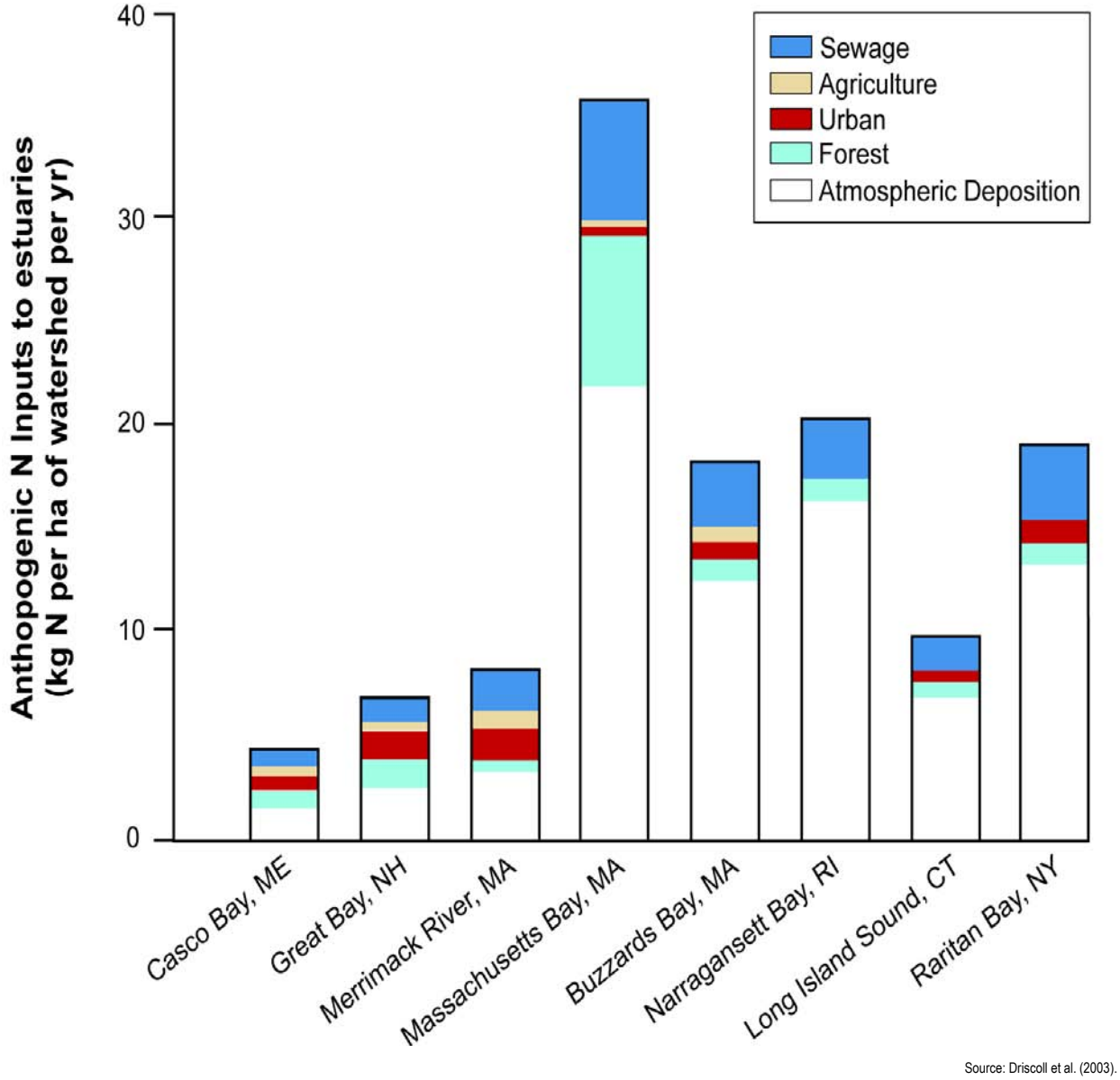
Watershed and In-Stream N Retention

Model validation efforts using measured N fluxes from the USGS National Stream Quality Accounting Network (NASQAN) have shown that WATERSN tends to overestimate N export from watersheds to estuaries (Castro, 2002). These differences are not unexpected since WATERSN does not account for watershed and in-stream N sinks. Attempts have been made to improve flux estimates by accounting for watershed and in-stream N retention (Castro, 2002; Castro, 2001; Castro, 2003; Castro, 2003). A summary of the N retention rates applied to WATERSN in these studies is given in Castro and Driscoll (2002) assumed that 30% of the total N that entered rivers above the fall line was lost during transport to the fall line and that inputs that enter the river below the fall line were not attenuated because of the relatively short travel times to the estuary See Table A-5. This 30% in-stream N retention value represents the median retention value obtained in previous studies of northeastern U.S. rivers (Castro, 2001) and falls within the range of retention values estimated by Howarth et al. (1996) and Alexander et al. (2000). Castro and Driscoll (2002) also incorporated watershed N retention fractions specific to individual land uses. They assumed that 60% of the excess N from agricultural land and septic systems was lost (retained within the watershed) due to watershed processes. Support for this value of N retention was given by several reports of riparian N removal rates from agricultural land, ranging from about 50 to 90% (Jordan, 1993; Jacobs, 1985; Peterjohn, 1984; Lowrance, 1983). After incorporating these assumptions, predicted fluxes closely matched ($r^2 = 0.909$) measured fluxes.

Table A-5. Summary of N retention rates used in recent WATERSN studies.

Study	Retention Type	% N Retention
Castro et al. (Castro, 2001)	In Stream*	30%
	Agriculture	50%
Castro and Driscoll (Castro, 2002)	In Stream*	30%
	Agriculture	60%
Castro et al. (2003)	Agriculture	40%
	Septic System	40%
	In Stream	Adjusted until predicted N flux matched observed fluxes

*In-stream N retention was only applied to lengths of river located above the "fall line." Below fall line N inputs to streams were assumed to not be attenuated due to the relatively short travel time to the estuary. The "fall line" is defined as the boundary between the Piedmont and Coastal Plain physiographic provinces in the eastern U.S. Source: Castro and Driscoll (Castro, 2002).



Source: Driscoll et al. (2003).

Figure A-10. WATERSN model estimates of anthropogenic N inputs to the estuaries of the northeastern U.S., in kilograms per hectare per year.

Driscoll et al. (2003) applied WATERSN to investigate anthropogenic N loading to estuaries in the northeastern U.S. The objectives of the study were to apply WATERSN to (1) quantify the inputs of reactive N to the region (**Error! Reference source not found.**), (2) discuss the ecological effects of regional elevated anthropogenic reactive N inputs, and (3) evaluate management options aimed at mitigating the effects of these elevated anthropogenic N inputs. Modeled N reduction scenarios included reductions atmospheric N emissions, increased N removal efficiencies of wastewater treatment plants, offshore pumping of wastewater, reductions in agricultural N runoff to surface waters, and an integrated management scenario consisting of a combination of N reductions from multiple sources. Other studies

have applied WATERSN to address similar issues related to N loading to estuaries in other regions of the U.S. (Whitall, 2004; Castro, 2003) Whitall, 2006).

A.3.2. Additional Effects Models Used Widely in Europe

The models of the effects of S and N deposition described below have been used primarily in Europe. These descriptions are derived in part from the UNECE Convention of Long-Range Transboundary Air Pollution Modelling and Mapping manual (Posch, 2003).

A.3.2.1. The Very Simple Dynamic Model

The Very Simple Dynamic (VSD) soil acidification model is frequently used in Europe to simulate acidification effects in soils when observed data are sparse. It only includes weathering, cation exchange, N immobilization processes, and a mass balance for cations, sulfur and N. It resembles the model presented by Reuss (1980) which, however, did not consider N processes. In the VSD model, the various ecosystem processes have been limited to a few key processes. Processes that are not taken into account include (1) canopy interactions, (2) nutrient cycling processes, (3) N fixation and NH_4 adsorption, (4) SO_4^{2-} transformations (adsorption, uptake, immobilization, and reduction), (5) formation and protonation of organic anions, and (6) complexation of Al.

The VSD model consists of a set of mass balance equations, describing the soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. The soil solution chemistry in VSD depends solely on the net element input from the atmosphere (deposition minus net uptake minus net immobilization) and the geochemical interaction in the soil (CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). Soil interactions are described by simple rate-limited (zero-order) reactions (e.g., uptake and silicate weathering) or by equilibrium reactions (e.g., cation exchange). It models the exchange of Al, H, and Ca + Mg + K with Gaines-Thomas or Gapon equations.

Solute transport in VSD is described by assuming complete mixing of the element input within one homogeneous soil compartment with a constant density and a fixed depth. Since VSD is a single layer soil model neglecting vertical heterogeneity, it predicts the concentration of the soil water leaving this layer (mostly the rootzone). The annual water flux percolating from this layer is taken as being equal to the annual precipitation excess. The time step of the model is one year, and therefore seasonal variations are not considered. A detailed description of the VSD model can be found in Posch and Reinds (2003).

A.3.2.2. SMART

The Simulation Model for Acidification's Regional Trends (SMART) model is similar to the VSD model, but somewhat extended. It is described in De Vries et al. (1989) and Posch et al. (1993). As with the VSD model, the SMART model consists of a set of mass balance equations, describing soil input-output relationships, and a set of equations describing the rate-limited and equilibrium soil processes. It includes most of the assumptions and simplifications given for the VSD model; and justifications for them can be found in De Vries et al. (1989).

SMART models the exchange of Al, H, and divalent base cations using Gaines Thomas equations. Additionally, SO_4^{2-} adsorption is modeled using a Langmuir equation (as in MAGIC) and organic acids can be described as mono-, di-, or tri-protic. Furthermore, it does include a balance for carbonate and Al, thus allowing application to a range of site conditions, from calcareous soils to completely acidified soils that do not have an Al buffer left. Recently, a description of the complexation of aluminum with organic acids has been included. The SMART model has been developed with regional applications in mind, and an early example of an application to Europe can be found in De Vries et al. (1994).

A.3.2.3. SAFE

The Soil Acidification in Forest Ecosystems (SAFE) model has been developed at the University of Lund (Warfvinge, 1993) and a recent description of the model can be found in Alveteg and Sverdrup (2002). The main differences between the SMART and MAGIC models are: (a) weathering of base cations is not a model input, but it is modeled with the PROFILE (sub-)model, using soil mineralogy as input (Warfvinge, 1992) ; b) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers (usually 4); and c) Cation exchange between Al, H, and (divalent) base cations is modeled with Gapon exchange reactions, and the exchange between soil matrix and the soil solution is diffusion-limited.

The standard version of SAFE does not include SO_4^{2-} adsorption although a version, in which SO_4^{2-} adsorption is dependent on SO_4^{2-} concentration and pH has recently been developed (Martinson, 2003). The SAFE model has been applied to many sites and more recently also regional applications have been carried out for Sweden (Alveteg, 2002) and Switzerland (Kurz, 1998).

A.3.3. Other Models

There are scores of models that can be useful in the context of developing a better understanding of the ecological effects of atmospheric S and N deposition. In the preceding sections, we have attempted to summarize a relatively small number of models that are most commonly used for this purpose in the U.S.

and Europe, in particular those that contribute to substantive conclusions presented in the ISA. There are many other models that are not covered in the discussion presented in this Annex. Several are highlighted in Table A-6.

Table A-6. Some examples of models that could contribute to development of a better understanding of the ecological efforts of atmospheric S and N deposition, but that are not explicitly addressed in this Annex.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
QUAL2K		A	S	1	QUAL2K is one dimensional river and stream water quality model. QUAL2K assumes: that he channel is well-mixed vertically and laterally; steady state hydraulics; diurnal water-quality kinetics. QUAL2K addresses point and non-point loads, BOD/DO, non-living particulate organic matter (detritus); denitrification; sediment-water interactions; bottom algae; pH (both alkalinity and total inorganic carbon).
WASP7	Water Quality Analysis Simulation Program	A	S	2	WASP is a dynamic compartment-modeling program for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1, 2, and 3 dimensional systems, and a variety of pollutant types. The time varying processes of advection, dispersion, point and diffuse mass loading and boundary exchange are represented in the model. WASP also can be linked with hydrodynamic and sediment transport models that can provide flows, depths velocities, temperature, salinity and sediment fluxes.
CE-QUAL-RIV1; CE-QUAL-R1; CE-QUAL-W2; CE-QUAL-ICM	Water quality models (river, reservoir, and estuary/ coastal) supported by USACE	A	N	3	CE-QUAL-R1 is a one-dimensional, vertical reservoir model and CE-QUAL-W2 is a two-dimensional (vertical and longitudinal), laterally averaged, hydrodynamic and water quality model. These two models are widely used by the Corps of Engineers, other federal and state agencies, the private sector, and agencies in other countries. CE-QUAL-RIV1 was developed for highly unsteady flow conditions, such as storm water flows and streams below peaking hydropower dams. CE-QUAL-ICM run in a 2D mode. This approach has been used for large, shallow waterways, harbors, and embayments.
RCA	Row Column AESOP	A	N	4	RCA evaluates the fate and transport of conventional and toxic pollutants in surface waterbodies in one, two, or three dimensions. RCA has been linked to various hydrodynamic models. Subroutines have been developed to model coliforms, pathogens, BOD/DO, simple and advanced eutrophication, wetland systems, and toxic contaminants. A sediment nutrient flux subroutine permits the coupling of the water column and sediment bed.
WARMS	Waterfowl Acidification Response Modeling System	A	N	McNicol et al. (1995), McNicol (2002)	WARMS includes an acidification model linked to fish and waterfowl models. WARMS uses pH, area, dissolved organic carbon, total P, and presence of fish to estimate preacidification, present and eventual steady-state values for pH, fish presence and waterfowl breeding parameters under proposed SO_2 emission scenarios.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
GT-MEL	Georgia Tech hydrologic model and the Multiple Element Limitation model	I	N	5	GT-MEL is a spatially distributed, process-based ecohydrology model that links a land surface hydrology model with a terrestrial biogeochemistry model. GT-MEL differs from other available ecohydrology models in its simplicity, flexibility, and theoretical foundation. The coupled GT-MEL simulates the cycling and transport of water and nutrients (C, N and P) within hillslopes and watersheds. The model runs on a daily time step and can be applied to user-defined landscape units that may vary in shape and size (m^2 to km^2). Thus, GT-MEL can provide detailed spatial and temporal information on nutrient acquisition and turnover in plants and soils, and terrestrial flow pathways and discharge of water and nutrients to surface waters. The same set of model equations applies to any terrestrial ecosystem – agricultural crops, forests, grasslands, wetlands, tundra, etc. GT-MEL simulates the effects of multiple interacting stressors, including changes in land use, land cover, climate, atmospheric CO_2 and N deposition.
ILWAS	Integrated Lake-Watershed Acidification Study	I	N	Gherini et al. (1985)	ILWAS was developed to predict changes in surface water acidity given changes in the acidity of precipitation and dry deposition. The model routes precipitation through the forest canopy, soil horizons, streams and lakes using mass balance concepts and equations which relate flow to hydraulic gradients. The physical-chemical processes which change the acid-base characteristics of the water are simulated by rate (kinetic) and equilibrium expressions and include mass transfers between gas, liquid and solid phases.
THMB/IBIS		I	N	6, 7	THMB is a mechanistic simulation model of large river systems that has been used recently in combination with a dynamic terrestrial ecosystem model IBIS to quantify nitrate flux in the Mississippi River Basin. The coupled models simulate time-varying flow and storage of water and N in rivers, wetlands, and reservoirs, based on major source inputs, subsurface drainage and N leaching, topography, and precipitation and evaporation. Evaluations of the model in the Mississippi basin indicated that the model accurately simulated inter-annual variability in the water and N budget from 1960 to 1994.
BIOME-BGC	Biome-BGC is a multi-biome generalization of FOREST-BGC	T	N	8	Biome-BGC is a computer program that estimates fluxes and storage of energy, water, carbon, and N for the vegetation and soil components of terrestrial ecosystems. The primary model purpose is to study global and regional interactions between climate, disturbance, and biogeochemical cycles.
DNDC	Denitrification-decomposition model	T	N	9	DNDC was initially developed to quantifying nitrous oxide (N_2O) emissions from agricultural soils in the U.S. The capability of the model to simulate soil biogeochemistry also allows DNDC to model emissions from other ecosystems through linkages with vegetation models; the model can be applied from field site to regional scales. The core of DNDC is a soil biogeochemistry model.
EPIC	Agricultural dynamic simulation model	T	N	11	EPIC is a widely used dynamic simulation model that describes the influence of agricultural management on crop productivity and erosion. The model has been used in studies of climate change, agricultural management and policy, and water-quality. EPIC simulates N cycling processes in soils-including mineralization, nitrification, immobilization, NH_3 volatilization and denitrification, runoff and subsurface leaching based on physical principles and parameter values derived from extensive model testing and specific field validation.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
GLEAMS	Groundwater Loading Effects of Agricultural Management Systems	T	N	12	GLEAMS was developed from both EPIC and CREAMS and employs a more explicit description of soil water content. In GLEAMS, the concentration of nitrate-N removed via denitrification is a function of the factors describing the soil water content, the soil temperature, and the organic C content. Under this formulation, denitrification only occurs if the soil water content is greater than a parameter related to the soil water content at field capacity and saturation. The fraction of soil nitrate- N lost to denitrification increases quickly as soil water content increases beyond the field capacity. The EPIC and GLEAMS method of simulating denitrification neglects denitrification that may occur in anaerobic micro-zones when the soil is not at field capacity or saturation.
Hole-in-the-pipe	Hole-in-the-pipe	T	N	Davidson et al. (2000)	The Hole-in-Pipe model relates the emissions of nitrous oxides to common soil processes. It regulates soil emissions of NO and N_2O at two levels: 1st, the rate of N cycling through ecosystems, which is symbolized by the amount of N flowing through the pipes, affects total emissions of NO and N_2O; 2nd, soil water content and perhaps other factors affect the ratio of N_2O:NO emissions, symbolized by the relative sizes of the holes through which nitric oxide and nitrous oxide "leak." Soil water content is so important because it controls the transport of O_2 into soil and the transport of NO, N_2O, and N_2
MERLIN	Model of Ecosystem Retention and Loss of Inorganic Nitrogen	T	N	Cosby et al. (1997), Kjonaas and Wright (1998)	MERLIN is a catchment-scale mass-balance model of linked carbon and N cycling in ecosystems for simulating leaching losses of inorganic N. It considers linked biotic and abiotic processes affecting the cycling and storage of N. The model is aggregated in space and time and contains compartments intended to be observable and/or interpretable at the plot or catchment scale. The structure of the model includes the inorganic soil, a plant compartment, and two soil organic compartments. Fluxes in and out of the ecosystem and between compartments are regulated by atmospheric deposition, hydrological discharge, plant uptake, litter production, wood production, microbial immobilization, mineralization, nitrification, and denitrification. N fluxes are controlled by carbon productivity, the C:N ratios of organic compartments and inorganic N in soil solution. Inputs include time series, constants, rates, source terms, and soil characteristics (Cosby, 1997).
NLM	Waquoit Bay Nitrogen Loading Model	T	N	RTI International (2001)	The Waquoit Bay Nitrogen Loading model estimates inputs from different N sources to defined land use categories and then estimates losses of N in various compartments of the watershed ecosystem, including the groundwater. This empirical N loading model produces long-term avg output. It is not currently endorsed by a federal agency but has been published in peer-reviewed journals. Most applications of the model have focused on the Cape Cod area of Massachusetts. The empirical data for this model are specific to that area and the model simulates N transport exclusively in the subsurface (i.e., overland transport is not considered).

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
Simple Mass Balance Method/Steady State Mass Balance	"Mass balance approach"	T	N	Bhattacharya et al. (2004), Likens et al. (1996), Rodriguez and Macias (2006)	Examples of two mass balance approaches are: Simple Mass Balance: This model is based on a balance of inputs and outputs of N according to the equation: Ndep + Nfix = Ni + Nu + Nad + Nde + Nfire + Neros + Nvol + Nle where the subscripts denote: dep (deposition); fix (fixation); i (immobilization); u (uptake); ad (adsorption); de (denitrification); fire (N loss during combustion); eros (erosion); vol (volatilization); le (leaching). Steady State Mass Balance: This method is the most commonly used method for analysis of critical loads of acid deposition. Its basic principle is based on identifying the long-term avg sources of acidity and alkalinity in order to determine the maximum acid input that will balance the system at a biogeochemical safe-limit. Several assumptions have been made in the steady state calculations. First, it is assumed that ion exchange is at steady state and there is no net change in base saturation or no net transfer of ANC from soil solution to the ion exchange matrix. It is assumed that for N there is no net denitrification, adsorption or desorption and the N cycle is at steady state. Sulfate is also assumed to be at steady state: no sulfide oxidation, sulfate uptake, sulfate permanent fixation or sulfate reduction are significant. Simple hydrology is assumed where there is straight infiltration through the soil profile.
HSPF/LSPC	Hydrological Simulation Program - FORTRAN	T*	S	12, 13	HSPF simulates watershed hydrology and water quality for conventional and toxic pollutants. HSPF incorporates watershed-scale ARM and NPS models into a basin-scale analysis framework that includes fate and transport in stream channels. It is a comprehensive model of watershed hydrology and water quality that allows the integrated simulation of land and soil contaminant runoff processes with In-stream hydraulic and sediment-chemical interactions. LSPC is a simplified version of HSPF. Although LSPC was designed to provide a less data intensive alternative to HSPF for modeling very large scale watersheds, it can also be used to model smaller, more detailed watersheds. The primary disadvantage of this simplified version of HSPF is that the developers eliminated the atmospheric deposition routines found in HSPF. For each model run, it automatically generates comprehensive text-file output by subwatershed for all land-layers, reaches, and simulated modules, which can be expressed on hourly or daily intervals. Output from LSPC has been linked to other model applications such as EFDC, WASP, and CE-QUAL-W2.
PLOAD	Pollutant Loading Model	T*	S	14	PLOAD is part of EPA's BASINS (Better Assessment Science Integrating Point and Nonpoint Sources) program and estimates nonpoint pollution sources on an annual basis. PLOAD can be combined with geographic information system (GIS)–based data coverages to rapidly estimate N loading to the bay using pass-through rates based on land uses from EPA guidance documents, literature, or other studies. This model is not precipitation driven; it does it include N speciation. However, the model does capture differences in N transport for different land uses in the watersheds.
SWAT	Soil and Water Assessment Tool	T*	S	van Griensven and Bauwens (2001), 15	SWAT is a public domain river basin scale model actively developed and primarily supported by the USDA (and included within EPA's BASINS framework), that quantifies the impact of land management practices in large, complex watersheds. SWAT is a physically based model that applies to all land uses and to include stormwater runoff in its calculations. The model simulates NH_3, nitrate, and organic N throughout the waterbodies and vegetation in the modeled system. At this time SWAT only accepts the nitrate concentration in the rain as the N atmospheric component.
WARMF	Watershed Analysis Risk Management Framework	T*	S	16	WARMF includes a GIS-based watershed model that calculates daily runoff, shallow groundwater flow, hydrology and water quality of a river basin. A river basin is divided into a network of land catchments (including canopy and soil layers), stream segments, and lake layers for hydrologic and water quality simulations. Inputs include meteorology, air quality, point source, reservoir release, and flow diversion data. WARMF also includes two watershed approach modules for Consensus building and TMDL calculation.

Model	Name	Type[1]	Support[2]	Reference[3]	Notes
DRAINMOD		T*	N	17	DRAINMOD quantifies N losses and transport from agricultural lands with shallow water tables where artificial drainage systems are used. Watershed-scale versions of DRAINMOD have been developed and evaluated based on data collected on a NC coastal plain. DRAINMOD is based on water balances in the soil and at the soil surface. It uses functional methods to quantify infiltration, subsurface drainage, surface drainage, evapotranspiration, seepage, freezing, thawing, snowmelt, and seepage. The model predicts the water Table depth and soil water contents above the water Table, drainage rates and the other hydrologic components on an hourly and daily basis for long periods of hydrologic record. Hydrologic predictions of the model have been tested and found to be reliable for a wide range of soil, crop, and climatological conditions.
INCA		T*	N	Wade et al. (2005)	INCA is a water and N mass balance simulation model; it estimates the integrated effects of point and diffuse N sources on stream nitrate and ammonium concentrations and loads and also estimates the N loads related to processes in the plant/soil system. It has been most commonly applied to watersheds within the UK, but more recently has been modified for use in other European watersheds. INCA quantifies plant uptake of nitrate and ammonium, nitrification, denitrification, and mineralization and immobilization within each land-use type and subcatchment. Biogeochemical reactions are limited to the soil zone from which water and N are leached to deeper groundwater.
LWWM	Linked Watershed/Waterbody Model	T*	N	18	The original release of the LWWM coupled the RUNOFF Block of the EPA's SWMM model (Version 4.21) with the EPA's Water Quality Analysis Program (WASP5). All components were accessed via a user-friendly operating shell. The LWWM included a GIS interface based on Arc/INFO to automate the reduction of spatial data within a watershed (i.e., land use and soils) for input into the RUNOFF Block of SWMM. The LWWM included pre-processors for inputting data into the RUNOFF Block of SWMM, WASP5 (Eutro and Toxi), and two hydrodynamic models associated with WASP5 (RIVMOD and DYNHYD5), as well as a graphical post-processor for the review of output from all model components. The post-processor was also the means by which nonpoint source loading files from RUNOFF were mapped to WASP segments.
ReNuM[a]	Regional Nutrient Management Model	T*	N	19	ReNuMa is based on the Generalized Watershed Loading Function (GWLF) model that has been used widely for purposes such as TMDL development. ReNuMa improves on GWLF by incorporating Net Anthropogenic N Inputs (NANI) accounting system. The model now considers atmospheric deposition, fertilizer application, septic system effluents, N fixation, and denitrification.
RHESS		T*	N	Boyer et al. (2006)	RHESS has been used to explore N dynamics at the watershed scale. RHESSys simulates the coupled effects of C, N, and hydrological processes by coupling biogeochemical dynamics from the BIOME_BGC and the NGAS model used in DAYCENT. Streamflow is based on the implementation of variable source-area concepts based on topography, quantifying routing of water through the landscape from patch to patch using either a lumped topographic approach adapted from TOPMODEL or a distributed approach adapted from the DHSVM model

Model	Name	Type[1]	Support[2]	Reference[3]	Notes

[1]Type: A = aquatic; I = integrated aquatic/terrestrial; T = terrestrial; T* = watershed
[2] Support: S = currently supported by EPA; N = currently not supported by EPA
[3]Websites:

1: River and Stream Water Quality Model (QUAL2K); http://www.epa.gov/athens/wwqtsc/html/qual2k.html
2: U.S.EPA's WASP Website; http://epawasp.com/
3: U.S. Army Core of Engineers Environmental Laboratory - Water Quality Models; http://el.erdc.usace.army.mil/products.cfm?Topic=model&Type=watqual
4: Hydroqual: Row Column AESOP (RCA) Modeling Code Description and Technical Capabilities; http://www.hydroqual.com/pdf/RCA_Desc_doc.pdf
5: Woods Hole Marine Lab, Ecosystems Center MEL home page http://ecosystems.mbl.edu/Research/Models/mel/welcome.htmll
6: IBIS (Integrated Biosphere Simulator); http://water.usgs.gov/software/hspf.html
7: THMB (Terrestrial Hydrology Model with Biogeochemistry) - formerly HYDRA; http://www.sage.wisc.edu/download/HYDRA/hydra.html
8: Biome-BGC: Terrestrial Ecosystem Process Model, Version 4.1.1; http://www.daac.ornl.gov/MODELS/guides/biome-bgc_guide.html
9: Denitrification Modeling Workshop: Model Summary; http://marine.rutgers.edu/BGC/RCNsite/WS1/WS1models/DNDC-2.pdf
10: EPIC Fact Sheet; http://www.brc.tamus.edu/epic/epfact2004.htm
11: GLEAMS Y2K Update Website; http://www.tifton.uga.edu/sewrl/Gleams/gleams_y2k_update.htm
12: U.S. EPA's HSPF Website; http://www.epa.gov/ceampubl/swater/hspf/
13: USGS's Water Resources Applications Software: HSPF Website; http://water.usgs.gov/software/hspf.htm
14: U.S. EPA's Better Assessment Science Integrating Point & Nonpoint Sources (BASINS) Website; http://www.epa.gov/waterscience/basins/
15: Soil & Water Assessment Tool; http://www.brc.tamus.edu/swat/
16: US EPA's Watershed Analysis Risk Management Framework (WARMF) Website; http://www.epa.gov/athens/wwqtsc/html/warmf.html
17: DRAINMOD Download Website; http://www.bae.ncsu.edu/soil_water/drainmod/
18: Linked Watershed Waterbody Model at the Southwest Florida Water Management District; http://www.swfwmd.state.fl.us/software/lwwm.htm
19: Regional Nutrient Management (ReNuMa) at Cornell University College of Agriculture and Life Sciences; http://www.eeb.cornell.edu/biogeo/nanc/usda/renuma.htm

A.3.3.1. Current Long-term Monitoring Data Sets Developed through the Hubbard Brook Ecosystem Study

CURRENT LONG-TERM MONITORING DATA SETS DEVELOPED THROUGH THE HUBBARD BROOK ECOSYSTEM STUDY

Physical/Hydrologic Monitoring

- Instantaneous streamflow (9 stations)
- Daily precipitation (24 stations)
- Class A weather station data
- Weekly snow depth on snow courses
- Daily soil temperature and moisture

Air Chemistry

- (SO_2, HNO_3, particulates, ozone)

Mirror Lake

- Instantaneous streamflow (3 inlets, outlet)
- Daily precipitation (2 stations)
- Weekly chemistry (3 inlets, outlet)
- Bi-monthly limnology (temp, chemistry, plankton)

Solution Chemistry

- Weekly bulk precipitation (6-10 stations)
- Monthly soil solution WS5, WS6
- Weekly stream at weirs of WS19
- Monthly stream within WS5, WS6

Organisms

- Bird populations
- Phytophagous insect populations WS2, WS4, WS5, WS6
- Vegetation biomass, chemistry

Soils

- Forest floor mass, chemistry (WS6, WS5; 5-yr intervals)
- Chemical and physical properties from soil pits (WS5)
- Chemical and physical properties from soil bags

ANNEX A - References

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Annex B. Acidification Effects

B.1. Effects on Biogeochemical Processes along Acidification Pathways

B.1.1. Atmospheric Deposition and Canopy Interaction

Inputs of N and S in wet, dry, and occult deposition first interact with the vegetative canopy. This interaction can occur a few centimeters above the ground in some alpine or grassland ecosystems to over 100 m above the ground in some forest canopies. In the canopy, deposited pollutants (especially N) can be taken up by the plants or by organisms that live within the canopy or on the leaf surface. Most of the deposited S moves as throughfall to the soil where it can be temporarily, or permanently, adsorbed on the soil. Sulfur that is not adsorbed on the soil moves readily into drainage water.

Earlier reviews (i.e., Hosker and Lindberg, 1982; Taylor et al., 1988) summarized information on the deposition of N to vegetation surfaces and interactions between pollutant deposition and canopy and leaf surfaces. Deposited N that is not taken up within the canopy then falls to the ground as throughfall, where plants, bacteria, and fungi compete for it. This competition for deposited N has long been known to play an important role in determining the extent to which N deposition will stimulate plant growth and the degree to which added N is retained within the ecosystem (U.S. Environmental Protection Agency, 1993). The available surface area of vegetation, onto which N gasses readily diffuse, has a significant effect on the dry deposition of N (Heil and Bruggink, 1987). Coniferous forests tend to increase deposition rates (both dry and wet) relative to deciduous forests, and landscape features such as elevation, aspect, and forest edge can play an important role in creating high levels of variability in deposition rates in complex terrain (Weathers et al., 2000).

B.1.2. Interactions with Soil

Air pollution is not the sole cause of soil acidity. High rates of soil acidification occur in low-deposition regions of the western U.S. because of internal soil processes, including tree N uptake and nitrification associated with extensive N fixation, for example on sites occupied by red alder trees (*Alnus rubra*) (Johnson et al., 1991b). Acidic deposition is not a necessary condition for having acidic soils, as evidenced by the common occurrence of acidic soils in unpolluted forests of the northwestern U.S. and Alaska (Johnson et al., 1991b).

B.1.2.1. Sulfur Retention and Release

Soils in the U.S. that most effectively adsorb SO_4^{2-} occur south of the maximum extent of glaciation that occurred during the most recent ice age (Rochelle and Church, 1987; Rochelle et al., 1987). Sulfate adsorption is strongly pH dependent, and a decrease in soil pH resulting from acidic deposition can enhance the ability of soil to adsorb SO_4^{2-} (Fuller et al., 1987).

Considerable effort in the 1980s went into the computation of S budgets for watersheds and forest plots, to evaluate 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 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). Through the 1990s little or no decrease in SO_4^{2-} concentrations occurred in streams below the glaciation line, despite regional decreases in atmospheric deposition of S (Webb et al., 2004). This lack of response has been generally attributed to the net release of adsorbed SO_4^{2-}, resulting from a shift in 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 and Morgan, 2000) also suggests 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. Additional information was obtained in the German study of Martinson et al. (2005) in which a "clean-roof" was used to exclude acidic deposition since 1989. Data collection enabled calibration of a model that predicted elevated concentrations of desorbed SO_4^{2-} in soil water for at least several decades. Although decreased levels of deposition are most likely resulting in net SO_4^{2-} desorption, limited research is available on sulfate desorption over time periods relevant to the time scale of decreased levels of S deposition (Johnson and Mitchell, 1998).

Numerous S budgets were also compiled in the 1980's for glaciated sites, and results generally indicated that inputs approximately equaled outputs on an annual basis (Rochelle et al., 1987). Little or no S retention at glaciated sites was attributed to relatively low SO_4^{2-} adsorption capacity in soils. Balanced S budgets implied that decreases in atmospheric deposition of S would lead directly to decreases in SO_4^{2-} leaching, and the strong correlation between decreases in atmospheric deposition and decreases in SO_4^{2-} concentrations in surface waters is widely recognized as an indication of this direct linkage (Stoddard et al., 2003). However, considerable evidence also indicates that S inputs in glaciated ecosystems do not behave conservatively, but instead are cycled through microbial and plant biomass (David et al., 1987; Alewell and Gehre, 1999; Likens et al., 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. (2001) estimated that annual S deposition at 11 sites in North America ranged from 1% to 13% of the organic S pool in soil.

Courchesne et al. (2005) measured a downward trend in water-soluble SO_4 from 1993 to 2002 in glaciated soils in Quebec, and attributed this response to net desorption of SO_4^{2-} rather than release of organically associated S. However, during this period, deposition of SO_4^{2-} was essentially unchanged. They attributed this discrepancy to a delay in the release of adsorbed SO_4^{2-} in response to a decrease in S deposition over the previous decade. These authors did not provide a mechanism to explain how desorption can continue under conditions of constant SO_4^{2-} inputs, however. On the basis of the abundant evidence of biological S cycling, it seems more likely that the delay observed by Courchesne et al. (2005) is the result of biological controls over the release of S.

Much of the organic S stored in soil is in carbon–bonded forms that are relatively unreactive, but can be mineralized to SO_4^{2-} in oxic conditions, typically found in moderately well-drained to well-drained soils (Johnson and Mitchell, 1998). 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., 2001). 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 et al., 2000; Lapenis et al., 2004). The study of Houle et al. (2001) did not find a relation between these factors, however. A Swedish “clean-roof” study also provides some insights into the role of organic S in possibly delaying recovery (Morth et al., 2005). After 9 years of pre-industrial levels of S deposition, the amount of S in runoff still exceeded inputs by 30%. Most of the S in runoff was attributed to mineralization of organic S in the O horizon.

B.1.2.2. Base Cation Depletion

Base cations are common in rocks and soils, but largely in forms that are unavailable to plants. There is a pool of bioavailable base cations (termed exchangeable base cations) that are adsorbed to negatively charged surfaces of soil particles. They can enter solution by exchanging with other dissolved cations including acidic cations such as H^+ or Al^{3+}. Base cations in this pool are gradually leached from the soil in drainage water, but are constantly resupplied through weathering. Weathering slowly breaks down rocks and minerals, releasing base cations to the pool of adsorbed base cations in the soil. The balance between base cation supply and base cation loss determines whether the pool of available base cations is increasing or decreasing in size. Net forest growth can also potentially lower exchangeable base cation concentrations through uptake of nutrient cations (Ca, Mg, and K), but these cations remain in the terrestrial ecosystem and can become available in the future through mineralization or canopy leaching. It has long been known that leaching of base cations by acidic deposition might deplete the soil of exchangeable bases faster than they are resupplied (Cowling and Dochinger, 1980). However, base cation

depletion of soils had not been demonstrated at the time of the last SO_X Air Quality Criteria Document (AQCD) (U.S. Environmental Protection Agency, 1982).

Data that clearly showed soil base cation depletion in the U.S. did not become available until the 1990s, although decreases in exchangeable Ca^{2+} concentrations between the periods 1947 to 1950 and 1987 to 1988 had been identified in European soils through repeated sampling (Billett et al., 1990; Falkengren-Grerup and Eriksson, 1990). In the only repeated sampling in the U.S. in which the original soil sample pre-dated acidic deposition, Johnson et al. (Johnson et al., 1994b) documented a decrease in exchangeable Ca^{2+} concentrations in both the O (combined Oa and Oe horizons) and B horizons from 1930 to 1984. Richter et al. (1994) also observed Ca^{2+} depletion in the B horizon from 1960 to 1990, in repeated sampling of Piedmont soil in South Carolina. The studies of Johnson et al. (Johnson et al., 1994b) and Richter et al. (1994) acknowledged the potential role of acidic deposition in causing the loss of Ca^{2+}, but focused on net forest growth as the primary cause.

Through reanalysis of archived soils, Lawrence et al. (1995) measured decreases in concentrations of exchangeable Ca^{2+} and acid-extractable Ca^{2+} in Oa horizons of spruce stands from 1969–70 to 1987–92 and presented relationships in soil chemistry that were not consistent with changes expected from vegetation uptake effects, but that could be explained by acidic deposition. Drohan and Sharpe (1997) also observed a decrease in Ca^{2+} concentrations in Oa and A horizons at 11 sites across Pennsylvania that were sampled in 1957 or 1959 and again in 1993, although effects of vegetation and acidic deposition were not distinguished.

The most thorough soil re-sampling study in the U.S. was conducted by Bailey et al. (Bailey et al., 2005) in northwestern Pennsylvania. Between 1967 and 1997, pronounced decreases, attributed largely to acidic deposition, were measured in exchangeable Ca^{2+} and Mg^{2+} concentrations in Oa/A horizons and throughout the B horizon. Courchesne et al. (2005) found higher concentrations of exchangeable Ca^{2+} in the O horizon (combined Oe and Oa horizons) in 2002 than in 1994 at one of three sampling areas within a 5.1 ha watershed, but no significant differences at the other two locations. No significant differences were found for exchangeable Mg^{2+} at the three locations in the O horizon. In the upper 10 cm of the B horizon, no significant differences were found in exchangeable Ca^{2+}, but at two of three locations, exchangeable Mg^{2+} concentrations were lower in 2002 than in 1994. The 8–year interval between sampling in this study is the shortest time in which changes in exchangeable base cations have been reported for North American soils.

In a regionally designed assessment of changes in soil-exchange chemistry, Sullivan et al. (2006a) found that base saturation and exchangeable Ca^{2+} concentrations in the Adirondack region of New York had decreased in the upper 10 cm of the B horizon between the mid 1980s and 2003, in watersheds of lakes with ANC less than 200 µeq/L. Soil chemistry in 36 lake watersheds in the mid 1980s was compared to soil chemistry in 32 lake watersheds in 2003. 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.

In a widely cited article, Likens et al. (1996) used a watershed mass balance approach to estimate changes in ecosystem Ca^{2+} pools at HBEF and found a sustained decrease in exchangeable Ca^{2+} concentrations from 1963 to 1993. The maximum depletion rate occurred in 1972, at the estimated peak in acidic deposition levels. The dependence on Ca:Na ratios to estimate Ca^{2+} weathering fluxes in this analysis adds uncertainty to the magnitude of changes reported for the exchangeable Ca^{2+} pool (Bailey et al., 2003). Two additional mass balance studies used Sr isotopes to evaluate changes in soil Ca^{2+} pools and fluxes. The study of Bailey et al. (1996) estimated substantial depletion rates in a watershed in the White Mountains of New Hampshire. Miller et al. (1993) estimated that inputs from weathering and atmospheric deposition approximately equaled leaching losses at a site in the Adirondack Mountains in New York. The different findings in these two studies are related to differences in the mineralogical composition of the respective soils. However, the Miller et al. (1993) study also estimated that 50 to 60% of the Ca^{2+} in vegetation and the forest floor was derived from the atmosphere, despite the fact that the weathering flux was estimated to be three times the rate of atmospheric inputs. This result suggests that Ca^{2+} supply from weathering in the lower profile is not reaching the upper soil where most root activity occurs, and that Ca^{2+} depletion has occurred in the upper soil.

The study of Yanai et al. (1999) investigated changes in Ca^{2+} and Mg^{2+} concentrations and content in northeastern hardwood stands over time intervals ranging from 10 to 21 years. The general conclusion of this study was that little or no change in O horizon (Oi, Oe, and Oa horizons) exchange chemistry occurred. However, a decrease in exchangeable Ca^{2+} concentrations in the Oa horizon was observed in this study at the HBEF from 1978 to 1997, although no change was observed in this soil in exchangeable Mg^{2+} concentrations, or Ca^{2+} or Mg^{2+} content in the Oa horizon. Results of this study were complicated by high spatial variability and differences in field sampling techniques between the original collection and the resampling (Yanai et al., 1999). Yanai et al. (2005) also found little difference over 15 years in exchangeable and extractable Ca^{2+} and Mg^{2+} concentrations in Oa horizons at 6 sites, and in O horizons (combined Oe and Oa horizons) at 13 sites, in hardwood stands in New Hampshire. In this study, it was also estimated that a difference greater than 50% would be needed to be statistically detected due to a large degree of spatial variability. Although most repeated sampling studies did identify decreases in exchangeable base cations in the Oa or O horizon, the results of Yanai et al. (2005) indicated that this change may not occur at all sites and may be difficult to detect in some soils due to inconsistencies in identifying horizon separations during sampling.

Through direct and inferred evidence of Ca^{2+} depletion, and additional research on soil processes, a detailed understanding of the mechanisms of Ca^{2+} depletion has developed over the past two decades.

Ulrich (1983) explained Ca^{2+} depletion as a three-stage process in which buffering of acidity in the mineral soil is first accomplished by weathering of carbonates and other mineral forms that weather relatively rapidly. Once these mineral forms are depleted, buffering is accomplished largely by cation exchange, in which H^+ is substituted for base cations and concentrations of exchangeable base cations decrease. Once the buffering capacity provided by cation exchange is depleted, acid neutralization is accomplished by weathering of crystalline minerals that contain large amounts of silicon (Si) and Al and relatively small amounts of base cations. At this stage, Al is mobilized within the soil and exchangeable Al concentrations increase. The shift in acid buffering from base cation exchange to alumino-silicate weathering and exchangeable Al was documented in Russian soils sampled three times over 75 years (Lawrence et al., 1995).

The effect of decreasing concentrations of exchangeable base cations on cation leaching in mineral soil was shown in simulation modeling by Reuss (1983). Below a base saturation of 20%, leaching of Ca^{2+} decreases substantially and becomes less sensitive to variations in acid inputs as base saturation decreases further. This relationship was later shown experimentally by Lawrence et al. (1999a). Samples from the upper B-horizon in nearly all of the Adirondack lake watersheds sampled by Sullivan et al. (2006a) had base saturation values less than 20%, as did soils at 11 sites in New York, Vermont, New Hampshire, and Maine in a regional study of mature spruce-fir forests (David and Lawrence, 1996). Exchangeable Ca^{2+} concentrations (expressed as a percentage of cation exchange capacity [CEC]) in the regional spruce-fir study were weakly correlated with an estimate of the relative weathering potential of parent material in the upper 10 cm of the B horizon ($r^2 = 0.44$). However, these factors were strongly correlated in the Oa horizon ($r^2 = 0.92$) (Lawrence et al., 1997). Because mineral weathering in the B horizon is the primary source of soil Ca^{2+}, a strong relationship between weathering potential and exchangeable Ca^{2+} concentrations would be expected in this horizon. The weak correlation suggests that concentrations of Ca^{2+} had decreased into the Al-buffering range sometime in the past. The parent material signature in the Oa horizon was likely maintained through vegetative recycling—uptake of Ca^{2+} from the O and B horizons, followed by transport back into the O horizon in litterfall.

In summary, evidence from repeated sampling and studies of soil processes indicate that decreases in exchangeable base cation concentrations in both Oa and B horizons are common and widespread in the eastern U.S. Factors such as logging and net forest growth are likely to have contributed to this decrease in varying degrees, but acidic deposition has played a major role (Lawrence et al., 1987; Huntington, 2000). The magnitudes and rates at which Ca^{2+} depletion has occurred are less clear.

These base cation depletion issues relate directly to the chemical recovery potential of acidified soils and surface waters. Replenishment of exchangeable base cation concentrations on soils will require that inputs from weathering and atmospheric deposition exceed losses from leaching and vegetative uptake. Inputs of Ca^{2+} from atmospheric deposition decreased sharply in the east through the 1980s

(Hedin et al., 1994), and have remained relatively stable since that time (http://nadp.sws.uiuc.edu/). Atmospheric deposition of SO_4^{2-} currently remains several factors higher than that of Ca^{2+} even at sites where SO_4^{2-} levels are relatively low (http://nadp.sws.uiuc.edu/), so chemical recovery at current acidic deposition levels will require inputs of base cations from weathering that are considerably greater than inputs from the atmosphere.

Because of the importance of weathering to the base-cation status of soils, a great deal of effort has been made to estimate in situ weathering flux with a variety of methods (Miller et al., 1993; Likens et al., 1996; Bailey et al., 2003). The complexity and variability of factors that affect weathering flux rates, such as soil mineralogy, particle surfaces, soil organic matter, moisture flux, and a host of other factors that are difficult to quantify, add large uncertainties to weathering flux estimates. Weathering rates estimated in geochemical models are generally assumed to be constant overtime, but lower weathering rates were observed in a soil sampled in 1987 than in the same soil sampled and archived in 1949–50 (Zulla and Billett, 1994). Further complexity in weathering flux rates results from the possible role of mycorrhizae in penetrating silicate minerals to extract base cations while remaining isolated from the soil solution (Van Breemen et al., 2000; Blum et al., 2002). Lastly, as yet unidentified sources of base cations may exist in forest soils. Bailey et al. (2003) found that elevated rates of Ca^{2+} loss from forest harvesting continued for 30 years after disturbance, but the source of the additional Ca^{2+} being lost could not be identified. Until estimates of in situ weathering fluxes are better constrained and more data become available from repeated soil sampling, predictions of recovery of exchangeable base cation concentrations will be highly uncertain.

B.1.2.3. Aluminum Mobilization

Through the natural process of podzolization, dissolved organic acids derived from partially decomposed organic matter in the O horizon move into the mineral soil where they weather soil particles and release Al into solution. As soil solution moves deeper into the profile, acidity is neutralized and Al is deposited as a secondary mineral or more likely as an organic Al (Al_o) complex (DeConinck, 1980). The limited mobility of organic anions results in retention of most Al within the mineral soil (often in the Bh horizon). Complexation with dissolved organic matter can increase the mobility of Al within the soil and lead to transport of organic Al into surface waters from shallow soils that are high in organic matter (Lawrence et al., 1986).

Increased concentrations of exchangeable 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. (1990), Falkengren-Grerup and Eriksson (1990), Bailey et al. (Bailey et al., 2005), and Lawrence et al. (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 et al., 1989; Lapenis et al., 2004), but Al depletion has not been documented in the U.S.

Increases in exchangeable Al concentrations in the O horizon have been documented over periods from 17 to 30 years (Lawrence et al., 1995; Drohan and Sharpe, 1997; (Bailey et al., 2005), although the study of Yanai et al. (2005) did not find consistent changes in Oa horizons over 15 years.

Numerous papers have evaluated solubility controls on Al in both the mineral soil and the O horizon. These papers have commonly related Al solubility to gibbsite ($Al(OH)_3$) or a gibbsite-like mineral to determine if inorganic Al concentrations could be predicted from gibbsite solubility constants and pH (e.g., Johnson et al., 1981; David and Driscoll, 1984; Cronan and Goldstein, 1989; Lawrence and David, 1977). These efforts have shown that inorganic Al concentrations are often undersaturated with respect to gibbsite and do not support Al-trihydroxide as the primary control in natural systems. Gibbsite solubility should therefore be considered a useful point of reference in evaluating Al-solubility rather a mineral form that is an important control of Al solubility in natural systems.

Through the 1990s, evidence accumulated to indicate that secondary Al in the mineral soil is in a form associated with organic matter, and in some soils, imogolite (Dahlgren and Walker, 1993; Mulder and Stein, 1994; Berggren and Mulder, 1995; Simonsson and Berggren, 1998; Skyllberg, 1999). Organic matter also plays a major role in controlling Al solubility in O horizons. This interaction has been described by Cronan et al. (1986) in O horizons through the bound Al ratio, which reflects the equivalents of adsorbed Al per mol of carboxyl groups (Cronan et al., 1986). Tipping et al. (1995) described Al solubility on organic and mineral soil horizons through equilibrium humic ion binding. Each of these approaches has had success in describing dissolved Al concentrations in organic soils as a function of pH through formulations that rely on concentrations of solid-phase organic bound Al. Further work has shown these relationships to be specific to the particular horizon, and the pool sizes of Al and humic substances (Lofts et al., 2001). However, inputs of acidity may alter concentrations of solid-phase organic bound Al (Lawrence and David, 1977). Changes in atmospheric deposition levels may therefore shift these relationships over time as soils further acidify or recover.

B.1.2.4. Soil Acidification

In the B horizon of soils north of the maximum extent of glaciation, CEC is largely derived from organic matter, whereas in older southern soils the surface charge of highly weathered clay minerals is the primary source of CEC. The CEC derived from organic matter is pH-dependent. Decreases in pH result in a decreases in CEC. In both cases, the CEC of the B horizon is much lower than in organic-rich surface horizons (Oa or A horizons). Less acidity from organic matter and a limited capacity for buffering due to low CEC makes the B horizon more susceptible to a lowering of pH from acidic deposition, and decreases in pH lower the CEC, further reducing the acid-buffering capacity from cation exchange. Two

studies in the U.S. have provided measurements to assess changes in soil pH in the B horizon from acidic deposition. Bailey et al. (Bailey et al., 2005) found lower pH values in the upper B horizon in northwestern Pennsylvania soils in 1967 than in 1997, at 50 cm depth ($p < 0.001$) and at 100 cm depth ($p < 0.001$), which were largely attributable to acidic deposition. Markewitz et al. (1998) also found pronounced decreases in soil pH down to 60 cm in highly weathered Piedmont soils from 1962 to 1990. The latter study was conducted in a former cotton field in which loblolly pines were planted in 1956–57. Forest regrowth undoubtedly played a large role in the soil pH changes that were measured, but atmospheric deposition was estimated to account for 38% of the H^+ inputs during the 28 years that elapsed between measurements.

Other studies in Europe have found similar decreases in soil pH of the B horizon that could be attributed, at least in part, to acidic deposition. These include the study of Lawrence et al. (Lawrence et al., 1995) in northwestern Russia, which documented decreases in soil pH in the B horizon down to 90 cm, from 1926 to 1964, and further decreases from 1964 to 2001. Acidic deposition was identified as the probable primary cause of decreasing pH in this study. The study of Lawrence et al. (Lawrence et al., 1995) also observed a decrease in CEC in this soil, as did a previous study of Russian soils (Lapenis et al., 2004). The decrease in pH was likely to have contributed to the decreased CEC of these soils, but a more important factor may have been a decrease in organic carbon concentrations that was also measured. To our knowledge, data to assess possible changes in CEC in soils in the U.S. has not become available, but change in CEC has implications for recovery potential of soils from acidic deposition effects (Sullivan et al., 2006b). Increased CEC driven by increases in pH could foster soil recovery by increasing the opportunity for adsorption of base cations, as soil solution becomes less acidic. Decreases in soil organic matter driven by climate and/or vegetation changes, such as those seen in Russian soils, would result in a decrease in acid-buffering capacity through cation-exchange. There are currently no data in the U.S. that indicate increases in soil pH associated with recent declines in acidic deposition levels. These data limitations make future projections of recovery of soil pH highly uncertain.

B.1.2.5. N Saturation

Severe symptoms of N saturation, have been observed in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains, as well as in the eastern hardwood watersheds at Fernow Experimental Forest near Parsons, WV and throughout the northeastern U.S. 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 et al., 1998).

Some examples of N-saturated forests in North America, including estimated inputs and outputs, are shown in Table B-1 (Fenn et al., 1998). The Harvard Forest hardwood stand in western Massachusetts

absorbed > 900 kg N/ha without significant NO_3^- leaching during an 8–year N amendment study (Fenn et al., 1998). In contrast, NO_3^- leaching losses were high at the Harvard Forest pine sites. In the 8–year experimental study, NO_3^- leaching was observed in the pine stand after the first year (1989) in the high-N application plots, and further increases were observed in 1995 and 1996. The hardwood stand did not show significant increases in NO_3^- leaching until 1996. The differences in response of the pine and hardwood stands indicate that the mosaic of community types across the landscape must be considered when evaluating landscape-scale responses to N deposition (Magill et al., 2000).

Utilization of N in the terrestrial ecosystem is accomplished through complex interactions between plants and microbes that are not fully understood (Schimel and Bennett, 2004). Long-term N retention is largely accomplished by incorporation of N into soil organic matter through biological assimilation (Aber et al., 1998), and to a lesser extent by abiotic processes that are not well understood (Dail et al., 2001). The forms in which N is assimilated by plants and microbes are determined by availability, as described in Schimel and Bennett (2004). In the most N-limited ecosystems, competition between plants and microbes is high and N is assimilated primarily in depolymerized organic forms, resulting in low mineralization rates and minimal buildup of inorganic N in the soil. Increased availability of N increases the mineralization rate, which enhances competition between plants and microbes for available NH_4^+ produced by mineralization. Further increase in the availability of N (for example by high levels of atmospheric N deposition) lessens competition for NH_4^+ between plants and microbes and leads to increased production of NO_3^- by autotrophic nitrifying bacteria. Some of this NO_3^- can be taken up by plants and microbes, but because much of the N demand is satisfied by NH_4^+ under these conditions, NO_3^- tends to be mobile within the soil, enabling it to leach to drainage water. Based on the definitions of Aber et al. (1989, 1998) and Stoddard (1994), the first stage of N saturation is reached when competition between plants and microbes for NH_4^+ has decreased to the point that net nitrification occurs.

Substantial leaching of NO_3^- from forest soils to streamwater can acidify downstream waters (Webb et al., 1995), eutrophy estuaries and marine waters (Fisher and Oppenheimer, 1991), and deplete soils of nutrient base cations, especially Ca^{2+} and Mg^{2+} (Likens et al., 1998). Considerable evidence is available to link N deposition to acidification of soils. Much of this evidence comes from the northeastern U.S., where increased accumulation of N in soil is suggested by a strong positive correlation between atmospheric deposition levels and total N concentration in the Oa horizon, at sites in New York, Vermont, New Hampshire, and Maine (Driscoll et al., 2001b). Further evidence that atmospheric deposition has increased availability of N in soil is shown by a strong negative correlation between atmospheric deposition levels and the C:N ratio of the Oa horizon in this region (Aber et al., 2003). If the C:N ratio falls below about 25, nitrification is stimulated, resulting in elevated NO_3^- in surface waters (Aber et al., 2003). Similar results were found in Europe, where a C:N ratio of 24 was identified as the critical level below which nitrification occurred (Emmett et al., 1998).

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. Stoddard (1994) presented a geographical analysis of patterns of watershed loss of N throughout the northeastern U.S. He identified approximately 100 surface water sites in the region with sufficiently intensive data to determine their N status. Sites were coded according to their presumed stage of N retention, and sites ranged from Stage 0 (background condition) through Stage 2 (chronic effects). The geographic pattern in watershed N retention depicted by Stoddard (1994) followed the geographic pattern of N deposition. Sites in the Adirondack and Catskill Mountains in New York, where N deposition was about 11 to 13 kg N/ha/yr, were typically identified as Stage 1 (episodic effects) or Stage 2. Sites in Maine, where N deposition was about half as high, were nearly all Stage 0. Sites in New Hampshire and Vermont, which received intermediate levels of N deposition, were identified as primarily Stage 0, with some Stage 1 sites. Based on this analysis, a reasonable threshold of N deposition for transforming a northeastern site from the "natural" Stage 0 condition to Stage 1 would correspond to the deposition levels found throughout New Hampshire and Vermont, approximately 8 kg N/ha/yr. This agreed with Driscoll et al.'s (1989) interpretation, which would probably correspond to total N inputs near 8 to10 kg N/ha/yr. This is probably the approximate level at which episodic aquatic effects of N deposition would become apparent in many watersheds of the eastern U.S.

Analysis of data from surveys of N outputs from 65 forested plots and catchments throughout Europe were conducted by Dise and Wright (1995) and Tietema and Beier (1995). Below the throughfall inputs of about 10 kg N/ha/yr, there was very little N leaching at any of the study sites. At throughfall inputs greater than 25 kg N/ha/yr, the study catchments consistently leached high concentrations of inorganic N. At intermediate deposition values (10 to 25 kg N/ha/yr), Dise and Wright (1995) observed a broad range of watershed responses. Nitrogen output was most highly correlated with N input ($r^2 = 0.69$), but also significantly correlated with S input, soil pH, percent slope, bedrock type, and latitude. A combination of N input (positive correlation) and soil pH (negative correlation) explained 87% of the variation in N output at the study sites (Dise and Wright, 1995).

The threshold level of atmospheric deposition that causes release of NO_3^- to surface waters was identified by Aber et al. (Aber et al., 2003) as approximately 7 kg N/ha/yr for the northeastern U.S. In watersheds receiving N deposition above this level, concentrations of NO_3^- in surface waters were positively correlated with atmospheric deposition, whereas most watersheds with deposition less than 7 kg/ha/yr had little or no NO_3^- (undetectable at most sites) in their surface waters (Aber et al., 2003). The threshold value of 7 kg/ha/yr was based on atmospheric deposition levels for the base of forested

watersheds. When scaled to include higher deposition levels expected at upper elevations this value was estimated to equal about 10 kg/ha/yr, similar to the European estimate of Dise et al. (1998).

The common deposition threshold for release of NO_3^- to surface waters in forested watersheds found in the northeastern U.S. and Europe represents an important advance in relating N inputs to ecosystem effects, but a considerable amount of variability in ecosystem response has also been demonstrated. Lovett et al. (2000b) found that 39 watersheds in the Catskill region of New York State retained from 49% to 90% of atmospheric N inputs. Castro and Morgan (2000) showed that NO_3^- export from watersheds in eastern North America can range from nearly 0 to over 400 eq/ha/yr in watersheds that receive similar levels of inorganic N in wet deposition in the range of 400 to 500 eq/ha/yr.

Experimental additions of N to plots and watersheds have also demonstrated variations in terrestrial retention of N. Additions of N (approximately twice ambient deposition) to hardwood 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 (Kahl et al., 1993a; Peterjohn et al., 1996). 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, whereas nitrification was not triggered until the third year in plots receiving 19.8 kg N/ha/yr (McNulty et al., 1996). Similar results to these were seen in two studies from Colorado. Additions of 25 kg N/ha/yr to old-growth spruce 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 (Rueth et al., 2003). A comparison study of old-growth spruce plots across a depositional gradient in Colorado 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 (Rueth and Baron, 2002). 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, which received additions of 150 kg N/ha/yr (Magill et al., 2004). Concentrations of ($NO_3^- + NH_4^+$) in hardwood plots receiving 50 kg N/ha/yr were not yet detectable in the 15th year of treatments. The same treatments were applied to red pine (*Pinus resinosa*) plots, which exhibited elevated concentrations of ($NO_3^- + NH_4^+$) in soil water after 1 year of 150 kg N/ha/yr doses, and after 5 years of 50 kg N/ha/yr doses.

In general, deciduous forest stands in the eastern U.S. have not progressed toward N-saturation as rapidly or as far as spruce-fir 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 spruce-fir forests. 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 excess inputs of N (Aber et al., 1998). Indeed, many of the lower elevation deciduous stands are N-deficient and are therefore likely to benefit (i.e., grow faster), at least up to a point, with increased inputs of N.

There are examples of N saturation in lower-elevation eastern forests, especially in West Virginia. For example, progressive increases in streamwater NO_3^- and Ca^{2+} concentrations were measured at the Fernow Experimental Forest in the 1970s and 1980s (Edwards and Helvey, 1991; Peterjohn et al., 1996; Adams et al., 1997, 2000). 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.

Varying responses to N additions reflect differences in N status of the treatment sites. These variations have most often been attributed to disturbance history, dating back a century or more (Goodale and Aber, 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. Nitrogen 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.

Although considerable progress has been made in understanding the factors that control N retention, efforts to quantify net N retention through known processes have not been fully successful. Assimilation of N by mycorrhizae followed by exudation as dissolved organic matter was proposed by Aber et al. (1998) as a possible explanation for unaccounted conversion of inorganic N into soil organic matter. However, Frey et al. (2004) found that elevated N inputs reduced active mycorrhizal biomass, fungal diversity and fungal:bacterial biomass ratios. These results suggested a decreased role for mycorrhizae in fixation of N under elevated N inputs.

Abiotic transformation of inorganic N into soil organic matter has also been proposed as a possible mechanism to explain high rates of N retention in soil, and some evidence has been presented to support this possibility. Dail et al. (2001) observed retention of $^{15}NO_3-$ and $^{15}NO_2$ in sterile soil, but the method of sterilization may have increased dissolved organic carbon (DOC) concentrations and artificially increased the opportunity for formation of soluble organic N compounds. Davidson et al. (2003) developed the ferrous wheel hypothesis to explain incorporation of inorganic N into organic matter. The hypothesized mechanism involves conversion of NO_3^- to NO_2^- through oxidation of Fe_2^+. Testing of this hypothesis *in situ* was not found in the literature, but the small amount of Fe_2^+ that typically occurs in the forest floor, where presumably much of the conversion to organic N occurs, may limit the importance of this pathway.

Fitzhugh et al. (2003) showed that NO_2^- produced in the first step of nitrification may be directly converted to soluble organic N rather than becoming fully oxidized to NO_3^-. However, concentrations of introduced $^{15}NO_2$ in this experiment were several orders of magnitude higher than that normally seen in forest soils. Therefore, the evidence at this time for abiotic retention of N is not fully convincing, and the importance of this process requires further research.

In addition to our limited understanding of N retention mechanisms, there is no direct information on ecosystem recovery from N saturation in the U.S. This may be at least partly because atmospheric deposition of N has been relatively stable in the eastern U.S. over the past two to three decades. An important source of information on N recovery responses has been provided by the European NITREX study, which reduced ambient N deposition for 5 years with roofs constructed over experimental plots in Germany and The Netherlands. At the German site, deposition was reduced from approximately 38 kg N/ha/yr to levels that varied from 10 to 20 kg N/ha/yr. At the Dutch site, deposition was reduced from 45 kg N/ha/yr to levels that varied from 1 to 10 kg N/ha/yr. At both of these sites, deposition levels before the experiment were approximately three to four times greater than the highest deposition levels commonly found in the eastern U.S., whereas after the reduction, levels at the Dutch site fell within the range of deposition in the eastern U.S. over the past two decades, and values at the German site were somewhat higher than this range (Ollinger et al., 1993); Emmett et al., 1998). The decrease in ambient N inputs resulted in a marked decrease in N outputs at each site within 2 to 3 years. The responses at the two sites were somewhat different, however. At the Dutch site, outputs of N exceeded inputs both before and after experimental reduction of inputs. At the German site, inputs exceeded outputs before and after reduction of inputs, but outputs were more similar to inputs after the reduction. At both sites, outputs after the reduction in deposition remained two to three times higher than outputs commonly measured in the eastern U.S.

Thus, atmospheric deposition of N has increased N availability in soils, which has led to increased nitrification and associated acidification of soil and soil water. The N retention capacity of soils is strongly dependant on land-use history, however, so the relationships between N deposition and ecosystem N status and percent of terrestrial retention are variable. In general, however, atmospheric deposition of 10 kg N/ha/yr or higher is required for appreciable amounts of NO_3^- to leach to surface waters in the eastern U.S. and northern Europe. Future projections of chemical recovery from N-driven acidification are uncertain because (1) retention mechanisms are not fully understood, and (2) there are only limited data on recovery responses. European experiments that reduced inputs of N found decreased outputs of N within 2 to 3 years, which indicates a relatively rapid response to decreased deposition levels. However, these studies are difficult to directly apply to the U.S. because deposition levels were much higher at the European sites prior to the experiment, and the 5–year duration of the experiments

only demonstrated recovery to levels of N saturation that are higher than the more heavily affected sites in the eastern U.S.

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 et al., 1994; Williams et al., 1996a,b), the Allegheny Mountains of West Virginia (Gilliam et al., 1996), the Catskill Mountains of New York (Murdoch and Stoddard, 1992; Stoddard, 1994), the Adirondack Mountains of New York (Wigington et al., 1996), and the Great Smoky Mountains in Tennessee (Cook et al., 1994). All of these regions, except Colorado, received relatively high (more than about 10 kg N/ha/yr) atmospheric deposition of oxidized N throughout the 1980s and 1990s. In contrast, the Front Range of Colorado receives less than about 4 or 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 these other locations. The cause of N-saturation at high-elevation western watersheds that receive low to moderate levels of atmospheric deposition has been a subject of debate. High concentrations of NO_3^- in surface waters in the western U.S. are not widespread. Nitrate concentrations during the fall sampling season were low in most western lakes sampled in the Western Lakes Survey (WLS). 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. Cold temperatures in such lakes undoubtedly play an important role in maintaining high NO_3^- concentrations by limiting biological uptake processes. The high NO_3^- concentrations are likely to affect acid-base chemistry only where ANC is low. Eight lakes showed high NO_3^- (>10 µeq/L) and low ANC (<50 µeq/L), all of which occurred at elevations higher than 3,100 m. Four were located in Colorado, two in Wyoming, and one each in California and Utah. In all cases, pH was above 6.5 and ANC was greater than or equal to 15 µeq/L. Such lakes are sensitive to episodic pulses of NO_3^- acidity; such pulses have been reported from Colorado Front Range lakes (Williams and Tonnessen, 2000). Episodic acidification of western lakes could be important biologically.

In the Uinta Mountains of Utah and the Bighorn Mountains of central Wyoming, 19% of the lakes included within the WLS had $NO_3^- > 10$ µeq/L. This suggests that N deposition in these areas may have exceeded the capability of these systems 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.

Williams et al. (1996a,b) contended 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. Although biological N demand may be high in subalpine forests, uptake is limited in alpine areas by large N inputs from snowmelt, steep

watershed gradients, rapid water flushing, extensive areas having little or no soil development, and limitations on the growth of phytoplankton in some alpine lakes by factors other than N (e.g., phosphorus [P], temperature) (Baron et al., 1994).

B.1.2.6. Nitrate Leaching

Nitrate leaching losses from soils to drainage waters are governed by a complex suite of ecosystem processes in addition to N inputs from atmospheric deposition. In particular, mineralization and nitrification processes play important roles in regulating the quantity of, and temporal variability in, the concentration of NO_3^- in soil solution, and consequently leaching losses from the rooting zone (Reuss and Johnson, 1985; Joslin et al., 1987; Johnson et al., 1991b,c). Thus, NO_3^- leaching is mostly under biological control and typically shows pronounced seasonal variability (Van Miegroet et al., 1993). Peak concentrations of NO_3^- in soil solution appear to be largely responsible for the potentially toxic peaks in Al concentration that sometimes occur in soil solution, although SO_4^{2-} may also play a role by serving to elevate chronic Al concentrations (Eagar et al., 1996).

High leaching of NO_3^- in soil water and streamwater draining high-elevation spruce-fir forests has been documented in numerous studies in the Southern Appalachian Mountain region (cf. Joslin et al., 1992; (Joslin et al., 1992)Van Miegroet et al., 1992a,b; Joslin and Wolfe, 1994; Nodvin et al., 1995). This high NO_3^- leaching has been attributed to a combination of high N deposition, low N uptake by forest vegetation, and inherently high N release from soils. Forest age is another major factor-affecting uptake, with mature forests requiring minimal N for new growth and, hence, often exhibiting higher NO_3^- leaching that younger, faster growing stands (Goodale and Aber, 2001). Old-growth red spruce stands in the Southern Appalachians have been demonstrated to have significantly slower growth rates than stands younger than 120 years (Smith and Nicholas, 1999). The latter feature is associated with low C:N ratios in mineral soil, high N mineralization potential and high nitrification (Joslin et al., 1992)Eagar et al., 1996).

In most terrestrial ecosystems in the U.S., N is strongly retained and there is limited mobility of NO_3^-. Exceptions to this pattern tend to occur in spatially limited regions that receive high levels of total N deposition (higher than about 10 to 20 kg N/ha/yr) and in alpine and subalpine environments that have little soil or vegetative development over substantial portions of the watersheds.

B.1.3. Interactions with Transitional Ecosystems

B.1.3.1. S Storage and Release in Transitional Ecosystems

Although S is generally mobile in upland soils in most parts of the U.S., wetlands act as both sources and sinks of atmospherically deposited S. Wetlands retain and release S in response to variations

in hydrology, which in turn affect oxidation and the reduction process in wetland soils. Ito et al. (2005) evaluated the influence of land cover types on SO_4^{2-} fluxes in Adirondack lake watersheds. They found that SO_4^{2-} concentration in drainage water decreased in association with increased wetland area within the lake watershed (adj. $r^2 = 0.58$, $p \geq 0.001$). They attributed this observed pattern to dissimilatory SO_4^{2-} reduction in anaerobic wetland soils.

Sulfur storage in wetland soils to some degree prevents or delays the acidification of downstream surface waters with mineral acidity. However, the water table in wetland areas typically drops during drought conditions, and this allows development of aerobic conditions in surface wetland soils. Under aerobic conditions, stored S is re-oxidized to SO_4^{2-}, which can then be rapidly mobilized under high-flow conditions that occur in response to rainfall or snowmelt. This can cause substantial episodic pulses of acidity in surface waters that receive drainage water from wetlands. Thus, wetlands buffer downstream receiving waters against chronic acidity to some degree, but can be an important source of periodic episodes of more extreme acidity.

B.1.3.2. Organic Acidity in Transitional Ecosystems and Downstream Surface Waters

Organic acids in fresh water originate from the degradation of biomass in upland areas, wetlands, near-stream riparian zones, the water column, and stream and lake sediments (Hemond, 1994). The watersheds of surface waters that have high concentrations of organic matter (DOC > about 400 µM) often contain extensive wetlands and/or extensive organic-rich riparian areas (Hemond, 1990; Sullivan, 2000).

Organic acids contributed by wetlands to downstream drainage waters can influence surface water acid-base chemistry, particularly in dilute waters having moderate to high (greater than about 400 µM) DOC concentrations. Organic acids in surface waters include a mixture of functional groups having both strong and weak acid character. Some lakes and streams are naturally acidic as a consequence of organic acids contributed to solution by wetlands. The presence of organic acids also provides buffering to minimize pH change in response to changes in the amount of SO_4^{2-} and NO_3^- derived from acidic deposition.

There are many lakes and streams that are chronically acidic or low in ANC mainly due to the presence of organic acids. In many cases, the principal source of these organic acids is the wetlands within the watershed. The NAPAP (1991) concluded that about one-fourth of all acidic lakes and streams surveyed in the National Surface Water Survey (NSWS) (Linthurst et al., 1986a; Kaufmann et al., 1988) were acidic largely as a consequence of organic acids. A survey of 1400 lakes in the Adirondack Mountains by the Adirondack Lake Survey Corporation (ALSC) (Kretser et al., 1989), which included many small lakes and ponds (1 to 4 ha) having relatively high DOC, revealed that about 38% of the lakes

had pH < 5 due to the presence of organic acids, and that organic acids generally depressed the pH of Adirondack lakes by 0.5 to 2.5 pH units in the ANC range of 0 to 50 μeq/L (Baker et al., 1990b).

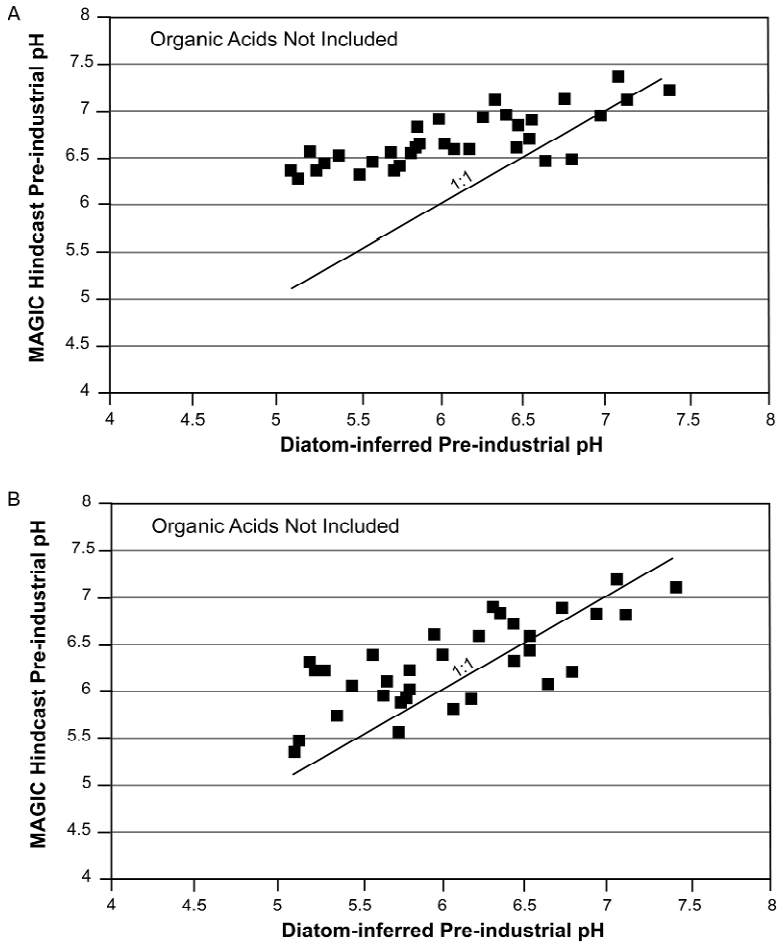
Specification of the acid-base character of water high in DOC is somewhat uncertain. Attempts have been made to describe the acid-base behavior of organic acids using a single H^+ dissociation constant (pK_a), despite the fact that organic acids in natural waters are made up of a complex mixture of acidic functional groups. A portion (perhaps one-third) of the acidity in organic acids is quite strong, with some ionization occurring at pH values well below 4.0 (Driscoll et al., 1994; Hemond, 1994). A number of modeling approaches have been used to estimate the acidity of organic acids in fresh waters, often as simple organic acid analogs having different pK_a values (Oliver et al., 1983; Perdue et al., 1984; Driscoll et al., 1994).

The importance of naturally occurring organic acids as agents of surface water acidification was reinforced by a modeling study (Sullivan et al., 1996a) that showed that inclusion of organic acids in the Model of Acidification of Groundwater in Catchments (MAGIC) had a substantial effect on model predictions of surface water pH, even in waters where DOC concentrations were only moderate. MAGIC hindcasts of pre-industrial lakewater pH of Adirondack lakes showed poor agreement with diatom inferences of pre-industrial pH when organic acids were not considered in the MAGIC model (Sullivan et al., 1996a). Revised MAGIC hindcasts of pre-industrial lakewater pH that included an organic acid representation (Driscoll et al., 1994) showed considerably closer agreement with diatom inferences (Figure B-1). The mean difference between MAGIC and diatom estimates of pre-industrial pH was reduced from 0.6 pH units to 0.2 pH units when organic acids were included in the model, and the agreement for individual lakes improved by up to a full pH unit (Sullivan et al., 1996a).

Rosenqvist (1978) and Krug et al. (Krug et al., 1985) hypothesized that a significant component of the mobile acid anions contributed from atmospheric deposition (e.g., SO_4^{2-}, NO_3^-) replace organic anions that were previously present in solution. Under this anion substitution hypothesis, the net result of acidic deposition is not so much an increase in cations (including potentially toxic H^+ and Al^{n+}) as much as an exchange of SO_4^{2-} and NO_3^- anions for organic anions, with little or no change in ANC and pH. This hypothesis has received some support from paleolimnological studies, which suggested historic decreases in DOC concentrations during the period of lakewater acidification in the 1900s (Davis et al., 1985a,b; Kingston and Birks, 1990; Dixit et al., 2001). Other studies have found a decrease in organic acidity which was at least partly attributable to the extent of organic acid protonation. David et al. (1999) measured a decrease in organic anion concentrations in stream water in response to the experimental whole-watershed acidification experiment at the Bear Brook Watershed in Maine. Wright et al. (1993) concluded that ANC increases in a small watershed in Norway, where rates of acidic deposition were experimentally reduced, were limited by the increasing role of organic acids that accompanied decreasing acid deposition load.

Complexation of organic acids by metals (Almer et al., 1974; Lind and Hem, 1975; Dickson, 1978; Cronan and Aiken, 1985) and pH-dependent changes in dissociation of organic acids (Oliver et al., 1983; Wright et al., 1988a) are probably important components of the organic acidity response. Loss of DOC in response to acidic deposition can also cause a shift in Al species composition towards lesser complexation with organic ligands. Such a shift from AL_o to Al_i increases toxicity of the Al to aquatic biota (Baker and Schofield, 1982). Changes in pH can alter the charge density of organic solutes and thus influence organic contributions to acidity (e.g., Wright et al., 1988a,b). David et al. (1999) found that the charge density of organic acids decreased by about 1 µeq/L/mg C at West Bear Brook in Maine, in response to 6 years of experimental acidification, probably due to greater protonation of organic acid anions at the lower pH. Similar results were reported by Lydersen et al. (1996) at Lake Skjervatjern in Norway. Values of the organic acid charge density in the ALSC lakes in the Adirondack Mountains increased with increasing pH between pH values of 5.0 to 7.0 due to the presence of weakly acidic functional groups (Driscoll et al., 1994).

Hedin et al. (1990) artificially acidified a small, moderately high-DOC (725 µM C) stream with H_2SO_4 at HBEF in New Hampshire. Streamwater pH (4.4) was near the range of reported average pK_a values for organic acids, suggesting that the capacity of organic acids to buffer mineral acidity should be high. The acid loading rate was adjusted to achieve an increased streamwater SO_4^{2-} concentrations of 150 µeq/L at the downstream sampling point 108 m below the point of acid addition. Adjustments were made for dilution by soil water or inflow from small tributaries. Although streamwater DOC did not change significantly, the concentration of organic anions (as calculated from the charge balance) decreased by 17 µeq/L. Thus, the overall capacity of organic anions to neutralize mineral acid inputs offset about 11% of the added acid (Hedin et al., 1990). This experiment only considered interactions between mineral acid and organic matter within the stream. Any additional buffering that may have been provided within the terrestrial catchment was not represented in the experimental design. Also, any possible catchment-mediated influences of the experimental acidification on organic acid properties or terrestrial DOC mobilization were excluded from the experiment because the acid was not applied to the catchment soils.



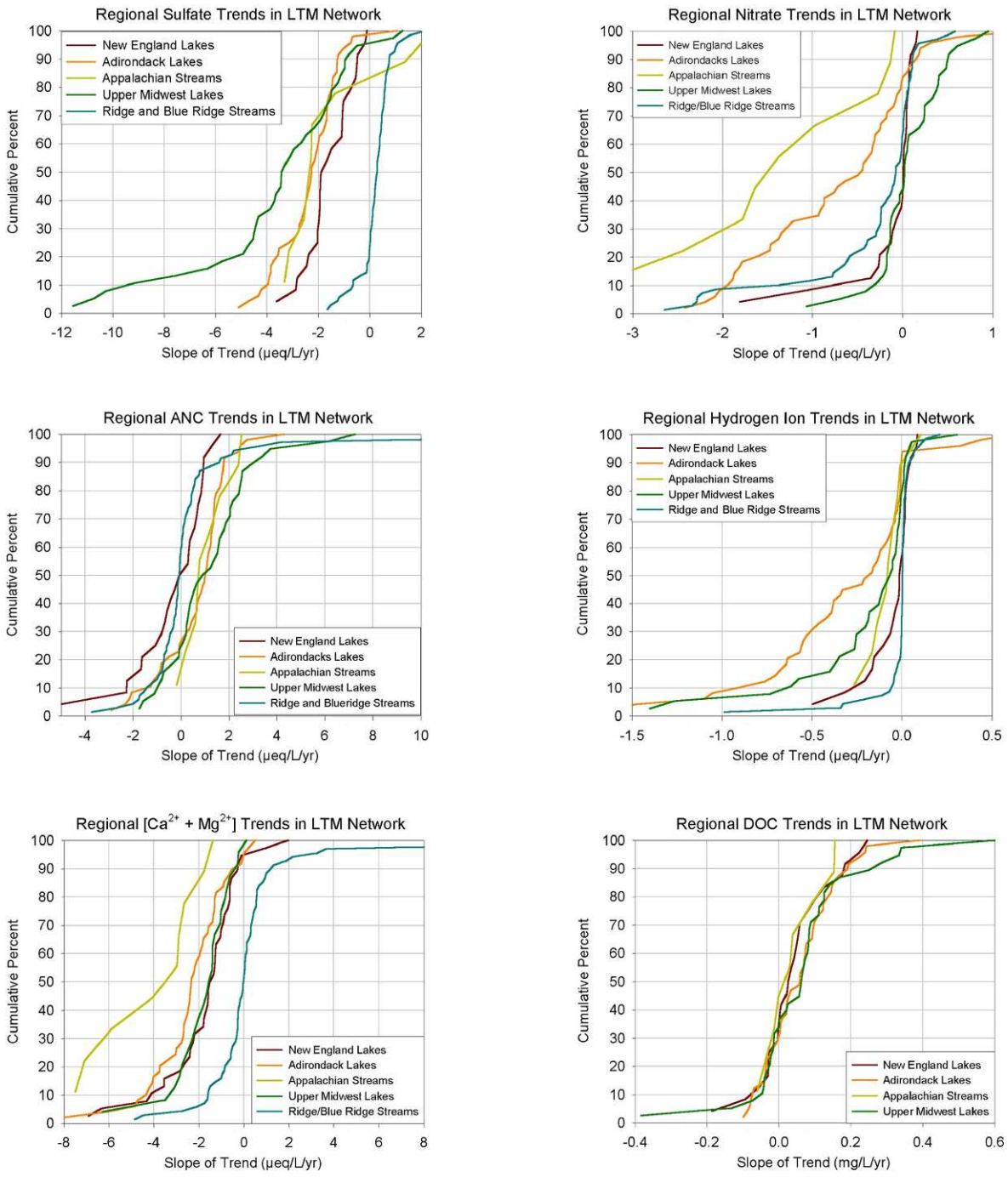
Source: Sullivan et al. (1996).

Figure B-1. MAGIC model hindcast estimates of pre-industrial pH versus diatom-inferred pH for 33 statistically selected Adirondack lakes: a) without including organic acid representation in the MAGIC simulations, and b) including a triprotic organic acid analog model in the MAGIC simulations.

Results of a resurvey of 485 Norwegian lakes sampled in both 1986 and 1995 provided evidence in support of an increase in organic acid anion concentrations in association with decreased lakewater SO_4^{2-} concentration (Skjelkvåle et al., 1998). The organic acid anion concentration increased by an amount equal to between 9% and 15% of the decrease in SO_4^{2-}concentration in the four regions of the country most heavily affected by the decrease in S deposition during the intervening 10 year period. Lakewater SO_4^{2-} concentrations decreased by 9 µeq/L (western and northern Norway) to 20 to 21 µeq/L (eastern and southern Norway). Only in mid-Norway, where average SO_4^{2-} concentration decreased by only 6 µeq/L, did the organic acid anion concentration remain unchanged between 1986 and 1995 (Skjelkvåle et al., 1998).

Recent monitoring data have shown that DOC and organic acid anion concentrations in many lakes and streams in the U.S. have increased in association with decreased S deposition. It is likely that a high percentage of this DOC originates from wetland soils within the monitored watersheds. This result

appears to be partly responsible for the limited lakewater ANC and pH recovery that has occurred at many locations. The response of surface waters to changes in acidic deposition has included a general increase in surface water DOC (Figure B-2). All regions of the eastern U.S. analyzed by Stoddard et al. (2003) that had sufficient DOC data for analysis exhibited increases in DOC concentrations during the 1990s. All regional trends were significant with the exception of the Northern Appalachian Plateau, the region with the lowest median DOC concentration. The median increase in DOC of 0.05 mg/L/yr reported by Stoddard et al. (2003) corresponds to an overall increase of about 10% across study regions, similar to trends reported elsewhere in the northern hemisphere (Evans and Monteith, 2001; Skjelkvåle et al., 2001). This suggests a common cause. Both climate warming and decreasing acidic deposition are possible causal agents.



Source: Stoddard et al. (2003).

Figure B-2. Cumlative frequency diagram (distribution) of slopes for SO_4^{2-} , NO_3^-, Gran ANC, hydrogen ion, [Ca^{2+} + Mg^{2+}], and DOC concentrations in LTM surface water monitoring sites, by region, for the period 1990–2000. The Ridge/Blue Ridge Province did not have sufficient DOC data to allow trend analysis.

B.2. Factors That Determine Ecosystem Sensitivity

B.2.1. Transitional Ecosystems

B.2.1.1. Wetlands and Peatlands

Wetlands and peatlands often contain highly acidic soils. Their acidity is mainly attributable to the presence of large quantities of naturally occurring organic materials. Fulvic and humic acids, formed during the breakdown of organic matter, contribute substantial organic acidity to soil and surface waters in wetland and peatland environments. In the case of ombotrophic bogs and poor fens, there is also a scarcity of base cations, which would serve to buffer both organic and mineral acidity.

Because wetland and peatland vegetative communities are adapted to high levels of natural organic acidity, it is unlikely that S or N deposition would cause any acidification-related effects at levels of acidic deposition commonly found in the U.S. Nevertheless, wetlands are closely tied to a number of important biogeochemical processes that regulate watershed response to acidic deposition. The major interactions are described below.

High concentrations of DOC in brownwater lakes and streams are often due to the influence of wetlands on hydrography within the watershed. This presence of high concentrations (higher than about 500 µM) of DOC can substantially reduce the pH and ANC of surface waters, buffer those waters against pH changes in response to added mineral acidity, and form stable complexes with dissolved Al, thereby reducing its toxicity to aquatic life. Therefore, the response of surface waters to acidic deposition is strongly influenced by the extent of upstream and shoreline wetland development.

Wetlands also serve as a (sometimes-temporary) sink for atmospheric S and N. Chemical reduction reactions and biological uptake contribute to S and N storage in wetland soils. Oxidation during drought periods, when water levels recede, followed by flushing from wetland to downstream surface water during subsequent storm flow, can cause substantial pulses of mineral acidity in downstream receiving waters. On a chronic basis, the concentration of SO_4^{2-} (and associated acidity) in surface water can be substantially lower as a consequence of dissimulatory S reduction in upslope wetlands. On an episodic basis, wetlands can contribute to wide fluctuations in downstream surface water acid-base chemistry. Such fluctuations can include pulses of acidity that may be toxic to aquatic biota.

Wetlands provide anaerobic substrate for S-reducing bacteria. These bacteria are also partly responsible for the increased rate of mercury (Hg) methylation that is known to occur in wetlands. As a consequence, fish in lakes drained by wetlands often have much higher concentrations of tissue methyl Hg, as compared with fish in lakes that lack watershed wetlands (Driscoll et al., 2007).

B.2.1.2. Ponds

The factors that determine the sensitivity of ponds to acidification from acidic deposition are generally similar to those that determine the sensitivity of lakes (discussed in the following section). In general, however, ponds and small lakes tend to exhibit low ANC and pH at a greater frequency than do larger lakes (Sullivan et al., 1990). This pattern is mainly a consequence of the higher concentrations of DOC frequently found in ponds as compared with larger lakes. In addition, because larger bodies of water tend to have larger watersheds, there is a greater likelihood that they will integrate conditions across a broader landscape, increasing the possibility of receiving at least a moderate level of base cation supply (Sullivan et al., 1990). Thus, where lakes are acid-sensitive, it is likely that ponds are also acid-sensitive. However, synoptic databases of pond acid-base chemistry are generally not available.

B.2.2. Streams and Lakes

Acidic deposition that falls as precipitation directly on the lake surface may eventually be neutralized by in-lake reduction processes which are controlled in part by hydraulic residence time (Baker and Brezonik, 1988). Natural hydrologic events also alter acidification and neutralization processes during snowmelt and change flowpaths during extended droughts (Webster et al., 1990).

Leaching of base cations by acidic deposition can deplete the soil of exchangeable bases. The importance of this response has recently been widely recognized because most watersheds are not exhibiting much ANC and pH recovery of drainage water in response to recent large decreases in S deposition. This limited recovery can be at least partially attributed to decreased base cation concentrations in surface water. This understanding of the base cation response has developed slowly. During the 1980s, the generally accepted paradigm of watershed response to acidic deposition was analogous to a large-scale titration of ANC (Henriksen, 1984). Atmospheric inputs of acidic anions were believed to result in movement of those anions through soils into drainage waters with near proportional loss of surface water ANC. This view was modified by Henriksen (1984), who suggested that a modest component of the added SO_4^{2-} (up to a maximum of about 40%) could be charge-balanced by increased mobilization of base cations from soils, and the remaining 60% to 100% of the added SO_4^{2-} resulted in loss of ANC in surface waters. During the latter part of the 1980s, it became increasingly clear that a larger component (> 40%) of the added SO_4^{2-} was in fact neutralized by base cation release in most cases and the ANC (and therefore also pH) of surface waters typically did not change as much as was earlier believed. This understanding developed in large part from paleoecological studies (e.g., Charles et al., 1990; (Sullivan et al., 1990), which indicated that past changes in lakewater pH and ANC had been small relative to estimated increases in lakewater SO_4^{2-} concentrations since pre-industrial times (Sullivan, 2000). The belief that changes in acidic deposition were accompanied mainly by changes in ANC and pH

has been replaced by the realization that changes in SO_4^{2-} were accompanied mainly by changes in base cations. Thus, surface waters have not been acidified as much by historical deposition as was earlier believed. Furthermore, surface water ANC and pH should not be expected to show substantial chemical recovery upon reduced emissions and deposition of S and N. The magnitude of the base cation response has clearly limited the extent of surface water acidification caused by acidic deposition. However, this same response has contributed to base cation deficiencies in some soils, with associated adverse terrestrial effects.

B.2.3. Other Types of Ecosystems

There has been little work on the rates of atmospheric deposition to urban ecosystems despite extensive data on concentrations and chemical reactions of air pollutants in cities (U.S. Environmental Protection Agency, 2004). Nevertheless, urban ecosystems are often subjected to large rates of deposition of anthropogenic pollutants (Lovett et al., 2000a). Decades of research on urban air quality indicate that cities are often important sources of emissions of NO_X, SO_X, and dust. Urban N deposition may affect nutrient cycles and soil acid-base chemistry in vegetated areas in and around cities, but such possible effects have not been studied sufficiently to draw conclusions about sensitivities or effects.

To determine the patterns of atmospheric deposition and throughfall in the vicinity of a large city, Lovett et al. (2000a) measured bulk deposition, oak forest throughfall, and particulate dust at sites along a transect within and to the north of New York City. They found that throughfall N was twice as high in the urban areas compared with suburban and rural areas. Most of the urban dry deposition of NO_3^- was from gaseous NO_X. Because there is limited biological uptake of throughfall N in an urban setting, it is believed that a relatively high (but unknown) percentage of N deposited to the urban landscape leaches to surface waters. Aquatic effects associated with N leaching from urban environments would be expected to be most pronounced near coastal cities. This is because atmospheric deposition to near-coastal urban environments can provide a substantial N load to estuaries and near shore oceanic environments, which tend to be N-limited. See further discussion in ISA Section 3.3.2.4.

B.3. Distribution and Extent of Ecosystem Effects

B.3.1. Terrestrial Ecosystems

Coniferous forests, with soils that are naturally more acidic, generally have lower pH and base saturation than soils in deciduous forests (Fernandez et al., 2003). In a paired watershed study at Bear

Brook Watershed in Maine, one watershed with mixed coniferous and deciduous species received $(NH_4)_2SO_4$ corresponding to about 25 kg N/ha/yr and 29 kg S/ha/yr. After a decade of experimental acidification, the treated watershed had 66 kg/ha/yr less exchangeable Ca^{2+} and 27 kg/ha/yr less exchangeable Mg^{2+} than the untreated watershed (Fernandez et al., 2003). Soils under conifers (red spruce, balsam fir [*Abies balsamea*], hemlock [*Tsuga canadensis*]) appeared to be more sensitive to acidification than those under hardwoods (American beech [*Fagus grandifolia*], yellow birch [*Betula alleghaniensis*], sugar, and red maples [*Acer rubrum*]). The hardwoods demonstrated no significant effects from $(NH_4)_2SO_4$ addition. Differences in response to acid treatment among vegetation covers were most pronounced in upper soil (O horizon and upper 5 cm of the B horizon). The study did not distinguish between effects from NH_4^+ versus SO_4^{2-} additions.

Kozlowski (1985) suggested that plants and soils act as sinks for SO_2 deposition at low exposures of 1 to 4 $\mu g/m^3$, with no discernible effects on ecosystem structure at those levels. Shugart and McLaughlin (1985) cautioned that forest responses to SO_2 and other stressors are strongly controlled by the successional dynamics of impacted forests. Thus, efforts to better understand and quantify forest dynamics and development will be paramount to predicting chronic pollution effects.

Results of N fertilization studies have been used to infer the response of forests to atmospheric N deposition. Such studies were reviewed by Johnson (1991) and EPA (1993), illustrating that forests can respond differently to periodic large pulsed fertilizer inputs, as compared with steady, low-level inputs from atmospheric deposition. For example, multiple or continuous inputs of N may stimulate populations of nitrifying bacteria (U.S. Environmental Protection Agency, 1993). This might be expected to modify the competitive interactions between trees and microbes and affect both the forest growth response and the extent of NO_3^- leaching and associated acidification.

In the southern Appalachian Mountains, acidification sensitivity has been evaluated for two common tree species: red spruce (sensitive) and loblolly pine (*Pinus taeda*; insensitive). Dendro-chronological analyses of tree cores collected for permanent plots in the Great Smoky Mountains National Park (37 trees cores from low elevation [~1500 m]; 35 tree cores from high elevation sites [~2000 m]), demonstrated a positive correlation between temporal and spatial trends in red spruce growth and acidic deposition, with a greater response in trees on ridges than in draws. Ridges are naturally more acidified, receive higher levels of acidic deposition, and have shallower soils with lower base saturation (Webster et al., 2004).

Loblolly pine seems to have low susceptibility to adverse effects from acidic deposition. A simulated acid addition experiment showed no significant effect of acidification on foliar nutrition in loblolly pine seedlings, at application levels of 21 to 26 kg/ha SO_4-S and 8 to 10 kg/ha NO_3-N (Baker et al., 1994). Loblolly pines grown on old agricultural fields showed signs of N deficiency over 25 years of growth despite atmospheric deposition of 5 to 10 kg N/ha/yr (Richter et al., 2000).

In the northeastern U.S., two species of coniferous tree (red spruce and red pine) have been shown to be sensitive to acidification. Aber et al. (2003) reported a decrease in C:N ratio from about 35 to about 25 along an increasing N deposition gradient of 3 to12 kg N/ha/yr across the Northeast. At the Harvard Forest LTER site, at chronic experimental N addition levels of 50 and 150 kg N/ha/yr, Magill et al. (2004) found 31% and 54% decreases, respectively, in red pine growth after 15 years of chronic N application. No additive effect of S was seen after 11 years of a combined N and S treatment, with an application of 74 kg S/ha/yr and 50 kg N/ha/yr. There were no significant differences in baseline measurements between the low N and combined N and S treatments.

Recent evidence indicates that mortality in red spruce in the southern Appalachian Mountains is not abnormal when compared to historical rates, and that Fraser fir stands killed by the balsam woolly adelgid (*Adelges piceae*) are largely being replaced by vigorous re-growth of young stands of that species (Van Miegroet et al., 2007). To what extent spruce or fir mortality in the southern Appalachian Mountains will be replaced with a species mix similar to that existing prior to the mortality remains to be seen.

At the Fernow Experimental Forest in West Virginia, $(NH_4)_2SO_4$ inputs of 54 kg N/ha/yr and 61 kg S/ha/yr (application plus ambient atmospheric deposition), each about three times the ambient deposition level, were applied to one watershed for 4 years. Few differences in soil and forest floor chemistry were found in response to the N addition, although pH was significantly lower in the treatment watershed, corresponding to increased base-flow concentrations of NO_3^- and Ca^{2+} (Gilliam et al., 1996).

Deciduous forests show variable responses to acidification depending on the tree species present. Along an increasing N deposition gradient in the northeastern U.S., from 4.2 to 11.1 kg N/ha/yr, Lovett and Rueth (1999) found a twofold increase in mineralization in soils of sugar maple stands, but no significant relationship between increased deposition and mineralization in American beech stands. This difference might be attributable to the lower litter quality in beech stands. Thus, sugar maple appears to be more susceptible to effects of increasing deposition and concomitant soil acidification from either direct leaching of NO_3^- or enhanced nitrification. For northeastern hardwoods, Aber et al. (Aber et al., 2003) found a decrease in C:N ratio from 24 to 17 over a deposition gradient of 3 to 12 kg N/ha/yr. This decrease was similar but less steep than the decrease seen in conifers.

Across an 800 km pollution gradient (3 to 11 kg SO_4 -S/ha/yr; 2 to 4 kg NO_3 -N/ha/yr) in northern hardwood forests, with maples dominant, Pregitzer et al. (1992) found a 200 to 300 µg/g increase in foliar S, and litter fall S content ranged from 872 to 1356 µg/g. While foliar N did not change across the gradient, litterfall N was correlated with changing deposition. Pregitzer and Burton assert that their data did not suggest a causal link between acid deposition and forest decline. Decline would be impossible to document in the short 5–year time frame of their study. They did, however, assert that their results supported the plausibility of altered tree nutrition across large geographic regions due to atmospheric deposition.

B.3.2. Transitional Ecosystems

Wetlands are common in many areas that contain acid-sensitive surface waters. For example, wetlands constitute about 14% of the land surface in the Oswegatchie/Black River watershed in the southwestern Adirondack Mountains (Ito et al., 2005), one of the regions of the U.S. most affected by surface water acidification from acidic deposition. There are no studies, however, that have documented the extent or magnitude of acidification effects of S and N deposition on wetland ecosystems in the U.S.

The topic of acidification effects on wetlands is not well represented in the literature, and therefore the distribution of ecosystem effects for these systems is not presented. Because levels of natural organic acidity tend to be high in wetland soils and water, it is not likely that such ecosystems are affected by the levels of acidic deposition commonly encountered in the U.S. It is more likely that atmospheric deposition affects wetlands via nutrient N enrichment pathways. (See Discussion in ISA Sections 3.3.2.2 and 3.3.5.2) Gorham et al. (1987) hypothesized that acidic deposition to mineral-poor fens might cause depletion of exchangeable base cations and decreased pH of soil water. This mechanism was suggested as a possible cause of transition from mineral-poor fen to *Sphagnum* bog. Such an effect has not been observed in response to acidic deposition at levels found in the U.S.

Synoptic surveys of ponded waters generally are restricted to lakes larger than 1 ha, 4 ha, or 10 ha. Reasons for this limitation are varied and can include the perception that larger lakes are more important, the failure of regional topographic map coverages to include the smaller lakes and ponds, and the fact that smaller lakes tend to be much more numerous than larger lakes within the major lake districts of the U.S. In general, if the larger lakes in a given region are sensitive to acidification, the smaller ponds would also be expected to be sensitive. In most cases, data to demonstrate this are not available.

Ponds that have been observed to be sensitive to acidic deposition have been found in the Adirondack Mountains in New York (Kretser et al., 1989) and the Mount Zirkel Wilderness Area located in the Colorado Rockies (Campbell et al., 2004). Acid-sensitive ponds are likely to be found elsewhere as well.

B.3.3. Aquatic Ecosystems

In most regions of the U.S., the majority of lakes and streams are not highly sensitive to existing levels of ambient air pollution. In addition, air pollution levels are generally decreasing in many parts of the country, especially in the eastern U.S., in response to federal and state air pollution control regulations. Therefore, the highly sensitive, and acidified, systems tend to be restricted to a relatively small percentage of the overall aquatic resource base. There are exceptions to this generalization, such as for example in Monongahela National Forest, WV, where a high percentage of the streams are acid-sensitive and highly acid-affected (cf. Sullivan et al., 2002). Similarly, a high percentage of Adirondack

lakes (and presumably also streams) are acid-sensitive and have been acidified by atmospheric deposition of S and N (Driscoll et al., 1991).

Studies to assess relationships between atmospheric deposition loading (N and S) and the estimated or expected extent, magnitude, and timing of aquatic acidification effects (U.S. Environmental Protection Agency, 1995; cf. Van Sickle and Church, 1995; NAPAP, 1998) often employ a "weight of evidence" evaluation of the relationships between deposition and effects, as followed by NAPAP in the Integrated Assessment (IA) (NAPAP, 1991).

Several kinds of evidence were used in the IA to assess the extent and magnitude of acidification in sensitive regions of the U.S. These included:

- results of watershed simulation models that projected past or future chemical changes in response to changes in S deposition
- empirical biological dose/response models
- improved relationships between surface water chemistry and ambient acidic deposition
- trend analyses of long-term monitoring chemical data in regions that have experienced large recent changes in acidic deposition levels
- paleolimnological reconstructions of past water chemistry using fossil remains of algae deposited in lake sediments
- results from whole-watershed or whole-lake acidification or deacidification field experiments

Evidence from each type of study contributes to understanding of the quantitative importance of acidification and neutralization processes and their effects on the chemistry and biology of affected ecosystems.

B.3.3.1. Status of Surface Waters – Regional Overview

In the NSS, DOC concentrations were much higher in lowland coastal streams, compared with inland streams. National Stream Survey data also supported the hypothesis that atmospheric sources and watershed retention of S control regional patterns in streamwater SO_4^{2-} concentrations. Most NSS watersheds retained the vast majority of the total N loading from wet deposition. The 1986 data suggested, however, that some atmospherically deposited N may have been reaching streams in the northern Appalachians (Kaufmann et al., 1991).

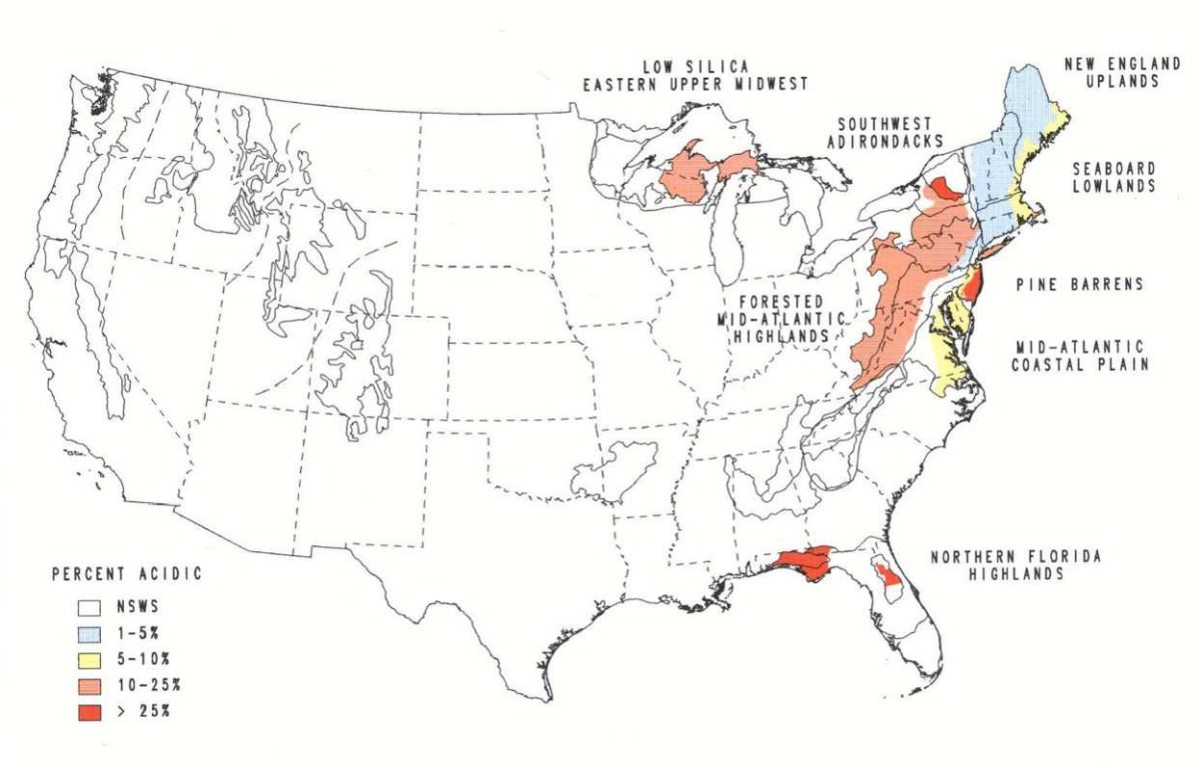
In the 1990 NAPAP State of Science/Technology (SOS/T) summary, Baker et al. (1991a) identified six high interest subpopulations that accounted for most of the U.S. surface waters that were acidic with acidic deposition having been identified as the likely source (Figure B-3; Table B-2):

- Southwestern Adirondacks
- New England Uplands
- Low Si Eastern Upper Midwest
- Forested Mid-Atlantic Highlands
- Mid-Atlantic Coastal Plain
- Northern Florida Highlands

Stream data for the NSS was unavailable for three of these high-interest areas: the Adirondacks, New England, and Upper Midwest. The national WSA data indicated that acidic streams in the Upper Midwest are likely to be rare but there are acidic streams in the Adirondacks/New England region. Specific areas of interest within the other three high-interest regions are described below.

In addition to the large water chemistry databases developed by the EPA, there are also some important supplemental databases in some regions. For example, based on results of lake surveys conducted during the 1980s, about 70% of the known acidic lakes in Maine were either seepage type or high elevation (Kahl et al., 1991). *The Maine seepage lake* dataset includes 120 of the estimated 150 lakes in Maine that meet the following criteria: (1) located in sand and gravel mapped by the USGS or Maine Geological Surveys; (2) depth at least 1 m; and (3) area at least 0.4 ha (1 ac). Sampling was conducted in 1986–87 and 1998–2000, and included at least one fall index sample for each lake. There were 87 lakes with Gran ANC less than 100 µeq/L.

The Maine high elevation lake dataset includes 90 lakes above 600 m elevation. Sampling was conducted during the periods 1986–88 and 1997–99. The study included the vast majority of Maine lakes that are at least 1 m deep and at least 0.4 ha (1 ac) in area. There were 64 lakes with Gran ANC less than 100 µeq/L.



Source: Baker et al. (1990b).

Figure B-3. Location and percentage of acidic surface waters in U.S. high-interest subpopulations with respect to acidic deposition effects. Estimates are for the upstream reach ends in the NSS data. Population estimates in the Mid-Atlantic Highlands apply only to the forested watersheds, while estimates in the eastern Upper Midwest apply only to low-silica (≥ 1 mg/L) lakes. Figure taken from Figure 9–106 in the 1990 NAPAP SOS/T report.

B.3.3.2. Recent Changes in Surface Water Chemistry

Surface water acid-base chemistry monitoring throughout the eastern U.S. occurs primarily in two EPA programs: the Temporally Integrated Monitoring of Ecosystems (TIME) project (Stoddard, 1990) and the Long-Term Monitoring (LTM) project (Ford et al., 1993; Stoddard et al., 1998). Both projects are operated in cooperation with numerous state agencies, academic institutions and other federal agencies. Each is described below.

The regions represented by the LTM and TIME monitoring programs (Annex A) are estimated to contain 95% of the lakes and 84% of the streams in the U.S. that have been anthropogenically acidified by acidic deposition. The Adirondacks had a large proportion of acidic surface waters (14%) in the NSWS; from 1984 to 1987, the ALSC sampled 1,469 Adirondack lakes greater than 0.5 ha in size and estimated that many more (26%) were acidic (Driscoll et al., 1991). The higher percentage of acidic lakes in the ALSC sample was due to inclusion of smaller lakes and ponds (1 to 4 ha in area), many of which were acidic as a consequence of naturally occurring organic acids (Sullivan et al., 1990). The proportions of

lakes estimated by NSWS to be acidic were smaller in New England and the Upper Midwest (5% and 3%, respectively), but because of the large numbers of lakes in these regions, there were several hundred acidic waters in each of these two regions.

The Valley and Ridge Province and Northern Appalachian Plateau had 5% and 6% acidic sites, respectively. The only potentially acid-sensitive region in the eastern U.S. not assessed in the Stoddard et al. (2003) report was Florida, where the high proportion of naturally acidic lakes, and a lack of long-term monitoring data, make assessment of the effects of acidic deposition problematic (Stoddard et al., 2003).

The TIME project is structured as a probability sampling. Each site is chosen statistically to be representative of a target population. In the Northeast (New England and Adirondacks), this target population consists of lakes with Gran ANC < 100 µeq/L, which are those likely to be most responsive to changes in acidic deposition. In the Mid-Atlantic, the target population is upland streams with ANC < 100 µeq/L. Each lake or stream is sampled annually, and results are extrapolated to the target populations (Larsen and Urquhart, 1993; Larsen et al., 1994; Stoddard et al., 1996; Urquhart et al., 1998). The TIME project began sampling northeastern lakes in 1991. Data from 43 Adirondack lakes can be extrapolated to the target population of about 1,000 lakes having ANC < 100 µeq/L, out of a total population of 1,830 lakes with surface area > 1 ha. Data from 30 lakes representing about 1,500 lakes having ANC < 100 µeq/L, out of a total population of 6,800 lakes, are included in the TIME program in New England.

As a compliment to lake and stream sampling in the statistical populations of lakes in TIME, the LTM project samples a subset of sensitive lakes and streams with long-term data, many dating back to the early 1980s. Each LTM site is sampled 3 to 15 times per year, and the resulting data are used to characterize the response of the most sensitive aquatic systems in each region to changing levels of acidic deposition. In most regions, a small number of higher ANC (e.g., Gran ANC > 100 µeq/L) sites are also sampled. Because of the long-term records at most LTM sites, their trends can also be placed in a better historical context than those of TIME sites, where data are only available from the 1990s. Monitoring results from the LTM project have been widely published (Kahl et al., 1991, 1993b; Driscoll and Van Dreason, 1993; Murdoch and Stoddard, 1993; Stoddard and Kellogg, 1993; Webster et al., 1993; DeWalle and Swistock, 1994; Driscoll et al., 1995; Stoddard et al., 1998). Overall results were summarized by Stoddard and Kellog (1993).

Monitoring data from the LTM and TIME projects were used to evaluate recent changes in lake and stream chemistry from 1990 to 2000 in many of the sensitive areas of the eastern U.S. including New England, the Adirondack Mountains, the Northern Appalachian Plateau, the Ridge and Blue Ridge provinces of Virginia, and the Upper Midwest (Stoddard et al., 2003). There are also substantial numbers of acid-sensitive streams in the Blue Ridge Province in North Carolina and portions of South Carolina and Tennessee that have been affected by acidic deposition but that were not included in this analysis. In

general, the results of the TIME/LTM data analysis suggest that about one-quarter to one-third of the lakes and streams that were chronically acidic in the 1980s were no longer chronically acidic in the year 2000. However many still had low ANC and were potentially susceptible to episodic acidification (Stoddard et al., 2003).

Stoddard et al. (2003) found little evidence of regional change in the acidity status of lakes in New England or streams in the Ridge/Blue Ridge regions. Furthermore, none of the study regions showed an increase in the number of chronically acidic waters, even though there was a decline in base cation concentrations and a likely increase in natural organic acidity (Stoddard et al., 2003). An important caveat in this analysis is that changes in Gran ANC used in the analysis were based on the median change of all sites in a region (Table B-4). However, as shown in (Table B-5), the rates of ANC increase were generally more rapid in chronically acidic lakes with ANC less than 0 µeq/L and streams with ANC between 0 and 25 µeq/L. If acidic sites are recovering more rapidly than the population of sites as a whole, then the estimates of change in the number of acidic lakes and streams presented would be conservative.

While general estimates for large regions are useful in providing a broad picture of the extent and status of surface water acidity, specific results from studies within those regions can help isolate trends and determine the specific mechanisms that contribute to change. The following sections report on the current status, past acidification, and potential future conditions for lakes and streams in acid sensitive areas of the Northeast, Southeast, Upper Midwest, and Western U.S.

B.3.4. Regional Assessments

B.3.4.1. Northeastern Surface Waters

Current Status

The Adirondacks and New England are two of the most acid sensitive and intensively studied regions in the Northeast. The glaciated soils and location downwind from emissions sources have made these areas the subject of intense scientific study over the past four decades. Most of this research has focused on lake ecosystems, though important stream studies have been undertaken at specific research sites and more regional stream survey work is being conducted. As discussed below, the surface water chemistry in these areas integrates atmospheric deposition, local geology, and upland watershed characteristics.

Available surface water datasets for Adirondack lakes include TIME, the Environmental Monitoring and Assessment Program (EMAP), and ALSC, each of which is useful for documenting chemical status and recent chemical changes. Population estimates from the TIME dataset suggest that 13.0% of Adirondack lakes (238 lakes) were chronically acidic in the early 1990s during baseflow

conditions in the summer. By applying an approximate rate of change in Gran ANC of +0.8 μeq/L/yr to these estimates (based on trend slopes for TIME and LTM data, (Table B-6), Stoddard et al. (2003) projected that approximately 8.1% of the population (149 Adirondack lakes) remained chronically acidic in 2000. This finding suggests that roughly 38% of lakes in the Adirondacks that were chronically acidic in the early 1990s were not chronically acidic a decade later. Certain caveats need to be included with the results of this analysis, however. Summertime baseflow sampling reflects the least acidic conditions experienced throughout the year. In addition, LTM trends, which are based on year-round sampling, may not be representative of trends in the summer-only sampling of the TIME program, and the rate of change determined through the TIME program was not controlled for possible differences in flow conditions between the two sample periods. Lastly, the ANC value of 0 μeq/L/year used to define acidic waters has been shown to be below the level needed to protect aquatic ecosystems in the Adirondack region (Baldigo et al., 2007; Lawrence et al., 2007).

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. The EMAP survey is 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. 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 ALSC conducted a comprehensive survey of Adirondack lakes greater than 0.2 ha in surface area between 1984 and 1987 (Kretser et al., 1989). 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., 2007).

For the New England region, the TIME population data indicates that 5.6% of the population (386 lakes) in New England exhibited Gran ANC < 0 μeq/L during the period of 1991 to 1994. This result is similar to the EMAP findings which indicate that 5% of lakes in New England and in the eastern Catskill region of New York had ANC values less than 0 μeq/L. 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).

Both TIME and LTM data from the New England region indicate that only a small increase in Gran ANC had occurred during the reported monitoring period (+0.3 μeq/L/yr). As a result, it is estimated that the proportion of chronically acidic lakes decreased only 0.1% from 5.6% to 5.5% over the previous 10 years (Table B-4) (Stoddard et al., 2003).

State surveys within New England provide additional information on the variation in lakewater chemistry across the region. In Maine, approximately 100 clearwater lakes in that state have been

classified as acidic, based on surveys conducted by EPA and the University of Maine (Kahl et al., 1999). An estimated 13% of the high-elevation lakes in Maine are acidic, compared to less than 1% of Maine lakes (>4 ha) represented in EPA's Eastern Lakes Survey (ELS) (Linthurst et al., 1986a; Kahl et al., 1991). Most acidic lakes in Maine are either seepage lakes located in sand and gravel deposits, or high-elevation lakes located above 600 m elevation. Roughly 60% of the acidic lakes are seepage lakes. The acid-sensitive seepage lakes are located in mapped sand and gravel deposits, are at least 1 m deep, and are at least 0.4 ha (1 acre) in surface area. About 45 of the 150 lakes of this type in Maine are acidic (Kahl et al., 1999).

Whereas lakes in the Adirondacks and New England have been intensively studied, there are no published data which describe the status of streamwater acid-base chemistry at a regional scale, except for the Catskill Mountains.

In the absence of regional streamwater studies, insights can be gained from site-specific long-term studies in the region. The HBEF has one of the longest continuous records of precipitation and streamwater chemistry in the U.S. Compared to model hindcast approximations, current conditions at HBEF indicate that soil percent base saturation has decreased in response to acidic deposition and because of accumulation of nutrient cations by forest vegetation. Further, acidic deposition has contributed to a nearly fourfold increase in stream SO_4^{2-} concentration; a decrease in ANC from positive to negative values; a decrease in stream pH to 5.0; and an increase in stream Al, largely occurring as the inorganic form which has been shown by Lawrence at al. (2007) to be an unequivocal indication of the effects of acidic deposition. Driscoll et al. (2001b) estimated that roughly 6% of lakes and streams in the Northeast are considered more sensitive to acidic deposition than the stream monitored at HBEF (Driscoll et al., 2001b).

Past Acidification

There are limited surface water data that directly document historic conditions and the response to atmospheric deposition since the time of the Industrial Revolution ((Charles, 1991). To address this gap, scientists use sediment cores from lakes and detailed computer models to try to reconstruct past conditions as well as understand the mechanisms that contribute to changing conditions.

Paleolimnological Studies

Paleolimnological studies use the remains of diatoms and other algae embedded in lake sediments to reconstruct historical water chemistry. In the Adirondack Mountains and northern New England, both diatom and chrysophyte algal remains in sediment cores have been used to evaluate patterns of past acidification in a large number of lakes.

Major findings of the Paleoecological Investigation of Recent Lakewater Acidification (PIRLA)-I and PIRLA-II research programs in the Adirondack Mountains suggested that: (1) Adirondack lakes had not acidified as much since pre-industrial times as had been widely believed prior to 1990; (2) many Adirondack lakes with ambient pH greater than 6.0 had not acidified historically, whereas many of the lakes having pH less than about 6.0 had acidified; (3) many of the lakes having high pH and ANC had increased in pH and ANC since the previous century; and (4) the average F-factor for acid-sensitive Adirondack lakes was near 0.8 (Charles et al., 1990; (Sullivan et al., 1990). The results of these studies had major effects on scientific understanding of the extent to which lakes had acidified in response to acidic deposition. The view of surface water acidification as a large-scale titration of ANC (Henriksen, 1980, 1984) was replaced by the realization that base cation concentrations typically changed more than ANC in response to acidic deposition. This realization also modified expectations for chemical recovery of surface waters as acidic deposition levels have decreased (Sullivan, 2000).

Diatom and chrysophyte reconstructions of pH and ANC for a statistically selected group of Adirondack lakes suggested that about 25% to 35% of the Adirondack lakes that are larger than 4 ha had acidified since preindustrial time (Cumming et al., 1992). Low-ANC lakes of the southwestern Adirondacks acidified the most, probably due to low initial buffering capacity and high rainfall and deposition of S and N in that area. Cumming et al. (1992) estimated that 80% of the Adirondack lakes that had ambient pH $\geq$ 5.2 had experienced large declines in pH and ANC since the previous century, and that 30% to 45% of the lakes with pH between 5.2 and 6.0 had also acidified.

Cumming et al. (1994) reported the results of chrysophyte inferences of pH in recently deposited lake sediments to assess acidification timing for 20 low-ANC Adirondack lakes. Lakes that were inferred to have acidified since about 1900 tended to be small, high-elevation lakes with lower inferred pre-industrial pH than the group of study lakes as a whole. These were probably the most acid-sensitive and were the first to acidify with increasing acidic deposition. Husar and Sullivan (1991) estimated that S deposition was about 4 kg S/ha/yr at that time. These lakes are located in the high peaks area and in the southwestern portion of Adirondack Park. A second category of acidification response included high-elevation lakes that were historically low in pH (<5.5) but that acidified further beginning about 1900. The third identified type of response included lakes with pre-industrial pH in the range of about 5.7 to 6.3 that started to acidify around 1900 but showed their greatest pH change around 1930 to 1950. The final category included lakes that were not inferred to have acidified. They had pre-industrial pH around 6.0 and are located at lower elevation.

Davis et al. (1994) conducted paleolimnological studies of 12 lakes in northern New England that were low in pH and ANC. Past logging, forest fire, and vegetation composition in the watersheds were estimated from oral and written historical information, aerial photographs, and tree ring analyses. Lake sediment cores were collected and analyzed for pollen, diatoms, and chemistry to reconstruct past lake

conditions for several hundred years. All 12 lakes were historically low in pH and ANC, with diatom-inferred pre-industrial ANC of –12 to 31 μeq/L. The inferred pH and ANC values of the lakes were relatively stable throughout the one to three centuries of sediment record prior to watershed disturbance by Euro-Americans. From the early 19th into the 20th century, however, all of the lakes showed increased diatom-inferred pH changes of about 0.05 to 0.6 pH units and increased diatom-inferred ANC of about 5 to 40 μeq/L. Most of these inferred increases in pH and ANC coincided with watershed logging. For all study lakes, recovery to pre-logging acid-base lake chemistry conditions was followed by continued decline in pH by 0.05 to 0.44 pH units and ANC by up to 26 μeq/L, probably because of acidic deposition. The 12–lake mean inferred decreases in pH and ANC in response to acidic deposition were 0.24 pH units and 14 μeq/L, respectively (Davis et al., 1994).

Modeling Studies

The most extensive regional modeling study that provides estimates of past acidification of Adirondack lakes is that of Sullivan et al. (2006a). They 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 lake watersheds in the Adirondacks 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 extrapolated to the regional Adirondack lake population, maximum past acidification occurred by about 1980 or 1990, with median ANC of the population under investigation of about 61 μeq/L (reduced from a median of 92 μeq/L estimated for the pre-industrial 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. Percentile values in 2000 illustrated limited chemical recovery (3 to 5 μeq/L) compared with simulated values in 1980 and 1990.

The MAGIC model simulations suggest that none of the target lakes were chronically acidic (had ANC < 0 μeq/L) under pre-industrial conditions, but that by 1980 there were about 204 acidic Adirondack lakes. That number decreased by an estimated 14% between 1980 and 2000. Similarly, the MAGIC model simulations suggested that there were no Adirondack lakes having ANC < 20 μeq/L in 1850, but by 1990 there were 263 such lakes. Many lakes (N = 191) were estimated to have had pre-industrial ANC below 50 μeq/L, and this estimate increased threefold by 1990, followed by a decrease to 399 lakes in 2000.

PnET-BGC model simulations generated output generally similar to results provided by MAGIC model simulations. PnET-BGC simulations suggested that lakewater SO_4^{2-}, NO_3^-, and base cation concentrations under pre-industrial conditions were much lower than current values. In 1850, simulated SO_4^{2-} concentrations in all study lakes were less than 25 μeq/L, and the median value was about 15 μeq/L. By 1980, the median simulated SO_4^{2-} concentration had increased more than sixfold to about

100 μeq/L. Simulated lake NO_3^- concentrations also increased markedly during that time, with the median value increasing from about 4 μeq/L in 1850 to 12 μeq/L in 1980. Simulated increases in the sum of divalent base cation concentrations were less than for SO_4^{2-} concentrations, with the median value increasing from 93 μeq/L in 1850 to 140 μeq/L in 1980. This large change in SO_4^{2-} + NO_3^- relative to the change in the sum of base cation concentrations was the major mechanism driving the decreases in ANC and pH associated with historical increases in acidic deposition.

Simulated lakewater ANC and pH and soil base saturation decreased from pre-industrial conditions to recent times. Results from PnET-BGC suggested that the median Adirondack lake, from among the estimated 1,320 lakes in the population larger than 1 ha that had measured recent ANC < 200 μeq/L, had pre-industrial ANC near 80 μeq/L; an estimated 10% of the lake population had pre-industrial ANC < 41 μeq/L; and one-fourth had pre-industrial ANC < 64 μeq/L. Percentiles for the year 2000 suggest decreases in SO_4^{2-}, NO_3^-, and sum of base cations, and small increases in ANC since 1990 for lower-ANC lakes.

Results from PnET-BGC suggest that none of the lakes in the Adirondack population had pre-industrial 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 pre-industrial ANC below 50 μeq/L, and this number increased 2.8 times by 1980 under the PnET-BGC simulations.

PnET-BGC has also been used to characterize past conditions at streams within the HBEF. Gbondo-Tugbawa et al. (Gbondo-Tugbawa et al., 2002) used relationships between current emissions and deposition, and estimates of past emissions to reconstruct historical deposition conditions. Their analysis also considered land disturbances such as logging in 1918–1920 and hurricane damage in 1938. Using this approach, they estimated that past soil base saturation in the mineral soil (circa 1850) was approximately 20%, stream SO_4^{2-} concentration was approximately 10 μeq/L, stream ANC was about 40 μeq/L, stream pH was approximately 6.3, and stream Al_i concentration was below 1 μmol/L (Driscoll et al., 2001b).

Recent Trends

Sulfur deposition has contributed to chronic soil and surface water acidification in the eastern U.S. to a much greater extent than has N deposition. Nitrate concentrations in acid-sensitive drainage waters in the eastern U.S. are generally much lower than SO_4^{2-} concentrations.

The concentration of SO_4^{2-} in precipitation has declined for about the past three decades throughout the northeastern U.S., in response to decreased atmospheric emissions and deposition. EPA's LTM Program has been collecting monitoring data since the early 1980s for many lakes and streams in acid-sensitive areas of the U.S., including the Northeast. These data allow evaluation of trends and

variability in key components of lake and streamwater chemistry prior to, during, and subsequent to Title IV implementation. Throughout the northeastern U.S., the concentration of SO_4^{2-} in surface waters has decreased substantially (Figure B-4) in response to decreased emissions and atmospheric deposition of S. Decreased concentrations of SO_4^{2-} in lakes and streams of a third, or more, have been commonly observed.

Lakewater SO_4^{2-} concentrations have decreased steadily in Adirondack lakes, at least since 1978 (Driscoll et al., 1995; Stoddard et al., 2003). Initially, there was not a systematic increase in lakewater pH or ANC in response to the decreased SO_4^{2-} concentrations. Rather, the decline in 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 (Driscoll et al., 1995). Similar findings were reported by Stoddard and Kellog (1993) for lakes in Vermont. F-factors for the nine ALTM lakes that showed significant declines in both the sum of base cations (SBC) and (SO_4^{2-} + NO_3^-) concentration ranged from 0.55 to greater than 1.0, with a mean of 0.93 (Driscoll et al., 1995). These high F-factor values for chemical recovery from acidification were similar to results of historical acidification obtained by Sullivan et al. (Sullivan et al., 1990), based on diatom reconstructions of historical change for 33 Adirondack lakes.

Trend analysis results for the period 1982 to 1994 were reported by Stoddard et al. (1998) for 36 lakes in the northeastern U.S. having ANC $\geq$ 100 µeq/L. Trend statistics among sites were combined through a meta-analytical technique to determine whether the combined results from multiple sites had more significance than the individual Seasonal Kendall Test statistics. All lakes showed significant declining trends in SO_4^{2-} concentration ($\Delta SO_4^{2-} = -1.7$ µeq/L/yr; $p \geq 0.001$). Lakewater ANC responses were regionally variable. Lakes in New England showed evidence of ANC recovery (Δ ANC = 0.8 µeq/L/yr; $p \geq 0.001$), whereas Adirondack lakes exhibited either no trend or further acidification, largely because of declines in base cation concentrations.

The observed changes in the concentration of NO_3^- in some surface waters have likely been due to a variety of factors, including climate. During the 1980s, NO_3^-concentration increased in many surface waters in the Adirondack and Catskill Mountains in New York (Driscoll and Van Dreason, 1993; Murdoch and Stoddard, 1993). There was concern that northeastern forests were becoming N-saturated, leading to increased NO_3^- leaching from forest soils throughout the region. Such a response could negate the benefits of decreased SO_4^{2-} concentrations in lake and stream waters. However, this trend was reversed in about 1990, and the reversal could not be attributed to a change in N deposition. Nitrate leaching through soils to drainage waters is the result of a complex set of biological and hydrological processes. Key components include N uptake by plants and microbes, transformations between the various forms of inorganic and organic N, and local precipitation patterns. Most of the major processes are influenced by climatic factors, including temperature, moisture, and snowpack development. Therefore, NO_3^- concentrations in surface waters respond to many factors in addition to N deposition and can be difficult

to predict. It is likely that monitoring programs of several decades or longer will be needed to separate trends in NO_3^- leaching from climatic variability in forested watersheds (Driscoll et al., 1995).

Monitoring data collected during the 1990s in the LTM and TIME projects illustrated that most regions included in the monitoring efforts showed large declines in SO_4^{2-} concentrations in surface waters over the 10 years of monitoring, with rates of change ranging from 1.5 to 3 µeq/L/yr (Figure B-4). These declines in lake and stream SO_4^{2-} concentration were considered consistent with observed declines in S wet deposition. Surface water NO_3^- concentrations also decreased, but only in the two regions that had the highest ambient surface water NO_3^- concentrations (Adirondacks and Northern Appalachian Plateau), but were relatively unchanged in regions with lower concentrations. DOC increased in each region over time. This finding suggests an increase in the contribution of natural organic acidity, which would partially offset the expected chemical recovery from decreased acidic deposition.

ANC increased in the Adirondacks at a rate of about +1 µeq/L/yr, despite a decline in surface water base cation concentrations ($Ca^{2+} + Mg^{2+}$; Figure B-4). The decline in base cations offset some of the decline in SO_4^{2-}, and thus limited the increase in ANC or pH that occurred in response to lower SO_4^{2-} concentrations. Surface water ANC and pH increased significantly in the 1990s; Al_i concentrations declined slightly. Regional surface water ANC did not change significantly in New England (Stoddard et al., 2003).

Moderate increases in surface water ANC during the 1990s reduced the estimated number of acidic lakes and stream segments in the northeastern U.S. Stoddard et al. (2003) estimated that there were 150 Adirondack lakes in the year 2000 that had ANC less than 0 (8.1% of the lake population), compared to 13% (240 lakes) in the early 1990s.

Lakewater SO_4^{2-} concentrations in the most acid-sensitive Maine lakes declined by about 12% to 22% during the period 1982 to 1998 (Kahl, 1999). Only in the seepage lakes, however, was there evidence of a small decline in lakewater acidity during that period (Table B-7).

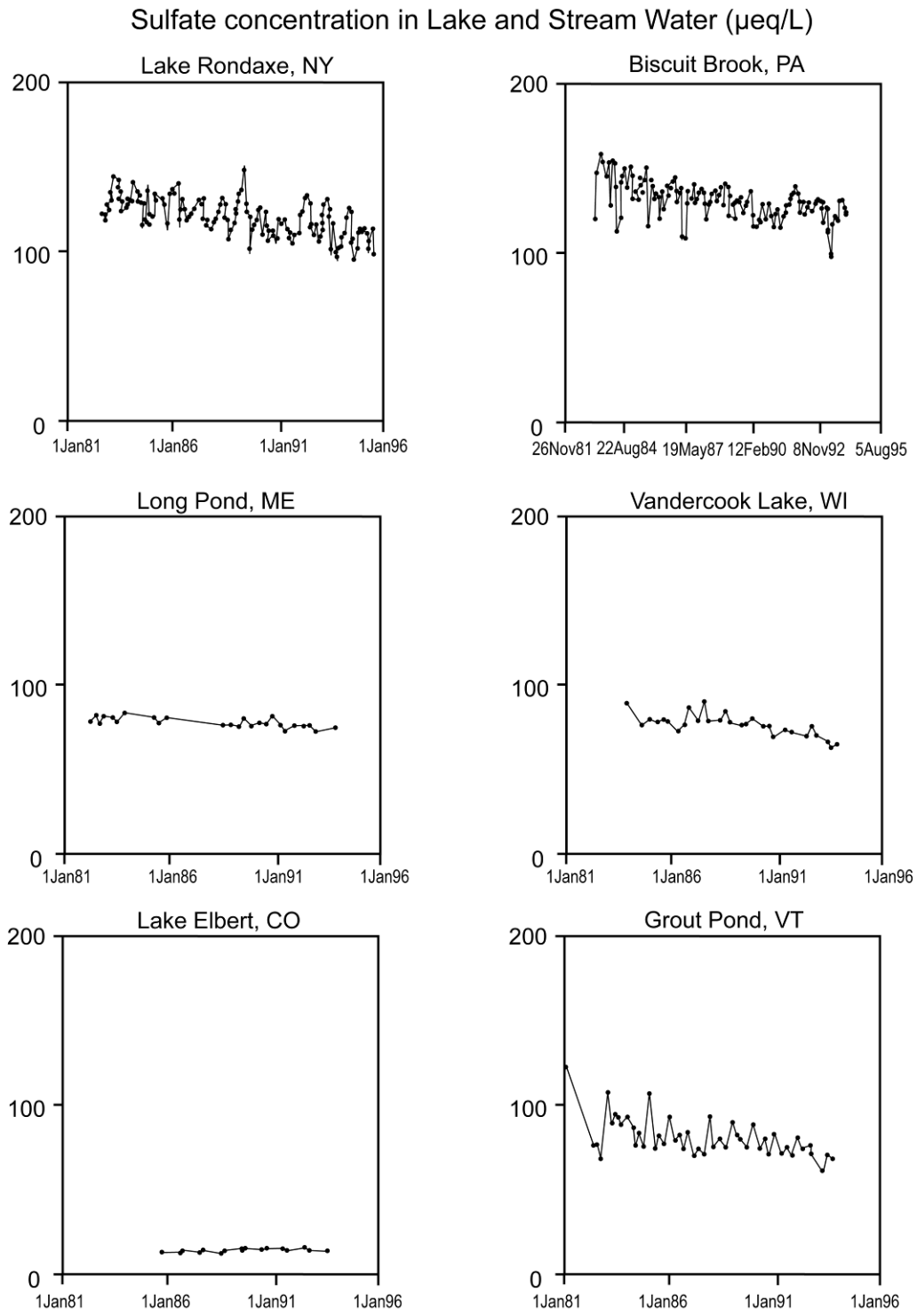


Figure B-4. Measured concentration of SO_4^{2-} in selected representative lakes and streams in six regions of the U.S. during the past approximately 15 years. Data were taken from EPA's Long-Term Monitoring (LTM) program.

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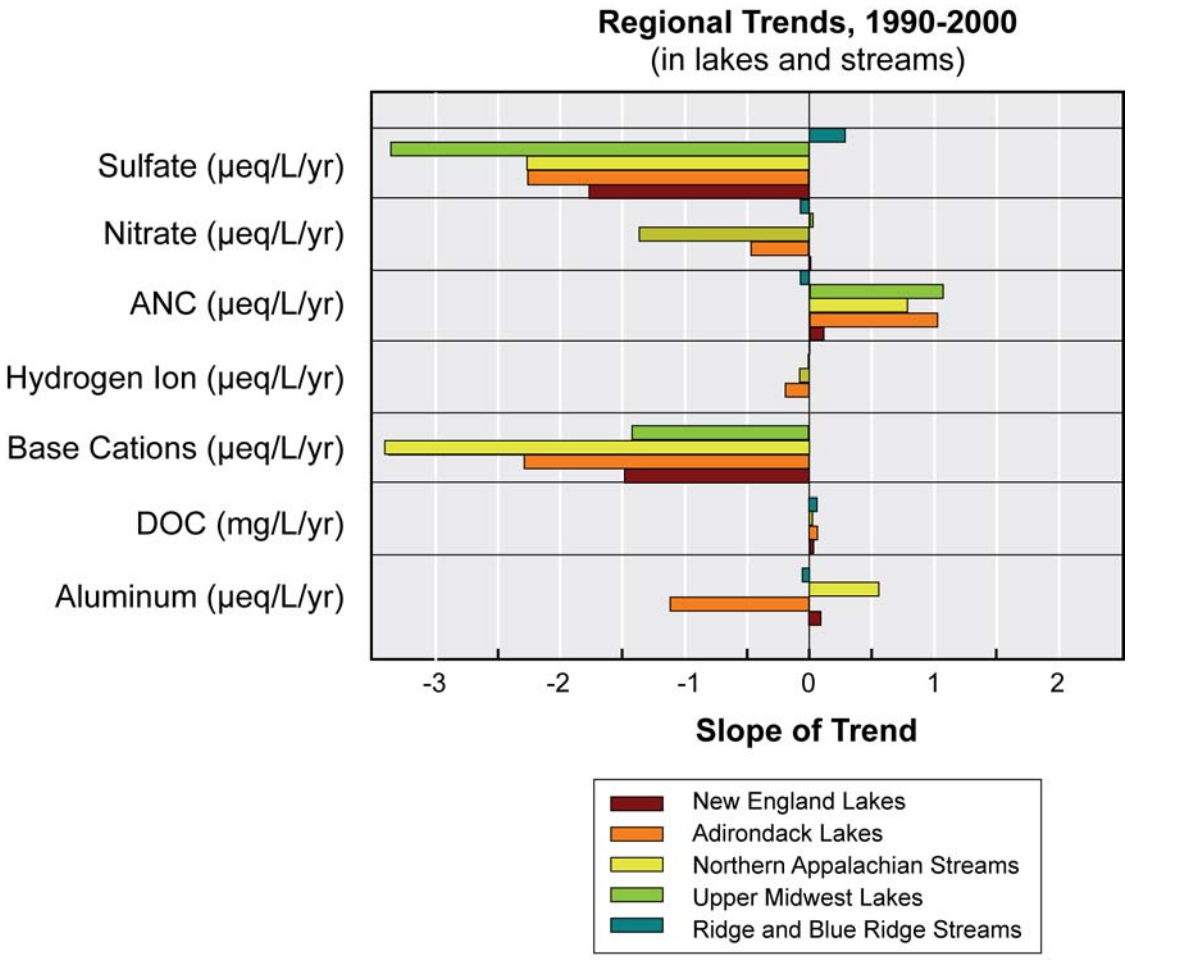


Source: Stoddard et al. (2003).

Figure B-5. Summary of regional trends in surface water chemistry from 1990 through 2000 in regions covered by the Stoddard et al. (2003) report.

However, evidence for reductions in lakewater ANC in seepage lakes from the mid-1980s to 1998 were based on a comparison of only two sampling points, which may have been influenced by climatic variation. Therefore, the conclusion of decreasing acidity of seepage lakes is considered preliminary. The seepage lakes are generally hydrologically isolated from their surrounding soil environment. They therefore did not show a clear decreasing trend in base cation concentrations, as has been found in drainage lakes throughout the Northeast. The high-elevation lakes, in contrast, showed small declines in lakewater acidity during the 1980s, but that trend slowed or reversed in the 1990s (Kahl, 1999). Both the seepage and high elevation lakes showed increased DOC concentrations of 10% to 20%, generally by about 0.5 to 1.0 mg/L. The increase in dissolved organic matter would be expected to limit the extent of ANC and pH recovery that would otherwise accompany the observed decreases in SO_4^{2-} concentration.

Whereas NO_3^- concentrations decreased during the 1990s in many lake chemistry datasets (cf. Stoddard et al., 2003), the high-elevation lakes in Maine continued to show high concentrations.

The reference stream of the Bear Brook Watershed Study (East Bear Brook) has the longest continuous, high-frequency data record of stream chemistry in Maine. Sulfate and NO_3^- concentration have both declined substantially since 1987. Base cations declined by an almost equivalent amount, and the increase in ANC has been limited (Kahl, 1999).

Long-term stream water data from the HBEF reveal a number of changes that are consistent with trends in lakes and streams across Europe and eastern North America (Stoddard et al., 1999, 2003; Evans and Monteith, 2001). Stream water draining the HBEF reference watershed (Watershed 6) had a 32% decline in annual volume-weighted concentrations of SO_4^{2-} (−1.1 µeq/L) between 1963 and 2000 (Driscoll et al., 2007). This decrease in stream SO_4^{2-} concentration corresponds to both decreases in atmospheric emissions of SO_2 and to bulk precipitation concentrations of SO_4^{2-} (Likens et al., 2001). In addition, there has been a long-term decrease in stream concentrations of NO_3^- that is not correlated with a commensurate change in emissions of NO_X or in bulk deposition of NO_3^-. The long-term declines in stream concentrations of strong acids ($SO_4^2 + NO_3^-$; −1.9 µeq/L/yr) have resulted in small but significant increases in pH, from 4.8 to 5.0 (Driscoll et al., 2007). Streams at HBEF remain acidic compared to background conditions, when stream pH was estimated to be approximately 6.0 (Driscoll et al., 2007). The increase in stream pH has been limited because of marked concurrent decreases in the sum of base cations (−1.6 µeq/L/yr; Driscoll et al., 2001b).

Future Projections

MAGIC model simulations were conducted for the NAPAP IA to forecast the response of lakes and streams in the eastern U.S. to S deposition. Results were reported by NAPAP (1991), Sullivan et al. (1992), and Turner et al. (1992). The projected median change in lakewater or streamwater ANC during 50–year simulations was similar among regions, except in the Southern Blue Ridge and Mid-Atlantic Highlands, where acidification was delayed due to S adsorption on watershed soils. MAGIC projected relatively small future loss of ANC in most northeastern watersheds under continued constant deposition. These modeled changes were due to a simulated slight depletion of the supply of base cations from soils (Turner et al., 1992).

On average, each kg/ha/yr change in S deposition was projected by MAGIC to cause a 3 to 4 µeq/L median change in surface water ANC. Such projected changes in ANC, while considerably smaller than was generally thought to occur in the 1980s, nevertheless suggested widespread sensitivity of surface water ANC to changes in S deposition throughout the northeastern U.S. (Sullivan, 2000).

Since 1990, adjustments have been made to the MAGIC model and its application method in response to model testing using paleolimnological data (Sullivan et al., 1992, 1996a) and the results of

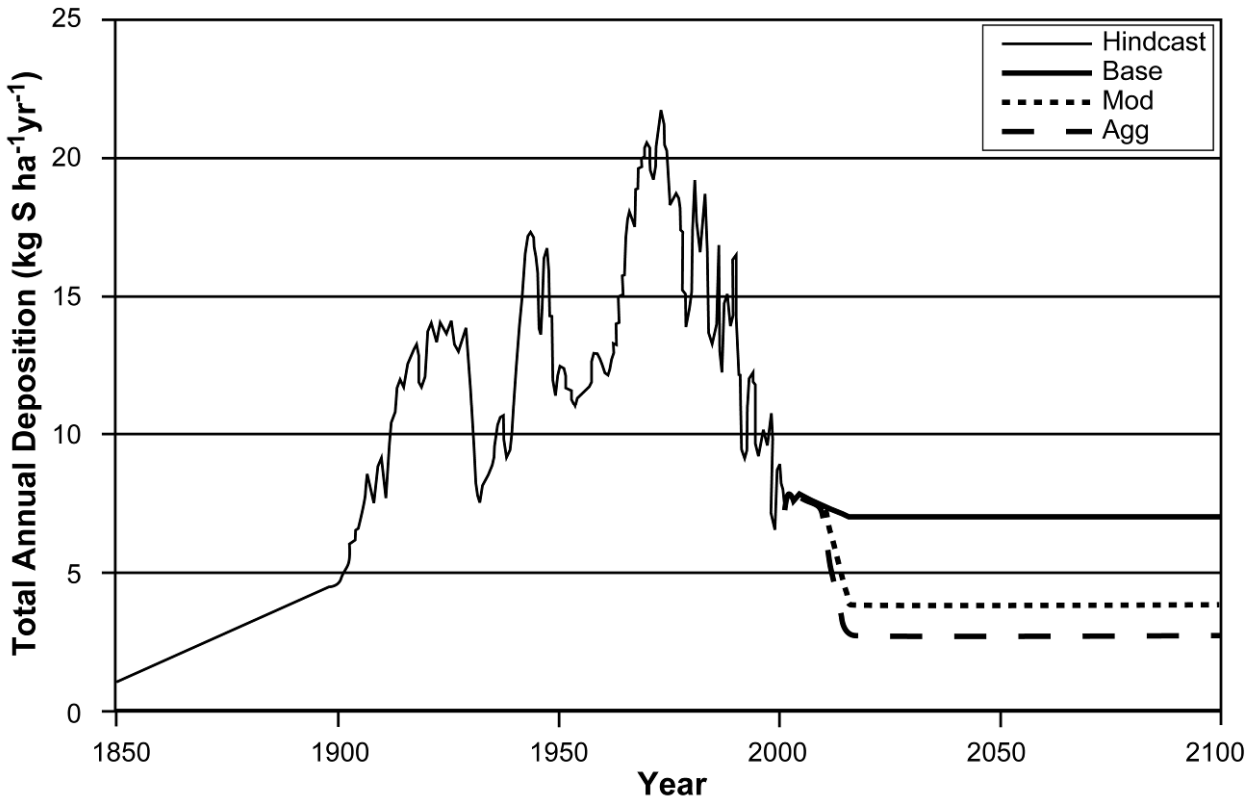
acidification and deacidification experiments (Norton et al., 1992; Cosby et al., 1995, 1996) and empirical studies (Sullivan and Cosby, 1998). The net effect has been that the model projects somewhat less sensitivity of Adirondack lakes to change in S deposition as compared with the version of MAGIC applied in 1990 (Sullivan and Cosby, 1998).

Model projections of future acid-base chemistry under three scenarios of future atmospheric emissions controls were presented by Sullivan et al. (2006b) and Zhai et al. (2008) for lakes in the Adirondack Mountains 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 B-6 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 B-7 for the past (1850), peak acidification period (1990), and future (2100). Results for the future are given for each of the scenarios.

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 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.

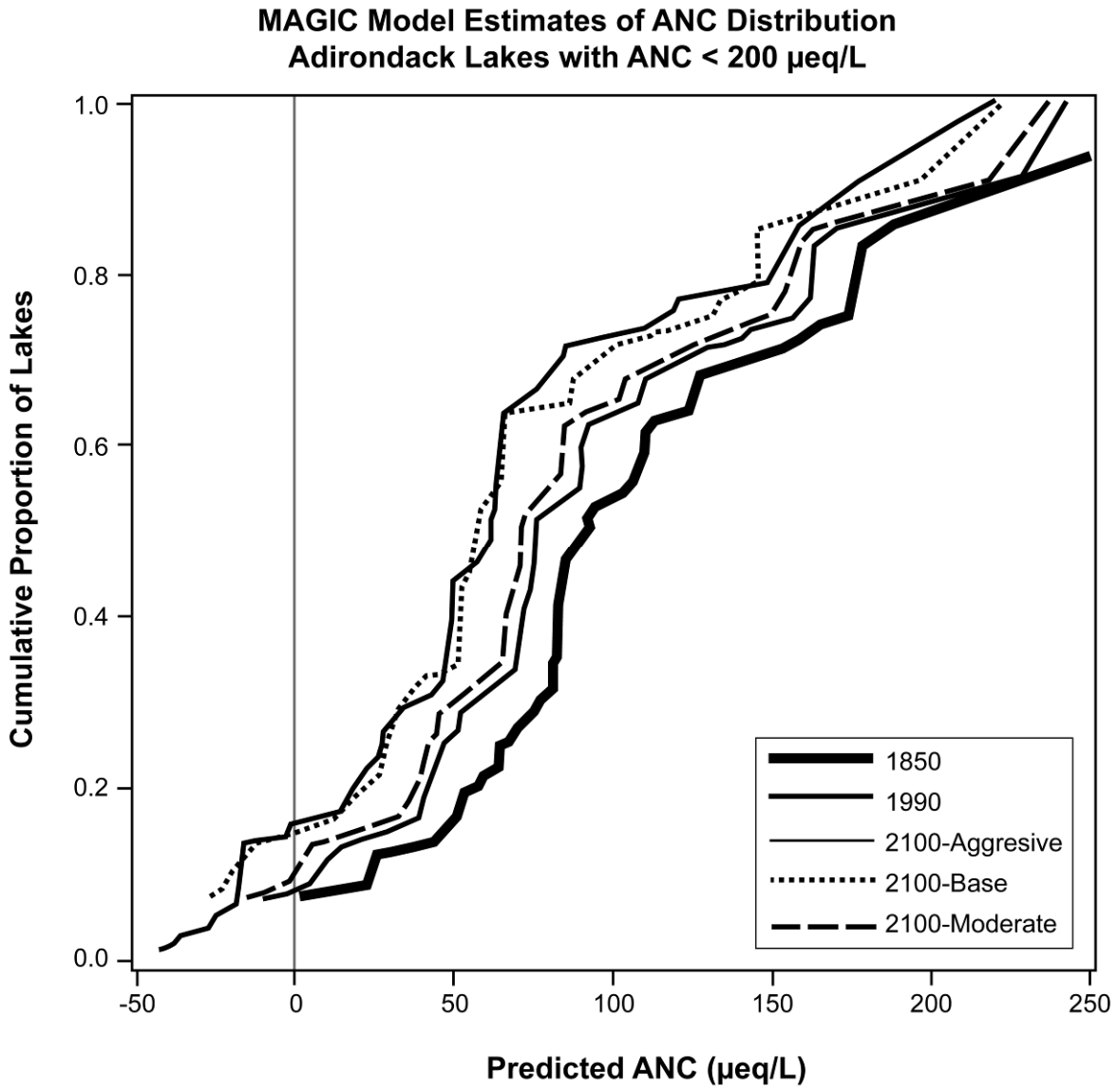
Simulations suggested that re-acidification might be prevented with further reductions in emissions and deposition.

Chen and Driscoll (2005) applied the PnET-BGC model to 44 EMAP lake watersheds in the Adirondacks. PnET-BGC was used to predict the acid-base chemistry of soils and surface waters, and to assess the fisheries status during pre-industrial conditions (~1850) and under three future acidic deposition scenarios.



Source: Sullivan et al. (Sullivan, 2003).

Figure B-6. Estimated time series of S deposition at one example watershed in the SW Adirondack Mountains used by Sullivan et al. (2006) as input to the MAGIC model for projecting past and future changes in lakewater chemistry attributable to acidic deposition. Future deposition estimates were based on three emissions control scenarios (Base Case, Moderate Additional Controls, Aggressive Additional Controls).



Source: Sullivan et al. (2006b).

Figure B-7. Simulated cumulative frequency distributions of lakewater ANC at three points in time for the population of Adirondack lakes.

Model hindcasts using PnET-BGC indicated that acidic deposition has greatly altered surface waters and soils in the Adirondacks over the past 150 years, and that some ecosystems are continuing to acidify despite decreases in S deposition. 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 stream 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

experienced increasing ANC and pH. The rate of soil base saturation regeneration 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.

There are few streams in the northeastern U.S. for which future acid-base chemistry status has been modeled. One notable exception is the modeling conducted for streams at the HBEF and in the Catskill Mountains. Calculations performed by Driscoll et al. (2003c) using the PnET-BGC model suggested that "aggressive reductions in N emissions alone will not result in marked improvements in the acid-base status of forest streams." For example, in response to an aggressive utility emissions control scenario (hypothesized 75% reduction in utility N emissions beyond the CAAA), the ANC values of Watershed 6 at HBEF in New Hampshire and Biscuit Brook in the Catskill Mountains in New York were only projected to increase by 1 and 2 μeq/L, respectively, by the year 2050 (Driscoll et al., 2003c). Projected changes in water chemistry in response to differing levels of N deposition were small in comparison with model projections of variations resulting from climatic factors (Aber and Driscoll, 1997; Driscoll et al., 2003c).

B.3.4.2. Southeastern Surface Waters

The two regions in the Southeast that were identified by Charles (Charles, 1991) as containing low-ANC surface waters are the Appalachian Mountains and Northern Florida. The Appalachian Mountain region contains many streams that have low ANC, and it receives one of the highest rates of acidic deposition in the U.S. (Herlihy et al., 1993). Streamwater acid-base chemistry has been extensively studied in this region (e.g., Church et al., 1992; Herlihy et al., 1993; Van Sickle and Church, 1995; Sullivan et al., 2002, 2003).

Northern Florida contains the highest percentage of acidic lakes of any lake population in the U.S. (Linthurst et al., 1986a,b). Most lakes in Florida are located in marine sands overlying carbonate bedrock and the Floridan aquifer, a series of limestone and dolomite formations that underlies most of Florida. Most of the acidic and low-ANC lakes are located in the Panhandle and north central lake districts.

The current status, past acidification and recent trends in surface waters chemistry for both the Appalachian Mountains and northern Florida are discussed below.

Appalachian Mountains

Current Status

One of the most important processes affecting watershed acid-neutralization throughout much of the Southeast is S-adsorption on soil. If S adsorption on soil is high, relatively high levels of S deposition

have little or no effect on stream acid-base chemistry, at least in the short-term. However, this S-adsorption capacity can become depleted over time under continued S deposition, and this causes a delayed acidification response.

Sulfur-adsorption varies by physiographic province. It is highest in the soils of the Southern Blue Ridge, where typically about half of the incoming S is retained. Adsorption is lower in the Valley and Ridge watersheds and especially in the Appalachian Plateau (Herlihy et al., 1993). In general, S adsorption is higher in the southern portions of the Appalachian Mountain region.

The Mid-Atlantic Highlands consists of the portions of the Blue Ridge Mountains, Ridge and Valley, and Appalachian Plateau ecoregions between the Virginia-North Carolina border and the Catskill Mountains in southeastern New York. Acid mine drainage (AMD) is a major source of acidity to streams in the Mid-Atlantic Highlands but in many cases is easy to identify due to the high concentrations of SO_4^{2-} in the streams that are influenced by AMD (Herlihy et al., 1991). Acidic and low-ANC streams affected by AMD were removed before analyses of acid-base chemistry population statistics.

Streams in the Appalachian Mountain portion of the mid-Atlantic region receive some of the largest acidic deposition loadings of any region of the U.S. A compilation of survey data from the mid-Appalachians yields a consistent picture of the acid-base status of streams. Acidic streams, and streams with very low ANC, are almost all located in small (watershed area < 20 km^2), upland, forested catchments in areas of base-poor bedrock. Acidic surface waters in this region are nearly always found in forested watersheds because the thin soils and steep slopes that make these watersheds unsuitable for agriculture and other development also contribute to their sensitivity to acidic deposition (Baker et al., 1991a).

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 (Table B-4). Sulfate from atmospheric deposition was the dominant source of acid anions in acidic mid-Appalachian streams. In these acidic streams, the low pH (median 4.9) and high levels of Al_i (median 129 µg/L) leached through soils by acidic deposition were considered to be sufficiently high to cause damage to aquatic biota. Acidic streams in this subpopulation typically had low DOC (mean 1.5 mg/L).

Localized studies have clearly shown that streamwater ANC is closely related to bedrock mineralogy (Herlihy et al., 1993). Sullivan et al. (2007) delimited a high-interest area for streamwater acidification sensitivity within the Southern Appalachian Mountain region (Virginia/West Virginia to Georgia) based on geological classification and elevation. It covered only 28% of the region, and yet included almost all known acidic and low ANC (<20 µeq/L) streams, based on evaluation of about 1,000

streams for which water chemistry data were available. They found that the vast majority of low ANC sample streams were underlain by the siliceous geologic sensitivity class, which is represented by such lithologies as sandstone and quartzite. Low ANC streamwater throughout the region was also found to be associated with a number of watershed features in addition to lithology and elevation, including ecoregion, physiographic province, soil type, forest type and watershed area.

Sulfate mass balance analyses indicated that, because of watershed SO_4^{2-} retention, soils and surface waters of the region have not yet realized the full effects of elevated S deposition. On average, based on NSS data, sites in the Blue Ridge Mountains retain 35% of incoming SO_4^{2-} from atmospheric deposition. The amount of SO_4^{2-} retention was strongly related to ecoregion in the order, Piedmont > Blue Ridge and Ridge & Valley > Appalachian Plateau.

Herlihy et al. (1993) believed that the observed differences were due to the effects of cumulative loadings from atmospheric S deposition and not due to inherent ecoregional differences in the soils. They also concluded that S retention will likely continue to decrease in the future, resulting in further losses of stream ANC.

Both mineral acids and organic acids play important roles in the acid-base status of streams in the Mid-Atlantic Coastal Plain (Baker et al., 1991a). Acidic streams in the New Jersey Pine Barrens (Table B-2) are largely inorganically dominated, but most likely they were naturally organically acidic in the past. It is uncertain what effect the addition of inorganic acids from acidic deposition has had on these low ionic strength colored systems. Over half the streams in the Pine Barrens included in the NSS were acidic, and virtually all (96%) had ANC less than 50 µeq/L. Human disturbances in the Pine Barrens often result in the alkalinization of streams (increases in pH and ANC) that alter the natural Pine Barrens aquatic biota. Outside of the Pine Barrens in the NSS, the remainder of the acidic streams in the Coastal Plain were all high DOC organically dominated systems. Low DOC (<4 mg/L), acidic streams have been observed, however, in other Mid-Atlantic Coastal Plain surveys.

The Virginia Trout Stream Sensitivity Study (VTSSS) surveyed streamwater chemistry for 344 (~80%) of the native brook trout (*Salvelinus fontinalis*) streams in western Virginia. About half of the streams included in the VTSSS had ANC < 50 µeq/L. In contrast, the NSS (Kaufmann et al., 1988) data for western Virginia suggested that only about 15% of the streams in the NSS target population had ANC < 50 µeq/L. These differences may reflect the smaller watershed size, more mountainous topography, and generally more inert bedrock of the VTSSS watersheds, as compared with the overall NSS stream population.

In the Appalachian Plateau of West Virginia there are two wilderness areas located in close proximity in an area of base-poor bedrock -- Dolly Sods and Otter Creek Wilderness Areas. Most streams draining these wilderness areas are acidic or low in ANC.

In the Great Smoky Mountains National Park in North Carolina and Tennessee, Cook et al. (1994) reported high NO_3^- concentrations (~100 µeq/L) in upland streams which were correlated with elevation and forest stand age. The old growth sites at higher elevation showed the highest NO_3^- concentrations. This pattern could have been due to the higher rates of N deposition and flashier hydrology at high elevation, and also decreased N uptake by trees in older forest stands. High N deposition at these sites has likely contributed to both chronic and episodic acidification of streamwater (Flum and Nodvin, 1995; Nodvin et al., 1995).

Recent Trends

Population estimates from TIME surveys of streams in the Northern Appalachian Plateau region suggested that 5014 km of streams (11.8% of the stream length) were acidic in 1993−94, but that only 3600 km of streams (8.5% of the stream population) remained acidic in this region in 2000. The approximate rate of estimated change in Gran ANC in the region (Table B-5) was +0.79 µeq/L/yr. On this basis, Stoddard et al. (2003) estimated that roughly 3600 km of stream (8.5%) remained acidic 10 years later. This represents about a 28% decrease in acidic stream length over the preceding decade.

Future Projections

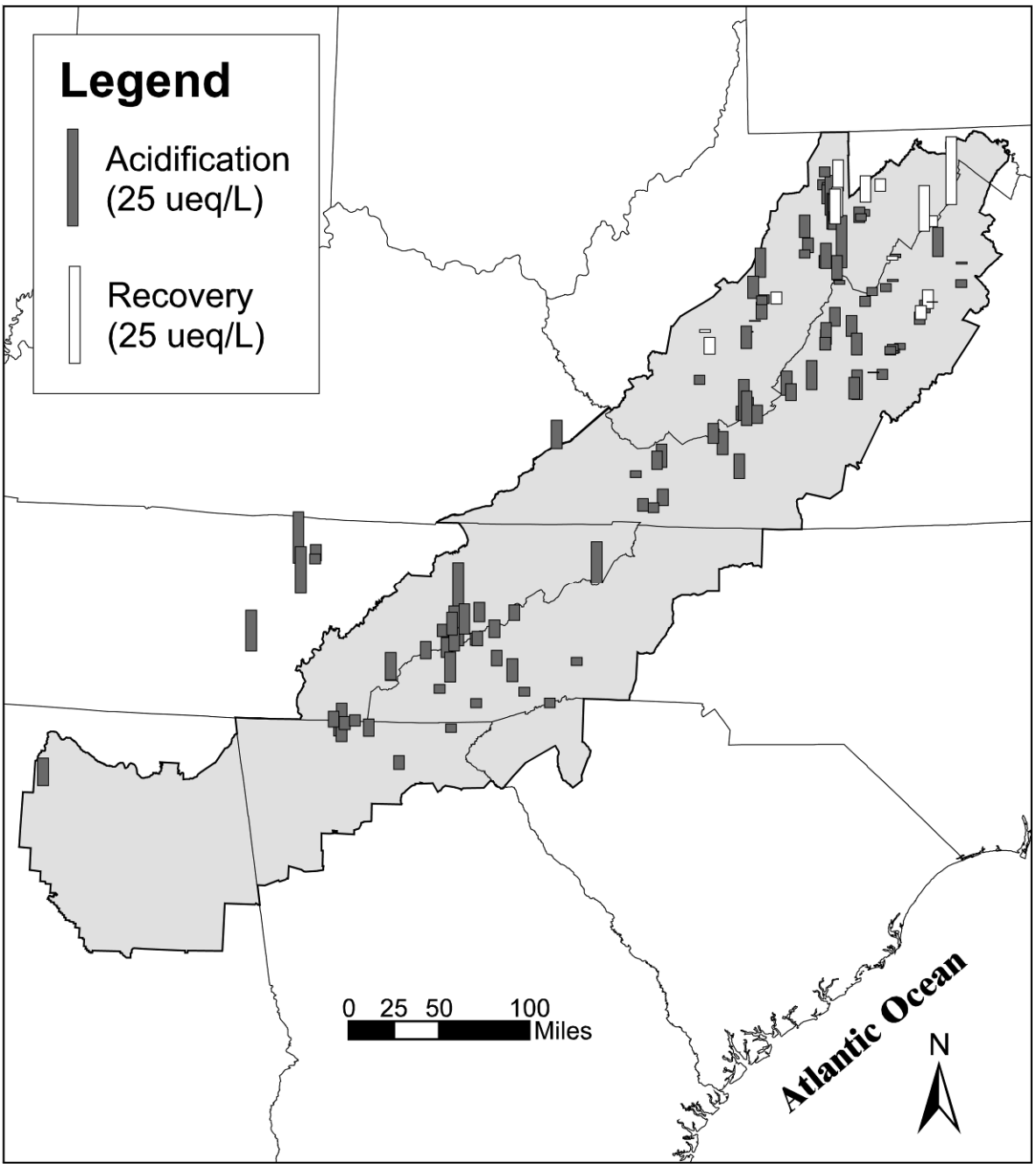
Model projections of future changes in acid-base chemistry of streams in the southeastern U.S. were presented by Sullivan et al. (2002, 2003, 2005). In the eight-state Southern Appalachian Mountains region, Sullivan et al. (2005) modeled future effects of atmospheric S and N deposition on aquatic resources. Modeling was conducted with the MAGIC model for 40 to 50 sites within each of three physiographic provinces, stratified by stream water ANC class. Simulations were based on assumed constant future atmospheric deposition at 1995 levels and on three regional strategies of emissions controls provided by the Southern Appalachian Mountains Initiative (SAMI), based on the Urban to Regional Multiscale One-Atmosphere model (Odman et al., 2002).

The NSS statistical frame (Kaufmann et al., 1991) was used to estimate the number and percentage of stream reaches in the region that were projected to change their chemistry in response to the emissions control strategies. There was a small decline in the estimated length of projected acidic ($ANC \geq 0$) streams in 2040 from the least to the most restrictive emissions control strategy, but there was little difference in projected stream length in the other ANC classes as a consequence of adopting one or another strategy. However, projections of continued future acidification were substantially larger under a scenario in which S and N deposition were held constant into the future at 1995 levels. Turner et al. (1992) also reported MAGIC model simulation results that suggested substantial acidification

(~20 μeq/L) of aquatic systems would occur in the southeastern U.S. if deposition remained constant at 1985 levels. Those model analyses were conducted as part of the NAPAP (1991) IA.

The SAMI emissions control strategies used in the modeling represented air regulatory requirements being implemented at the time of SAMI's formation, expected reductions under recent federal regulatory actions, and additional emissions controls applied to all emissions sectors in the eight SAMI states. The spatial variability of these emissions controls resulted in varying estimated future changes in S and N deposition at different locations within the SAMI region. The SAMI strategies were designated A2, B1, and B3. A2 is the reference strategy that represented SAMI's 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). Emissions reductions under the A2 strategy included the acid rain controls under Title IV of the 1990 Amendments to the CAAA, the 1–h 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 A2 strategy was applied for all eastern states and focused on the utility and highway vehicle sectors. The B1 and B3 strategies assumed progressively larger emissions reductions, targeted only to the eight SAMI states but covering all emissions sectors.

Streams exhibited a broad range of response to the cumulative S deposition loadings received to date and the large simulated decreases in S deposition in the future under the emissions control strategies (Table B-8). Some streams showed modeled stream water SO_4^{2-} concentrations increasing in the future, even while S deposition was reduced by more than two-thirds. These were mostly sites that had relatively low SO_4^{2-} concentrations in 1995 (≥ about 50 μeq/L) because of S adsorption on soils. They generally showed simulated future acidification, which was most pronounced for the A2 strategy. Other streams were simulated to show relatively large decreases in future stream water SO_4^{2-} concentrations and concurrent increases in ANC in response to the strategies, with progressively larger changes from the A2 to the B3 strategy. These tended to be streams that had relatively high concentrations of SO_4^{2-} (>50 μeq/L) in 1995, suggesting that they were closer to steady state with respect to S inputs and outputs. Some streams were projected to exhibit future decreases in both SO_4^{2-} and NO_3^- concentrations but nevertheless to continue to acidify. This response was attributed by Sullivan et al. (2004) to large simulated decreases in base cation concentrations at these sites due to soil base cation depletion.



Source: Sullivan et al. (2004).

Figure B-8. Map showing simulated changes in streamwater ANC from 1995 to 2040 in response to the SAMI A2 emmissions control strategy, representing existing emissions control regulations.

Most simulated changes in stream water ANC from 1995 to 2040 were rather modest (Table B-8), given the very large estimates of decreased S deposition. Few modeled streams showed projected change in ANC of more than about 20 µeq/L. 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 negative ANC stream water, and therefore little biological benefit would be expected from the simulated improvement in chemistry. The model results suggested, however, that benefits would continue to accrue well beyond 2040 for all strategies, even if deposition was held constant at 2040 levels into the future.

Florida Surface Waters

Current Status

According to the ELS 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 clearwater (DOC < 400 µmol) seepage lakes in which the dominant acid anions were Cl^- and SO_4^{2-}. Most of the acidic and low-ANC lakes are located in the Panhandle and north central lake districts. In these areas, the Floridan aquifer is separated from overlying sand deposits by a confining layer called the Hawthorne formation. The major lake districts are located in karst terrain, where lakes formed through dissolution of the underlying limestone followed by movement of surficial deposits into solution cavities (cf. Arrington et al., 1987).

Flow of water from most of the lakes is downward, recharging the Floridan aquifer. Lake stage varies in response to long-term trends in precipitation, and perhaps in response to groundwater withdrawals. ANC generation in most lakes that have been studied appears to be due primarily to in-lake SO_4^{2-} and NO_3^- reduction (Baker et al., 1988; Pollman and Canfield, 1991). Retention of SO_4^{2-} by watershed soils may also be important. Lakes can be highly alkaline where groundwater interacts with the deeper aquifer. Lakes with hydrologic contributions from shallow aquifers in highly weathered sands can be quite acidic and may be sensitive to acidic deposition.

DOC concentrations are high in many Florida lakes, but organic anions are less important than SO_4^{2-} in most low-ANC and acidic lakes (Pollman and Canfield, 1991). Aluminum concentrations tend to be very low in Florida lakes despite the high lakewater acidity because most of the Al^{n+} is removed from soil solution by precipitation and ion exchange reactions within 75 cm depths (Grates et al., 1985), and relatively little Al^{n+} is transported in groundwater to lake waters.

Baker et al. (1988) reported that retention of inorganic N is nearly 100% in most Florida lakes. ANC generation from SO_4^{2-} retention may approach 100 µeq/L in some Florida lakes (Pollman and Canfield, 1991). These in-lake processes are important for generating ANC. Base cation deposition and NH_4^+ assimilation can also influence the acid-base status of lakes in Florida.

The Northern Florida Highlands high interest area identified by Baker et al. (1991a) consists of the northern portion (north of 29°N latitude) of the Central Lake District and the Florida Panhandle (Figure B-3). Acidic streams were located in the Florida Panhandle and were mildly acidic (mean pH 5.0) and extremely dilute, with very low sea salt-corrected SBC (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 DOC < 2 mg/L and were inorganically dominated. Inorganic monomeric Al concentrations in these acidic streams were very low (mean 11 µg/L). In these low DOC, low ANC Panhandle streams, it was suggested that the degree of SO_4^{2-} and NO_3^- retention was an important control on streamwater ANC (Baker et al., 1991a).

Past Acidification

Considerable research has been conducted on past acidification in Florida lakes. Historical analyses of lake chemistry (Battoe and Lowe, 1992), inferred historical deposition (Hendry and Brezonik, 1984; Husar and Sullivan, 1991), and paleolimnological reconstructions of lake pH (Sweets et al., 1990; Sweets, 1992) suggest evidence that some Florida lakes have acidified in response to acidic deposition. However, the role of acid deposition in lakewater acidification is not entirely clear (cf. Pollman and Canfield, 1991), and the interpretation is complicated by regional and local changes in land use and hydrology (Sullivan, 2000).

An alternative explanation for the apparent acidification of some lakes is the regional decline in the potentiometric surface of the groundwater (Sweets et al., 1990). Large groundwater withdrawals of the Floridan aquifer for residential and agricultural purposes may have reduced groundwater inflow of base cations into seepage lakes, and therefore caused less buffering of acidity. Other land use changes may have increased lake pH by providing inputs of fertilizer, which would increase lake productivity. Paleolimnological evidence of this effect was provided by Brenner and Binford (1988) and Deevey et al. (1986).

It is likely that lake chemistry in Florida has been heavily effected by land use changes. More than half of the Florida lakes included in the ELS showed evidence of disturbance based on deviations from expected geochemistry (Pollman and Canfield, 1991). Such effects complicate efforts to determine the role of acidic deposition in controlling lakewater acid-base chemistry.

Diatom-inferred pH reconstructions of lakewater chemistry of six seepage lakes in Florida were calculated as part of the PIRLA-I project and reported by Sweets et al. (1990). An additional 10 seepage lakes were cored as part of PIRLA-II, and results of those analyses were reported by Sweets (1992). Paleolimnological study lakes are located in the Panhandle, the Trail Ridge Lake District, and Ocala National Forest, generally in terraces of highly weathered loose sand that were deposited on top of the clay-confining layer.

Of the six lakes analyzed in PIRLA-I, two (Barco and Suggs) were inferred to have acidified since 1950 (Sweets et al., 1990). The timing of the onset of inferred acidification correlated with increases in SO_2 emissions and S deposition, which increased consistently between about 1945 and 1985 (Husar and Sullivan, 1991).

Of the 16 Florida seepage lakes studied in the PIRLA-II projects, 5 were located in or near the Trail Ridge Lake District, and all showed diatom-inferred acidification of at least 0.2 pH units (Sweets, 1992). Lakes located in the Panhandle region and Ocala National Forest generally did not show evidence of recent acidification. The exception was Lake Five-O, which was inferred to have decreased by 2 pH units. However, the diatom data suggested that this pH decline was associated with a sudden change in chemistry, probably caused by a catastrophic disturbance such as sinkhole development, rather than by acidification from atmospheric deposition (Pollman and Sweets, 1990; Sweets, 1992).

B.3.4.3. Upper Midwest

The Upper Midwest contains numerous lakes created by glaciation. The region has little topographic relief and with its deep glacial overburden, it also has little or no exposed bedrock. Acid-sensitive surface waters in the Upper Midwest are mainly seepage lakes (Eilers et al., 1983). Most drainage lakes and some of the seepage lakes in the Upper Midwest region receive substantial inflow from groundwater, which is generally high in base cation concentrations from dissolution of carbonate and silicate minerals. Relatively high concentrations of base cations in these lakes make them insensitive to acidification from acidic deposition. The seepage lakes that have low base cation concentrations, and that are therefore more acid-sensitive, generally receive most of their water input from precipitation directly on the lake surface (Baker et al., 1991b).

Current Status

Based on the ELS survey, the Upper Midwest has a large population of low ANC lakes, but relatively few chronically acidic (ANC $\geq$ 0) lakes (Linthurst et al., 1986a,b). 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 et al., 1988), but much higher in many of the drainage lakes that are less sensitive to acidification from acidic deposition.

Groundwater flow-through lakes in the Upper Midwest can be identified on the basis of having Si concentration greater than about 1 mg/L (Baker et al., 1991b). They generally have high pH and ANC, due to groundwater inputs of base cations (e.g., Baker et al., 1991b). Based on results from the ELS survey, only 6% of these lakes had ANC $\geq$ 50 µeq/L and none were acidic. Groundwater recharge lakes (those having Si concentration less than 1 mg/L) constituted 71% of the seepage lakes in the Upper Midwest, and were more frequently low pH and ANC. Five percent were acidic and 9% had pH $\geq$ 5.5. Nearly 90% of Upper Midwestern lakes that had ANC $\geq$ 50 µeq/L were in this category (Baker et al., 1991b). Such lakes tend to be susceptible to acidification from acidic deposition.

Sullivan (2000) summarized patterns in lakewater chemistry across the Upper Midwest from the ELS survey. Lakewater pH, ANC, base cations, and DOC all decreased from west to east across the region. Lakewater SO_4^{2-} concentrations did not show a comparable change, despite a substantial increase in wet SO_4 deposition from Wisconsin to Michigan. Cook and Jager (1991) attributed the absence of a more pronounced gradient in lakewater SO_4^{2-} concentration across the region to watershed sources of S in Minnesota and high anion retention in seepage lakes, which predominate in the eastern portion of the region. The retention of SO_4^{2-} by dissimilatory reduction is generally high for seepage lakes because of their long hydraulic retention times (τw). For example, an Upper Midwestern seepage lake with mean depth of 3 m and hydraulic retention time of 7.5 years would be expected to lose about 50 μeq/L of SO_4^{2-} from the water column by this process (Cook and Jager, 1991).

Lakewater concentrations of inorganic N reported by the ELS were low throughout the Upper Midwest. In addition, snowmelt would not be expected to provide any significant NO_3^- influx to lakes in the Upper Midwest because most snowmelt infiltrates the soil before reaching the drainage lakes, and because snowmelt input of N into seepage lakes would be limited mainly to the snow on the lake surface and immediate near-shore environment. Aluminum concentrations are far lower in the Upper Midwest than in lakes of similar pH in the Northeast.

Wetlands are common throughout the Upper Midwest. They contribute to high production of organic matter which is reflected in high DOC concentrations in many lakes. Despite the abundant wetlands, SO_4^{2-} is the dominant anion in the low-ANC ($\geq$ 50 μeq/L) groundwater recharge seepage lakes.

Base cation production is the dominant ion-enrichment process in most Upper Midwestern lakes. Even in low-ANC groundwater-recharge seepage lakes, base cation production accounts for 72% to 86% of total ANC production (Cook and Jager, 1991).

Past Acidification

Space-for-time substitution analysis was used to infer the general levels of past change in lake water acid-base chemistry in the Upper Midwest. Such an analysis assumes that study lakes were generally similar in acid-base chemistry prior to the onset of acidic deposition and that the only substantial driver of recent change in acid-base chemistry has been the level of acidic deposition. Across an increasing S depositional gradient from eastern Minnesota eastward to eastern Michigan, ANC expressed as (HCO_3^- - H^+) decreased and the ratio SO_4^{2-} to SBC increased in the groundwater recharge seepage lakes. In Michigan and Wisconsin, many lakes had SO_4^{2-} > SBC, indicating that the acidity was due to high SO_4^{2-} relative to SBC concentration. There were also many lakes that had high concentrations of DOC, and organic acidity probably accounted for many of these lakes having ANC < 0. The spatial pattern in (HCO_3^- - H^+) could not be attributed to DOC, which generally showed a decreasing trend with increasing acidic deposition.

The concentration of lakewater (Ca^{2+} + Mg^{2+}) also decreased with increasing acidic deposition, probably due to lower levels of base cation deposition and greater amounts of precipitation in the eastern portion of the region. Atmospheric deposition is an important source of base cations for groundwater recharge seepage lakes because of minimal groundwater inputs. In the eastern portion of the region, such lakes are more sensitive to pH and ANC depression in response to either elevated SO_4^{2-} or DOC. The spatial patterns for low ANC groundwater recharge lakes in the Upper Midwest are consistent with the following hypotheses (Sullivan et al., 1990)(Sullivan, 1990, 2000):

1. Sensitivity to mineral and organic acidity increased from west to east because of decreasing lakewater base cation concentrations, and this may have been due, in part, to changes in base cation deposition and precipitation volume along this gradient.

2. High concentrations of DOC were responsible for the acidic conditions in some of the lakes, and DOC may have decreased in response to acidic deposition.

3. Many of the lakes in eastern Michigan, and some in Wisconsin, were acidic because of high SO_4^{2-} relative to base cation concentration, and had probably been acidified by acidic deposition.

Diatom-inferred pH reconstructions were completed for 15 lakes in the Upper Midwest region, and summarized by Kingston et al. (1990) and Cook and Jager (1991). Four lakes, all of which had measured pH < 5.7, showed a diatom-inferred pH decline of 0.2 to 0.5 pH units during the preceding 50 to 100 years. Diatom-inferred pH increased in one lake by 0.2 pH units. No change was inferred for the other 10 lakes, including 4 lakes with pH > 6.0. No major, recent, regional acidification was indicated by the diatom-inferred pH reconstructions. Inferred changes in most lakes were small, and were no greater during the industrial period than during the pre-industrial period (Sullivan, 2000).

Although diatom data suggested that some Upper Midwestern lakes may have acidified since pre-industrial times, there is little paleolimnological evidence indicating substantial widespread acidification in this region (Cook et al., 1990; Kingston et al., 1990). Land use changes and other human disturbances of Upper Midwestern lakes and their watersheds have probably exerted more influence on the acid-base chemistry of lakes than has acidic deposition (Kingston et al., 1990; (Sullivan et al., 1990)Sullivan, 1990, 2000). The portion of the region most likely to have experienced acidification from acidic deposition is the Upper Peninsula of Michigan, where acidic seepage lakes are particularly numerous (Baker et al., 1991a); acidic deposition is highest for the region, and the $[SO_4^{2-}]$/[SBC] ratio is commonly >1.0. The percentage of acidic lakes in the eastern portion of the Upper Peninsula of Michigan (east of longitude 87°) was estimated to be 18% to 19% in 1984 (Schnoor et al., 1986; Eilers et al., 1988).

Recent Trends

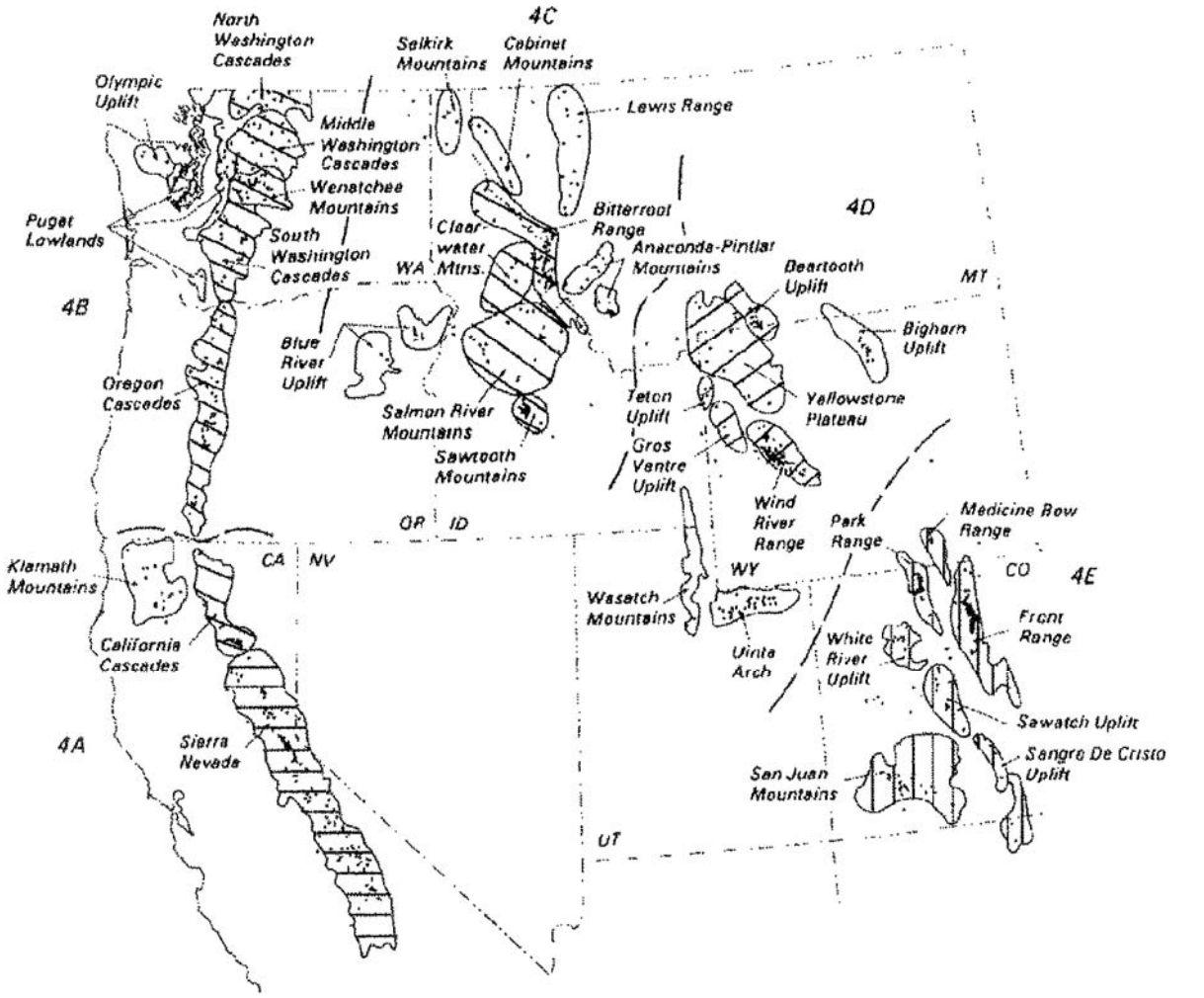
Regional trend values for long-term monitoring lakes during the period 1990 to 2000 suggested that SO_4^{2-} declined in lakewater by 3.63 µeq/L/yr, whereas lakewater NO_3^- concentrations were relatively constant. The large decrease in SO_4^{2-} concentration was mainly balanced by a large decrease in base cation concentrations (−1.42 µeq/L/yr) and an increase in ANC (+1.07 µeq/L/yr). All of these trends were significant at $p < 0.01$ (Stoddard et al., 2003). In the Upper Midwest, an estimated 80 of 251 lakes that were acidic in the mid-1980s were no longer acidic in 2000. This change may be due to reduced levels of S deposition (Stoddard et al., 2003).

B.3.4.4. West

Portions of the mountainous West contain large areas of exposed bedrock, with little soil or vegetative cover to neutralize acidic inputs. This is particularly true of alpine regions of the Sierra Nevada, northern Washington Cascades, the Idaho batholith, and portions of the Rocky Mountains in Wyoming and Colorado. However, the percentage of exposed bedrock in a watershed does not always indicate acid-sensitivity. If the bedrock contains even small deposits of calcareous minerals or if physical weathering such as that caused by glaciers causes a high production of base cations within the watershed (Drever and Hurcomb, 1986), surface waters may be alkaline, and are not sensitive to acidification from acidic deposition.

The areas that are sensitive to adverse effects from acidic deposition in the western U.S. form two nearly continuous ranges, the Sierra Nevada, which extends through most of the length of California, and the Cascade Mountains, which extend from northern California to northern Washington (Source: Landers et al. (1987).

Figure B-9). The sensitivity of the Rocky Mountains varies widely because the ranges are discontinuous with highly variable geological composition. For that reason, assessments of the sensitivity of Rocky Mountain aquatic resources to acidification should be specific to individual ranges (Turk and Spahr, 1991).



Source: Landers et al. (1987).

Figure B-9. Major geomorphic units and locations of lakes sampled in the Western Lake Survey. Those areas known to contain sensitive lake resources are shaded with cross-hatching.

The NAPAP SOS/T Reports and the IA (NAPAP, 1991) provided only a cursory treatment of aquatic effects issues in the West, largely because it was well known that atmospheric deposition of S and N were generally low compared to highly affected areas in the East (Sullivan, 2000) and because results from the WLS (Landers et al., 1987) indicated that there were virtually no acidic (ANC $\geq$ 0) lakes in the West. NAPAP (1991) indicated, however, that high-elevation areas of the West contained many of the watersheds most sensitive to the potential effects of acidic deposition.

Because of the proximity of western urban and industrial pollution sources to individual mountain ranges, it is important to consider emissions in the immediate vicinity of sensitive resources as well as regional emissions. Atmospheric deposition in the far western ranges (i.e., Sierra Nevada, Cascade Mountains) is largely influenced by local emissions, particularly emission sources to the west (upwind) of sensitive resources. In the Rocky Mountains, deposition chemistry is often influenced by a more complex

collection of emission sources. For example, in the Mt. Zirkel Wilderness of northwestern Colorado, SO_4^{2-} and NO_3^- in the snow appeared to originate largely from sources in the Yampa Valley, about 75 km to the west (Turk et al., 1992). Rocky Mountain National Park is affected by emissions from the Front Range to the southeast.

The acid base chemistry of lake and stream waters in Rocky Mountain National Park appears to be primarily a function of the interactions among several key parameters and associated processes: atmospheric deposition, bedrock geology, the depth and composition of surficial deposits and associated hydrologic flowpaths, and the occurrence of soils, tundra, and forest vegetation (Sullivan, 2000). Potential biological effects of acidic deposition on lakes in the Rocky Mountains are primarily attributable to acidification from high NO_3^- concentration. In general, such effects tend to be episodic, rather than chronic. Highest NO_3^- concentrations in both precipitation and surface waters are found above timberline in Colorado, where biological activity, and therefore NO_3^- uptake, by terrestrial and aquatic biota is lowest.

Current Status

The available information on acid-base chemistry of surface waters in the West is based mostly on synoptic data from the WLS (Landers et al., 1987) and some more localized studies. Acid anion concentrations in most western lakes are low during fall, but can be higher during snowmelt (Williams and Melack, 1991). Available data from intensive study sites in the West (e.g., Loch Vale, CO, Emerald Lake Basin, CA, and the Glacier Lakes Watershed, WY) suggest that episodic depression of stream pH may be more pronounced than for lakes. However, there are no available systematic regional stream chemistry data with which to assess regional sensitivity of streams to acidic deposition.

In most western lakes concentrations of SO_4^{2-} are low, although watershed sources of S are substantial in some cases (Table B-9). Turk and Spahr (1991) presented a conceptual model for expected SO_4^{2-} distributions in lakewaters in the West that can be used as an aid in identifying the proportion of watersheds with significant watershed sources of S. Considering that atmospheric sources can account for generally < 30 μeq/L of SO_4 in the West, it appears that many lakes, particularly in Colorado, receive variable amounts of watershed S (Sullivan, 2000; Figure B-10).

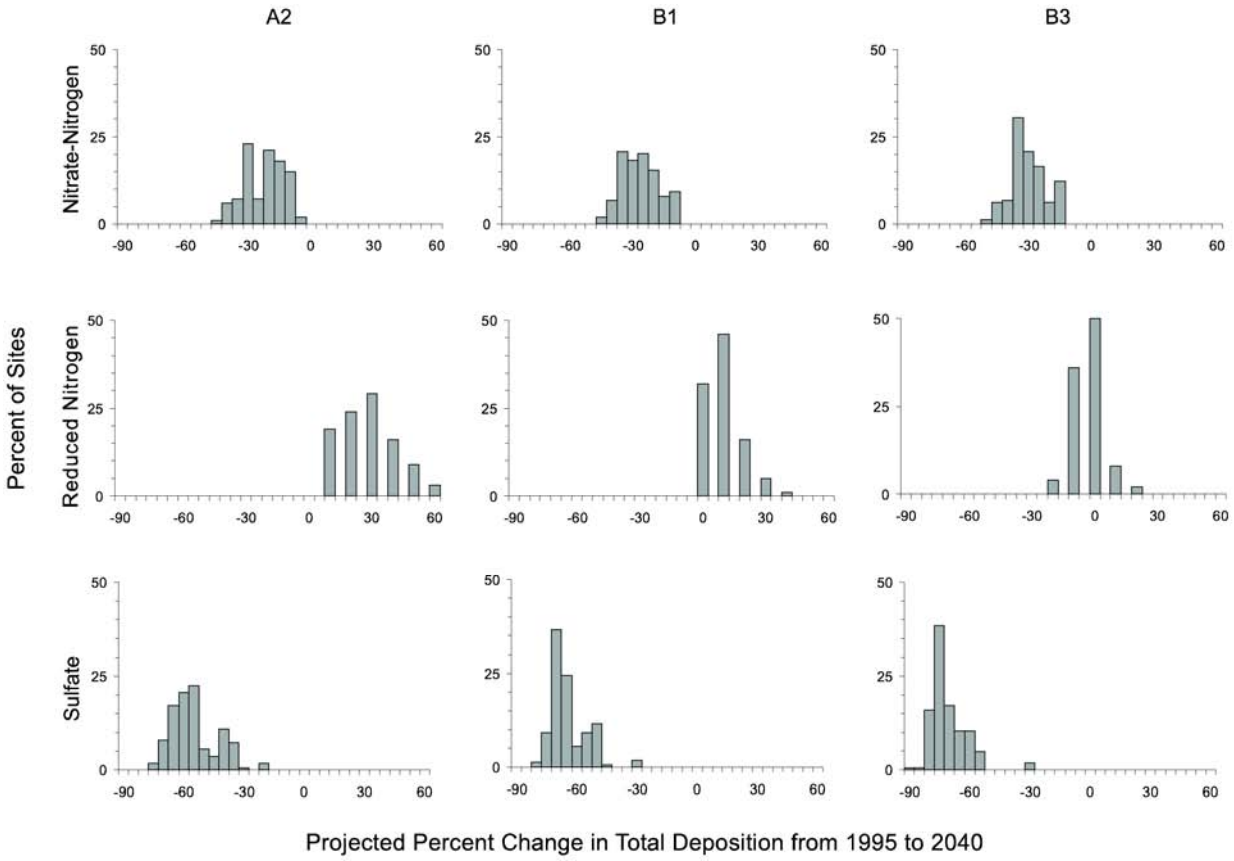


Figure B-10. Estimated percent changes in the total deposition of sulfur, reduced N, and nitrate-N at MAGIC modeling sites from 1995 to 2040 under each of the emissions control strategies.

Source: Sullivan et al. (2004).

Nitrate concentrations in most WLS lakes were near 0 during fall (Landers et al., 1987), although fall NO_3^- concentrations were high in some cases (Table B-10). For example, nearly one fourth of the lakes in northwest Wyoming had NO_3^- > 5 µeq/L and almost 10% had NO_3^- > 10 µeq/L (Table B-10). In both the Sierra Nevada and Colorado Rockies subregions, about 10% of the lakes had fall NO_3^- concentrations above 5 µeq/L (Table B-10).

It is important to note that even low to moderate concentrations of NO_3^- in western lakes might be significant in view of: (1) the low base cation concentrations in many lakes; (2) potential for continuing N deposition to eventually exhaust natural assimilative capabilities; and (3) the fact that these distributions are based on fall data. Time-intensive discharge and chemical data for two alpine streams in Loch Vale watershed identified strong seasonal control on streamwater NO_3^- concentrations (Campbell et al., 1995). In spite of the paucity of soil cover, the chemical composition of streams is regulated much as in typical forested watersheds. Soils and other shallow groundwater matrices such as boulder fields are more important in controlling surface water chemistry than their abundance would indicate. Spring streamwater NO_3^- concentrations ranged to 40 µeq/L, compared with summer minimum values near 10 µeq/L. Elution

of acidic waters from snowpack along with dilution of base cations originating in shallow groundwater caused episodes of decreased ANC in alpine streams (Campbell et al., 1995). A subalpine stream in the same watershed similarly displayed decreased ANC and elevated monomeric Al concentrations during snowmelt over 2 years of intensive sampling, related to elevated concentrations of SO_4^{2-}, NO_3^-, and DOC (Denning et al., 1991). Limited data collected during snowmelt suggest that spring concentrations could be several times higher than samples collected during the fall (e.g., Reuss et al., 1995).

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 resources (Table B-9 and Table B-10). Lakes in the Sierra Nevada are especially sensitive to effects from acidic deposition because of the predominance of granitic bedrock, thin acidic soils, large amounts of precipitation, coniferous vegetation, and dilute nature of the lakes (Melack et al., 1985; Melack and Stoddard, 1991). Surface waters in this region are among the 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 (pH about 5.5) snowpack.

During the 1980s, an Integrated Watershed Study (IWS) was conducted at seven lakes in the Sierra Nevada, including Emerald Lake and surrounding watersheds (~3,000 m elevation) to determine the effects of acidification on surface waters (Tonnessen, 1991). Three lakes (Lost, Pear, and Emerald) had volume-weighted mean ANC in the range of 15 to 30 µeq/L. Moderate ANC waters (Topaz, Spuller, and Marble Fork) exhibited mean ANC in the range of 30 to 50 µeq/L. Crystal and Ruby Lakes had mean annual ANC > 50 µeq/L.

Many Cascade and Rocky Mountain lakes are also highly sensitive to potential acidic 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). The data that would be needed for determining the extent and magnitude of episodic acidification have not been collected to a sufficient degree in acid-sensitive areas of the West to support regional assessment of episodic acidification (Sullivan, 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. The WLS data for lakes in Colorado and Wyoming demonstrate that surface waters in this area had fall concentrations of NO_3^- in the range of 10 to 30 µeq/L, and likely had substantially higher NO_3^- concentrations during spring.

The weight of evidence suggests many high-elevation lakes in the West receive N deposition sufficiently high to cause chronic NO_3^- leaching, and likely some degree of associated chronic and episodic acidification. However, existing data are insufficient to make a conclusive determination (Sullivan, 2000).

Past Acidification

The limited paleolimnological data available for lakes in the western U.S. suggest that widespread chronic acidification probably has not occurred. Some lakes may have experienced recent pH declines, but the magnitude of such changes has likely been small (Sullivan, 2000).

In the Sierra Nevada, paleolimnological reconstructions of lakewater pH and ANC were calculated by Holmes et al. (1989) at 24 depth intervals at Emerald Lake, for the period 1825 to the present. Significant trends were not found for either pH or ANC, and the authors concluded that Emerald Lake had not been acidified by acidic deposition. Whiting et al. (1989) completed paleolimnological analyses of three additional lakes in the Sierra Nevada. Eastern Book Lake (pH = 7.06) showed evidence of both long-term alkalization (~0.3 pH units over the past 200 years) and pH fluctuations since 1970. Lake 45 (pH = 5.16) may have acidified slightly (~0.2 pH units) over the last 60 years. Lake Harriet (pH = 6.52) showed no significant change.

In Rocky Mountain National Park, Colorado, Baron et al. (1986) investigated metal stratigraphy, diatom stratigraphy, and inferred pH profiles of four subalpine lakes. They found no evidence of historical influence on pH attributable to atmospheric deposition. Other paleolimnological studies of Rocky Mountain lakes report similar results: metals (primarily lead) exhibit temporal dynamics related to the increase and decline of precious metal mining in the region, but these are asynchronous with other metal or biological indicators of acidification (Wolfe et al., 2003). Both the study by Wolfe et al. (2003) and a study by Saros et al. (2003) showed no evidence of acidification of lake waters over time, but increasing evidence of eutrophication from atmospheric N deposition (see Annex C).

DayCent-Chem, a model that simulates the daily dynamics of plant production, soil organic matter, cation exchange, mineral weathering, elution, stream discharge, and stream solute concentrations, was able to recreate daily stream chemistry dynamics over 13 years for an alpine watershed in the Colorado Front Range (Hartman et al., 2007). Using the model to hindcast stream chemical dynamics back to 1900 revealed changes in simulated pH coincident with maximum SO_2 emissions in the late 1960s and early 1970s. Model simulations suggested annual mean pH values decreased to 5.6 to 5.8 during the years of maximum regional SO_2 emissions, and have since recovered to circumneutral values. Simulated ANC responded to both SO_2 and NO_X emissions, decreasing to annual values of 20 to 25 µeq/L during years of highest SO_2 or NO_X emissions compared with current mean annual ANC values near 50 µeq/L (Hartman et al., 2007).

Recent Trends

Limited monitoring data are available on recent trends in surface water chemistry in the western regions and are mostly limited to the recent past and a number of reconnaissance studies (Melack and Stoddard, 1991; Nelson, 1991; Turk and Spahr, 1991). Existing information on recent trends in surface water chemistry since the 1980s suggests that conditions vary widely across the West. Parts of Colorado, Wyoming and the western Cascades showed decreased ANC, while Emerald Lake experienced reduced NO_3^- concentrations.

Turk et al. (1993) reported the results of 5 years of monitoring for ten lakes in the Mt. Zirkel and Weminuche Wilderness areas in Colorado. Based on lake concentrations of SO_4^{2-} and Cl^- and on wet deposition concentrations of SO_4^{2-}, NO_3^-, and H^+, Turk and Spahr (1991) concluded that low-ANC lakes had lost no more than 5 µeq/L ANC in the Bitterroot Range of the Northern Rocky Mountains, 12 µeq/L ANC in the Wind River Range of Wyoming, and 10 µeq/L ANC in the Front Range of Colorado. It is likely that the actual ANC losses had been much less than these estimates (Sullivan, 2000).

Future Projections

The DayCent-Chem model was used to project a timeline to acidification for an alpine watershed of Rocky Mountain National Park (Hartman et al., 2007). At current levels of N deposition of 4 to 6 kg N/ha/yr, acidification does not occur over 48 years of simulation, but increasing deposition amounts lead to first episodic acidification over time at deposition of 7.0 to 7.5 kg N/ha/yr. MAGIC model simulation results suggested that a sustained N deposition load of 12.2 kg N/ha/yr would be required over a period of 50 years to cause chronic acidification of the Andrews Creek watershed in Rocky Mountain National Park (Sullivan et al., 2005).

B.3.4.5. Temporal Variability in Water Chemistry

Water chemistry changes on both intra-annual and inter-annual time scales in response to changes in environmental conditions. Because of this variability, many years of data are required to establish the existence of trends in surface water chemistry. Assignment of causality to changes that are found to occur is even more difficult.

Temporal variability in surface water and soil solution chemistry, and patterns in nutrient uptake by terrestrial and aquatic biota, influence acidification processes and pathways. Thus, conditions are constantly changing in response to episodic, seasonal, and inter-annual cycles and processes. In particular, climatic fluctuations that govern the amount and timing of precipitation inputs, snowmelt, vegetative growth, depth to groundwater tables, and evapoconcentration of solutes influence soil and surface water

chemistry and the interactions between pollution stress and sensitive aquatic and terrestrial biological receptors.

Decreases in pH with increases in flow are nearly ubiquitous in drainage waters throughout the U.S. (Wigington et al., 1991). Chemical changes during episodes are controlled in part by acidic deposition and in part by natural processes, including dilution of base cation concentrations, nitrification, flushing of organic acids from terrestrial to aquatic systems, and the neutral salt effect. Episodic acidification pulses may last for hours to weeks, and sometimes result in depletion of ANC in acid-sensitive streams and lakes to negative values and concomitant increases in Al_i in solution to toxic levels.

During episodes, which are driven by rainstorms and/or snowmelt events, both discharge (streamflow volume per unit time) and water chemistry change, sometimes dramatically. This is important because streams may in some cases exhibit chronic chemistry that is still suitable for aquatic biota, but nevertheless experience occasional episodic acidification with lethal consequences (cf. Wigington et al., 1993).

The most important factor governing watershed sensitivity to episodic acidification is the pathways followed by snowmelt water and stormflow water through the watershed. These pathways determine the extent of acid neutralization provided by the soils and bedrock in that watershed. High-elevation watersheds with steep topography, extensive areas of exposed bedrock, deep snowpack accumulation, and shallow, base-poor soils tend to be most sensitive to episodic acidification.

Rainfall and snowmelt typically pass through the soil profile prior to reach a stream channel. The typical soil profile in acid-sensitive watersheds has lowest pH in upper organic soil horizons, increasing down the profile to higher pH at depth. Drainage water chemistry during baseflow conditions is generally reflective of conditions in the lower soil horizons and the subsoil. During high flows during snowmelt or rainfall events, however, flow-routing favors water flowpaths through upper horizons. During such events, drainage water chemistry, therefore, typically reflects the lower pH, higher organic content, and lower ANC of these upper soil horizons (Sullivan, 2000). As such, storm flow and snowmelt are often associated with episodes of extreme surface water acidity due to an increase in the proportion of flow derived from water that has moved laterally through the surface soil without infiltration to deeper soil horizons (Wigington et al., 1991).

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 deep versus shallow soil horizons; the more subsurface contact, the higher the surface water ANC (Turner et al., 1991). This 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 and Corbett, 1989; Turner et al., 1991). Episodic acidification is often the limiting condition for aquatic organisms in streams that can be suitable for aquatic life under baseflow conditions.

Episodes are generally accompanied by changes in at least two or more of the following chemical parameters: ANC, pH, base cations, SO_4^{2-}, NO_3^-, Al^{n+}, organic acid anions, and DOC (Sullivan, 2000). The EPA's Episodic Response Project (ERP) confirmed the chemical and biological effects of episodic pH depressions in lakes and streams in parts of the U.S. (Wigington et al., 1993). The ERP illustrated that episodic processes are mostly natural, that SO_4^{2-} and especially NO_3^- attributable to atmospheric deposition play important roles in the episodic acidification of some surface waters, and that the chemical response that has the greatest effect on biota is increased Al_i concentration. Similar findings had been reported elsewhere, especially in Europe, but the ERP helped to clarify the extent, causes, and magnitude of episodic acidification in portions of the U.S. (Sullivan, 2000).

Water chemistry trends documented by long-term monitoring programs and reported here represent recovery from chronic acidification. Most surface waters exhibit seasonally lower ANC and pH values than would be captured by trend analysis that considers only chronic chemistry data. In many cases, sites that are relatively low in ANC, but not chronically acidic, undergo short-term episodic acidification to negative ANC values during spring snowmelt, or during intense rain events. Lawrence (2002) found that 16% of total stream reaches in the West Branch Neversink River, in the Catskill Mountains of New York, were chronically acidic, whereas 66% of total stream reaches has a high likelihood of becoming acidic during high flows.

Most research on episodic processes has been conducted on stream systems, which tend to be more susceptible to such effects than lakes. Spatial variability can be considerable in lakes, and this complicates efforts to quantify the magnitude of episodic effects (Gubala et al., 1991). Moreover, synoptic lake surveys are typically conducted during the autumn "index period," during which time lakewater chemistry exhibits low temporal variability. Although autumn is an ideal time for surveying lakewater chemistry in terms of minimizing variability, lakewater samples collected during autumn provide little relevant data on episodic processes, and in particular on the dynamics or importance of N as an agent of acidification. Nitrate concentrations in lakewater are elevated during the autumn season only in lakes having watersheds that exhibit fairly advanced symptoms of N saturation (Stoddard, 1994).

Mixing zones have received little attention despite the fact that they can be acutely toxic to aquatic biota. Whether an area of acidic water that comes in contact with non-acidic water is a safe haven or a toxic zone depends on many parameters, one of the most important of which is the amount and form of Al species produced at the boundaries. For example, Al hydroxide ($Al(OH_3)$) can precipitate out of solution if pH is suddenly increased within a mixing zone. This form of Al is acutely toxic to fish.

The mechanisms that produce acidic episodes can include dilution of base cations and flushing of NO_3^-, SO_4^{2-} and/or organic acids from forest soils to drainage water (Kahl et al., 1992; Wigington et al., 1996; Wigington, 1999; Lawrence, 2002). Acidic deposition can contribute to episodic acidification of surface water both by supplying N which can produce pulses of NO_3^- during high flow periods, contributing hydrologically mobile SO_4^{2-} through dry deposition, and by lowering baseline pH and ANC, so that episodes are sufficient to produce biologically harmful conditions (Stoddard et al., 2003).

Episodic acidification due to atmospheric deposition is most commonly associated with N deposition, and effects tend to be most pronounced during snowmelt. However, snowmelt can flush into surface waters N that was deposited from the atmosphere to the snowpack and also N that was mineralized within the soil under the snowpack during winter. A substantial component of the NO_3^- flux may have been derived from mineralization of organic N (Ley et al., 2004). Much of the N released from the snowpack during the melting period is retained in underlying soils and only a component of that is flushed to surface waters. Where soils are sparse, as in alpine regions of the western U.S., most snowpack N is flushed to surface waters, and even though there is evidence through use of isotopic tracers that much of the N was cycled microbially, snowpack N has been reported to caused temporary acidification of alpine streams (Williams and Tonnessen, 2000; Campbell et al., 2002).

Episodic pH and ANC depressions during snowmelt are largely driven by base cation dilution and NO_3^- enrichment in most areas (cf. Wigington et al., 1991, 1993; Campbell et al., 1995; Stoddard, 1995), although Denning et al. (1991) found a significant decline of both pH and ANC associated with DOC flushing from forest soils. Pulses of increased SO_4^{2-} during hydrological episodes are usually attributable to S storage and release in soils (for example, in the southeastern U.S.) or wetlands. More commonly, lake and streamwater concentrations of SO_4^{2-} decrease or remain stable during snowmelt. This is probably because most stream flow during episodes is derived from water previously stored in watershed soils that is then forced into streams and lakes by the piston effect.

In the Northeast, the most severe acidification of surface waters generally occurs during spring snowmelt (Charles, 1991). Stoddard et al. (2003) found that on average, spring ANC values in New England, the Adirondacks, and the Northern Appalachian Plateau were about 30 µeq/L lower than summer values during the period 1990 to 2000 (Figure B-11). This implies that lakes and streams in these regions would need to recover to chronic Gran ANC values above about 30 µeq/L before they could be expected to not experience acidic episodes (Stoddard et al., 2003). However, the estimate of 30 µeq/L is certain to be low because the comparison was made with non-episodic sampling in spring.

In the West, episodic acidification is an especially important issue for surface waters throughout high-elevation areas. A number of factors pre-dispose western systems to potential episodic effects (Peterson et al., 1998; (Sullivan, 2000), including:

- the abundance of dilute to ultradilute lakes which exhibit very low concentrations of base cations, and therefore ANC, throughout the year;

- large snowpack accumulations at the high-elevation sites, thus causing substantial episodic acidification via the natural process of base cation dilution; and

- short hydraulic retention times for many of the high-elevation drainage lakes, thus enabling snowmelt to rapidly flush lake basins with highly dilute meltwater.

Based on measurements of microbial biomass, CO_2 flux through the snowpack, and soil N pools, Williams et al. (1996b) concluded N cycling under the snowpack in Colorado during the winter and spring was sufficient to supply the NO_3^- measured in stream waters. Brooks et al. (1996) investigated soil N dynamics throughout the snow-covered season on Niwot Ridge, CO. Sites with consistent snow cover had a 3 to 8 cm layer of thawed soil under the snowpack for several months before snowmelt began. Nitrogen mineralization in this thawed layer contributed to N_r pools that were significantly larger than the pool of N stored in the snowpack. As snowmelt began, soil inorganic N pools decreased sharply, concurrent with a large increase in microbial biomass N. As snowmelt continued, both microbial N and soil inorganic N decreased, presumably due to increased demand by growing vegetation (Brooks et al., 1996).

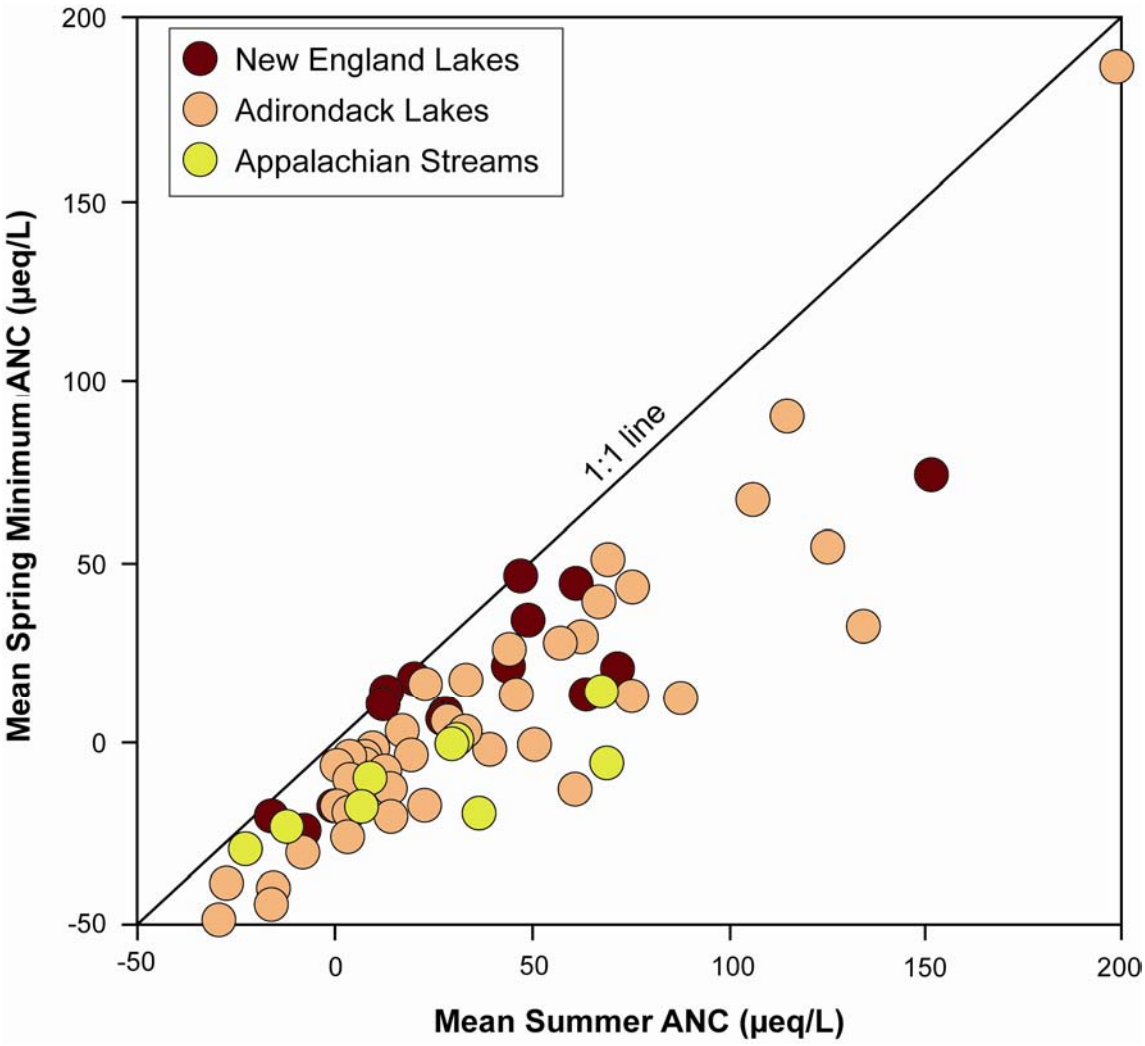


Figure B-11. Relationship between mean summer and spring ANC values at LTM sites in New England, the Adirondacks, and the Northern Appalachian Plateau.

Source: Stoddard et al. (2003).

In the Sierra Nevada, the hydrology of alpine and subalpine ecosystems is dominated by snowfall and snowmelt, with over 90% of the annual precipitation falling as snow. The relatively small loads of acidic deposition can supply relatively high concentrations of SO_4^{2-} and NO_3^- to lakes and streams during the early phase of snowmelt (Stoddard, 1995) through the process of preferential elution (Johannessen and Henriksen, 1978).

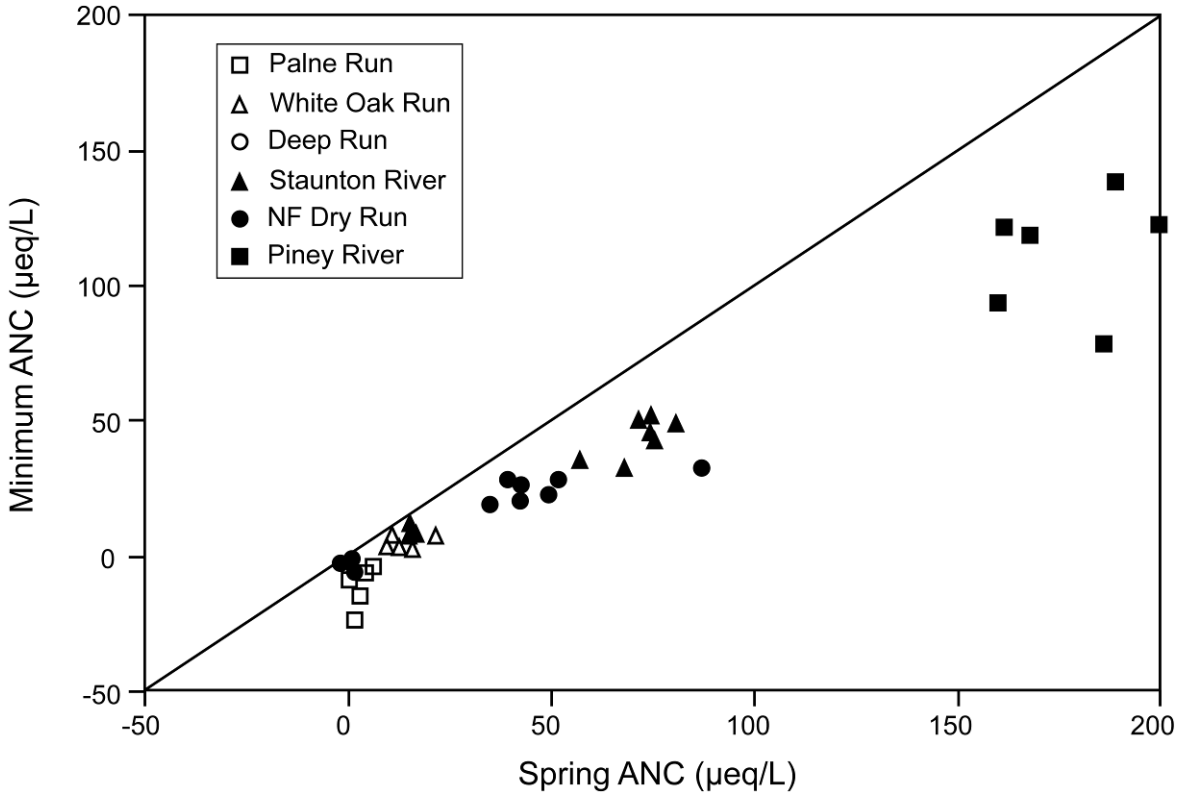
Lakewater pH and ANC in the Sierra Nevada generally decrease with increasing runoff, reaching minima near peak snowmelt discharge. Most other solutes exhibit temporal patterns that indicate dilution or a pulse of increased concentration followed by either dilution or biological uptake. Williams and Melack (1991) and Williams et al. (1995) documented ionic pulses (2 to 10 days in duration) in meltwater

concentrations in the Emerald Lake watershed twofold to twelvefold greater than the snowpack average. Sulfate and NO_3^- concentrations in meltwater decreased to below the initial bulk concentrations after about 30% of the snowpack had melted. The initial meltwater draining from the snowpack had concentrations of NO_3^- and NH_4^+ as high as 28 µeq/L, compared to bulk snowpack concentrations < 5 µeq/L (Williams et al., 1995). Streamwater NO_3^- concentrations peaked during the early snowmelt period, with maximum streamwater concentrations of 18 µeq/L. During summer, streamwater NO_3^- concentrations were always near or below detection limit.

Stoddard (1995) reported results for two lakes in the Sierra Episodes Study, one of which (Treasure Lake) typified the response of the majority of high elevation lakes in the study and one whose response was most extreme (High Lake). At Treasure Lake, ANC began to decline at the onset of snowmelt and reached a minimum at peak runoff, corresponding with minimum base cation, NO_3^-, and SO_4^{2-} concentrations. The lakewater did not become acidic. High Lake watershed contained a deeper snowpack, and began melting later in the season. ANC fell to 0 and below twice during the first 10 days of snowmelt. The ANC minimum corresponded with maximum concentrations of base cations, NO_3^- and Al. Nitrate concentrations increased to values greater than 40 µeq/L, exceeding concurrent increases in base cations and causing the lake to become acidic for brief periods. Stoddard (1995) concluded that High Lake appeared to be representative of the most extreme conditions of episodic acid-sensitivity in the Sierra Nevada.

Data regarding episodic variability in streamwater ANC for six intensively studied sites within Shenandoah National Park for the period 1993 to 1999 are presented in Sullivan et al (2003); (Figure B-12. The minimum measured ANC each year at each site (which generally is recorded during a large rain or snowmelt episode) is plotted against the median spring ANC for that year at that site. Sites that exhibited median spring ANC below about 20 µeq/L (Paine Run, White Oak Run, Deep Run) generally had minimum measured ANC about 10 µeq/L lower than median spring ANC.

In contrast, at the high-ANC Piney River site (median spring ANC > 150 µeq/L), the minimum measured ANC was generally more than about 40 µeq/L lower than the respective median spring ANC. At sites having intermediate ANC values, with median spring ANC in the range of about 30 to 90 µeq/L, the minimum ANC measured each year was generally about 20 to 30 µeq/L lower than the respective median spring ANC. Thus, there is a rather clear pattern of larger episodic ANC depressions in streams having higher median ANC and smaller episodic ANC depressions in streams having lower median ANC. The two sites that had median spring ANC between about 0 and 10 µeq/L consistently showed minimum measured values below 0. Streams having low chronic ANC can be expected to experience relatively small episodic ANC depressions. However, those depressions can result in minimum ANC values that are associated with toxicity to aquatic biota.



Source: Sullivan et al. (Sullivan, 2003).

Figure B-12. Minimum streamwater ANC sampled at each site during each year versus median spring ANC for all samples collected at that site during that spring season. Data are provided for all intensively studied streams within Shenandoah National Park during the period 1993−1999. A 1:1 line is provided for reference. The vertical distance from each sample point upwards to the 1:1 line indicates the ANC difference between the median spring value and the lowest sample value for each site and year.

A recent study by Deviney et al. (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 Shenandoah National Park catchments using catchment geology and topography. On the basis of the models, they conclude that large number of Shenandoah National Park streams have 6– to 168–h periods of low ANC values, which may stress resident fish populations (Deviney et al., 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 indeterminate (ANC 20 to 50), episodically acidic (ANC 0 to 20) or chronically acidic (ANC less than 0) for 72 continuous hours. Many catchments are predicted to have successive years of low-ANC values

potentially sufficient to extirpate some species (Deviney et al., 2006). The authors of the study reported that smaller catchments are more vulnerable to episodic acidification than large catchments underlain by the same bedrock. Catchments with similar topography and size are more vulnerable if underlain by less basaltic and carbonate bedrock.

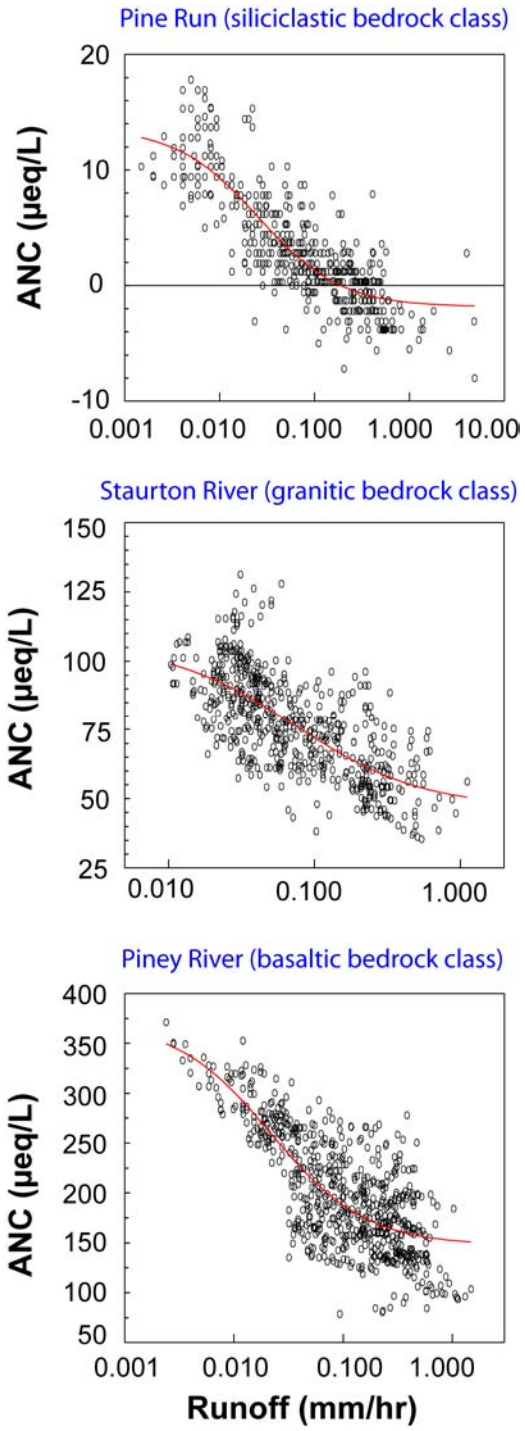
There are several different mechanisms of episodic acidification in operation in the streams in Shenandoah National Park, depending at least in part on the bedrock geology of the stream. The most acidic conditions in Shenandoah National Park streams occur during high-flow periods, in conjunction with storm or snowmelt runoff. The general relationship between flow level and ANC is evident in Source: Sullivan et al. (Sullivan, 2003).

, which plots ANC measurements against flow for three intensively studied streams representing the major bedrock types in the park. The response of all three streams is similar in that most of the lower ANC values occur in the upper range of flow levels.

Consistent with observations by Eshleman (1988), the minimum ANC values that occur in response to high flow are related to baseflow ANC values. Paine Run (siliciclastic bedrock) had a mean weekly ANC value of about 6 µeq/L and often had high-flow ANC values that were less than 0 µeq/L. Staunton River (granitic bedrock) had a mean weekly ANC value of about 82 µeq/L and had only a few high-flow ANC values less than 50 µeq/L. Piney River (basaltic bedrock) had a mean weekly ANC value of 217 µeq/L and no values as low as 50 µeq/L.

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 storm events 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) 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. 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).



Source: Sullivan et al. (Sullivan, 2003).

Figure B-13. Relationship between ANC and runoff for streamwater samples collected at intensively studied sites in Shenandoah National Park. The data represent samples collected during the 1992–1997 period.

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). Sulfate and NO_3^- 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).

Previous studies have shown that mobilization of dissolved Al during episodic acidification is a primary cause of fish mortality in streams that have low ANC under baseflow conditions (Wigington et al., 1993). Streams with higher ANC during baseflow are less likely to become sufficiently acidic during episodes to bring much Al into solution.

Figure B-14 provides an example of changes in ANC, pH, and total monomeric Al that occurred in Paine Run, Staunton River, and Piney River during a high-flow episode in January 1995. Under baseflow conditions, ANC at the Paine Run site was above 0 µeq/L, pH was above 5.5, and Al concentration was less than about 1 µM. Discharge levels increased dramatically during the episode, resulting in depression of ANC to less than 0 µeq/L, pH values less than 5.5, and an increase in Al concentration to near 3 µM, above the threshold for adverse effects on some species of aquatic biota.

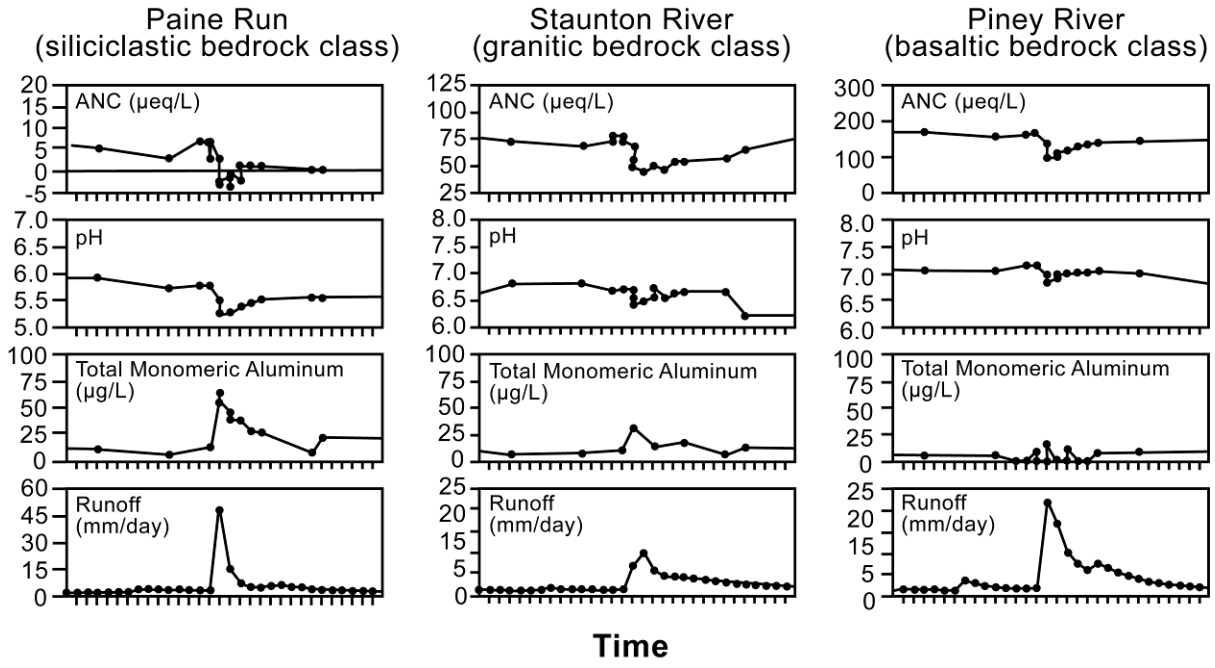


Figure B-14. Decrease in ANC and pH and increase in dissolved aluminum in response to a sharp increase in streamflow in three watersheds within Shenandoah National Park during a hydrological episode in 1995. The watersheds were selected to be representative of the three geologic sensitivity classes within the park. Data are shown for the month of January 1995.

Source: Sullivan et al. (Sullivan, 2003).

The same episode also resulted in substantial declines in ANC in the granitic (Staunton River) and basaltic (Piney River) watersheds. However, ANC values at these two sites were relatively high prior to the episode (about 75 and 175 µeq/L, respectively) and did not decline to below about 50 µeq/L during the episode at either site, and pH values remained above 6.0 and 6.5, respectively (Figure B-14).

In general, pre-episode ANC is a good predictor of minimum episodic ANC and also a reasonable predictor of episodic ΔANC. Higher values of pre-episode ANC lead to larger ΔANC values, but minimum ANC values of such streams are generally not especially low. Lowest minimum ANC values are reached in streams that have low pre-episode ANC, but the ΔANC values for such streams are generally small.

Webb et al. (1994) developed an approach to calibration of an episodic acidification model for VTSSS long-term monitoring streams in western Virginia that was based on the regression method described by Eshleman (1988). Median, spring quarter ANC concentrations for the period 1988 to 1993 were used to represent chronic ANC, from which episodic ANC was predicted. Regression results were very similar for the four lowest ANC watershed classes, and they were therefore combined to yield a single regression model to predict the minimum measured ANC from the chronic ANC. Extreme ANC values were about 20% lower than chronic values, based on the regression equation:

$$ANC_{min} = 0.79\ ANC_{chronic} - 5.88\ (r^2 = 0.97;\ \text{se of slope} = 0.02,\ p = 0.001)$$

Because the model was based on estimation of the minimum ANC measured in the quarterly sampling program, it is probable that the true minimum ANC values were actually somewhat lower than 20% below the measured chronic ANC. Nevertheless, regression approaches for estimation of the minimum episodic ANC of surface waters, such as was employed by Webb et al. (1994) for western Virginia, provide a basis for predicting future episodic acidification. It must be recognized, however, that future episodic behavior might vary from current behavior if chronic conditions change dramatically.

The relative importance of the major processes that contribute to episodic acidification varies among the streams within Shenandoah National Park, in part as a function of bedrock geology and baseflow streamwater ANC. Sulfur-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 soils surfaces. Dilution of base cation concentrations was most important at the high-ANC site.

The documented importance of NO_3^- to episodic acidification was a relatively recent development, attributed to the effects of gypsy moth (*Lymantria dispar*) infestation in many watersheds within Shenandoah National Park (Webb et al., 1995). Consumption of foliage by the moth larvae converted

foliar N, which is normally tied up in long-term N cycling processes, into more labile N forms on the forest floor.

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-episodic ANC, episodic decreases in pH and ANC and increases in toxic Al concentrations can have adverse effects on fish populations. Not all of the causes of episodic acidification are related to acidic deposition. Base-cation dilution and increase in organic acid anions during high-flow conditions are natural processes. The contribution of nitric acid, 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). However, significant contributions of sulfuric acid, 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).

B.4. Effects on Biota

Soil and surface water acidification involve changes in a number of chemical parameters, each of which has the potential to influence the health and vigor of biological communities and the species that comprise them. In most cases where biological effects of acidification have been documented, the most important chemical parameters involved in those effects have been pH, Al_i, and Ca^{2+}. Less commonly, one or more base cations other than Ca^{2+} (e.g., Mg^{2+}, K^+) or C are also involved. This is true for both aquatic and terrestrial effects.

A number of authors have examined the complex interactions between pH, Al, and Ca^{2+} that must be considered when attempting to determine the effects of acidification on both aquatic and terrestrial biota (e.g., Mount et al., 1988; Ingersoll et al., 1990b; Wood et al., 1990). Calcium concentration significantly affects the distribution of species and their ability to survive in acidified environments. Aluminum, leached by acid precipitation from soils in the watershed, complicates the response considerably because some forms of Al are highly toxic to both aquatic and terrestrial species. Aluminum and hydrogen ions interact both synergistically and antagonistically depending on conditions (Havas, 1985; Rosseland and Staurnes, 1994). In the presence of naturally occurring organic acids, Al toxicity can be reduced or eliminated. A number of authors have examined the complex interactions between pH, Al, and Ca2+ that must be considered when attempting to determine the effects of acidification on both aquatic and terrestrial biota (e.g., Mount et al., 1988; Ingersoll et al., 1990a; Wood et al., 1990).

B.4.1. Types of Effects of Acidification on Biota

Ecological effects occur at four levels of biological organization: (1) the individual, (2) the population, comprised of many individuals, (3) the biological community, composed of many species, (Billings, 1978), and (4) the ecosystem. Several metrics have been developed to describe the effects of acidification at each of these levels of organization. For the individual, effects are assessed in terms of sublethal effects on condition. At the population level, effects are measured by changes in the population of a certain species. At the community level, species richness and community structure can be used to evaluate effects, and at the ecosystem level, changes in nutrient cycling and ecosystem processes are assessed. Most of these indices have been applied primarily to aquatic ecosystems. Each is discussed below.

Baker et al. (1990a) conducted a rigorous review of the effects of acidification on aquatic biota for the 1990 NAPAP State of Science/Technology reports. They evaluated hundreds of laboratory, in situ bioassay, field surveys, whole-system field experiments, and smaller mesocosm studies on the effects of acidification on aquatic biota. Their 381–page report is the most exhaustive source summarizing the aquatic biological effects of acidification from acidic deposition. The summaries provided here in sections B.4 and B.6 rely heavily on this source.

In Shenandoah National Park, a statistically robust relationship between acid-base status of streams and fish species richness was documented. The three-year Fish in Sensitive Habitats (FISH) study of stream acidification in Shenandoah National Park demonstrated negative effects on fish from both chronic and episodic acidification (Bulger et al., 1999). Biological differences in low- versus high-ANC streams included 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 et al., 1995; Dennis and Bulger, 1995).

B.4.1.1. Individual Condition Factor

Relatively little is known about changes in the condition of fish or other aquatic biota resulting from acidification. It is expected that sublethal effects will occur in acid-sensitive species well before the species is eliminated from a particular lake, stream, or terrestrial habitat. For that reason, loss of an acid-sensitive species is not necessarily an ideal indicator of acid stress. Clearly, stress begins to occur prior to species elimination. Sublethal effects are more difficult to quantify, but are nevertheless important.

Condition factor is one measure of sublethal effect that has been used to quantify effects of acidification on fish. Condition factor is an index to describe 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 reserves (Everhart and Youngs, 1981; Goede and Barton, 1990; Dennis and Bulger, 1995). Condition factor is interpreted as depletion of energy resources such as stored liver glycogen and body fat (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 and Bulger, 1995). Condition factor has been developed and applied mainly for blacknose dace. This 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 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 condition factor and pH in streams in Shenandoah National Park (Figure B-15). Dennis and Bulger (1995) found a reduction in the condition factor for blacknose dace in waters near pH 6.0. The four populations shown in Figure B-15 with the lowest condition factor have 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 length-adjusted 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 (Schofield and Driscoll, 1987) and Kretser et al. (1989) suggest that pH in the low-pH Shenandoah National Park streams is near or below the limit of occurrence for blacknose dace populations in the Adirondack region of New York (Sullivan et al., 2003).

Chronic sublethal stress caused by pH below about 6.0 may have serious effects on a variety of wild fish populations. 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). Because of the steep gradient in Na^+ and Cl^- concentrations between fish blood and freshwater, there is constant diffusional loss of these ions, that must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-), and Al elevates losses of Na^+ and Cl^- above the levels that occur due to acid stress alone (Wood, 1989).

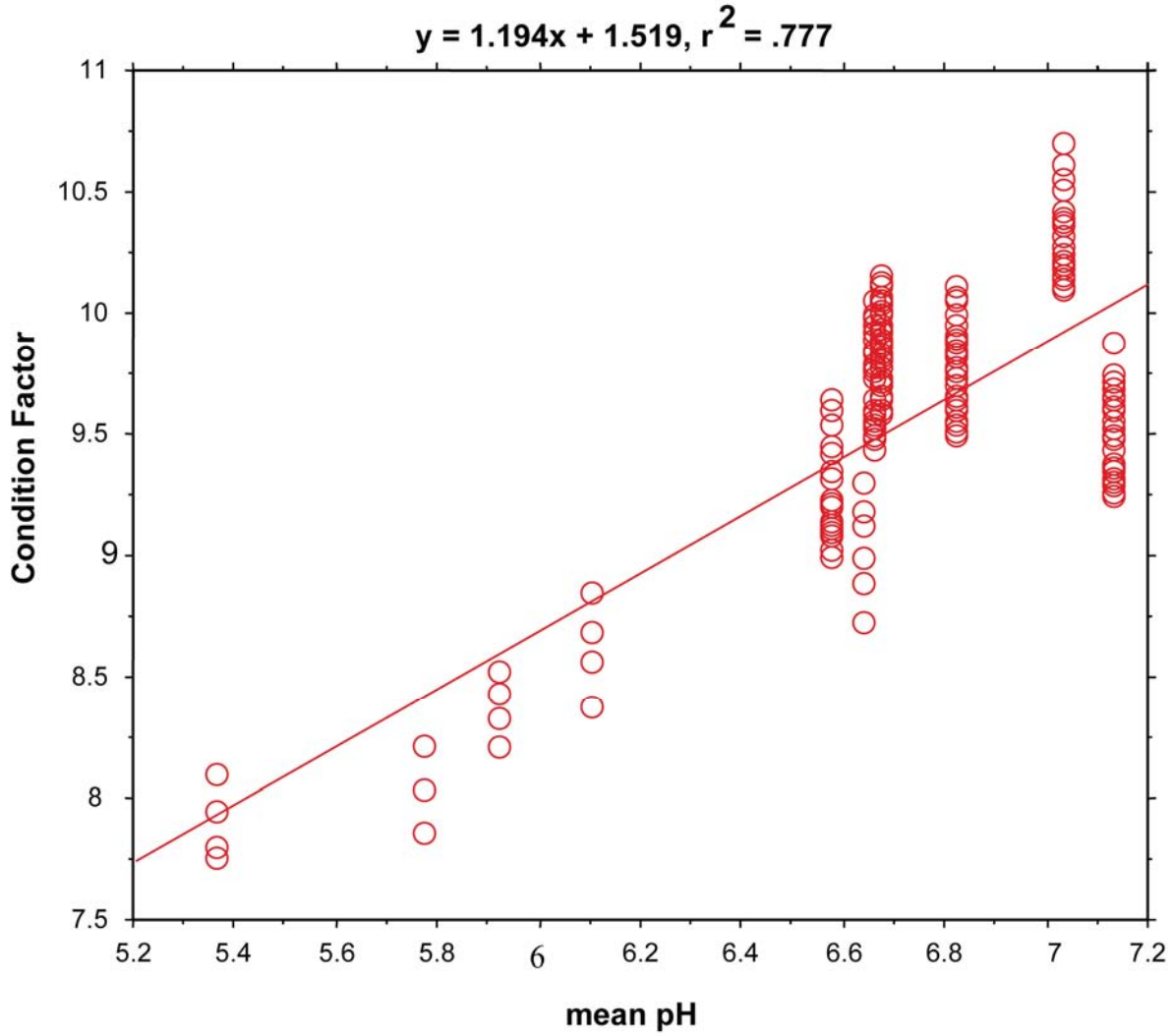


Figure B-15. Length-adjusted condition factor (K), a measure of body size in blacknose dace (*Rhinichthys atratulus*) compared with mean stream pH among 11 populations (n = 442) in Shenandoah National Park. Values of pH are means based on quarterly measurements, 1991–94; K was measured in 1994. The regression analysis showed a highly significant relationship ($p < 0.001$) between mean stream pH and body size, such that fish from acidified streams were less robust than fish from circumneutral streams.

Source: Bulger et al. (1999).

It is also possible that the loss of sensitive individuals or early life stages within species may reduce competition for food among the survivors, resulting in better growth rates, survival, or condition. Similarly, competitive release (increase in growth or abundance subsequent to removal of a competitor) may result from the loss of a sensitive species, with positive effects on the density, growth, or survival of competitor population(s) of other species (Baker et al., 1990b). However, in some cases where acidification continued, transient positive effects on size of surviving fish were shortly followed by extirpation (Bulger et al., 1993).

Acid stress is at least partly responsible for the lower condition of blacknose dace populations in Shenandoah National Park, though reduced access to food or lower food quality (Baker et al., 1990b), either resulting from the nature of soft water streams or exacerbated by acidification, cannot be ruled out. Primary productivity is low in headwater streams and lower still in soft water headwaters, which are more likely to be acidified. Production of invertebrates is likely to be low in such streams as well (Wallace et al., 1992). Thus, lower food availability cannot be discounted as a potential contributor to lowered condition in Shenandoah National Park blacknose dace populations in low-pH streams. Nevertheless, reduced growth rates have been 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*).

B.4.1.2. Species Composition

Species composition refers to the mix of species that are represented 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 acidic 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 effects of acidification are continuous, with more species being affected at higher degrees of acidification. Therefore, the degree of alteration of surface water biological community composition increases as surface waters become more acidic. There is a consistent pattern of lower community diversity with increased acidification.

B.4.1.3. Taxonomic Richness

Taxonomic richness is a metric that is commonly used to quantify the effects of an environmental stress such as acidification or eutrophication. The richness metric can be applied at various taxonomic levels. For example, the number of fish species can be used as an index of acidification (cf. Bulger et al., 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 et al., 2003).

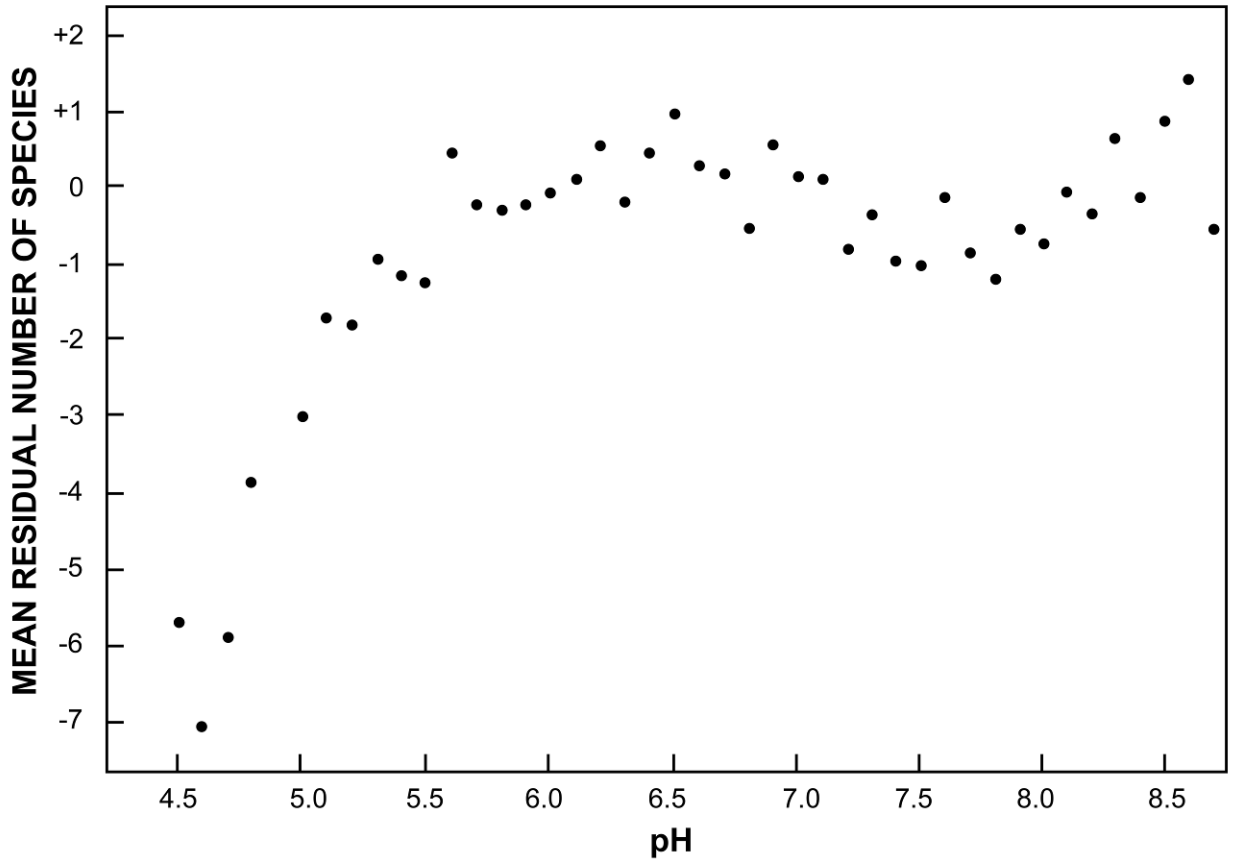
Acidification results in the loss of acid-sensitive species, with more species lost with higher degrees of acidification. A direct outcome of population loss caused by acidification is a decline in species richness (the total number of species in a stream or lake). This is a highly predictable outcome of regional acidification, although the pattern and rate of species loss varies from region to region.

Decreases in ANC and pH and increases in Al_i concentration contribute to declines in species richness and abundance of zooplankton, macroinvertebrates, and fish (Schindler et al., 1985; Keller and Gunn, 1995). Species richness is positively correlated with pH and ANC (Rago and Wiener, 1986; Kretser et al., 1989) because of the elimination of acid-sensitive species (Schindler et al., 1985). Knowledge of the spatial distribution of pH and other water quality variables is necessary to explain the presence or absence of species within heterogeneous environments. Organisms that are mobile and can sense the pH of their environment can move to areas (called refugia) that have more favorable water chemistry. Although some species are favored by increased acidity, species diversity generally decreases as surface water acidity increases.

Decreases in species richness have been observed for all major trophic groups of aquatic organisms (Baker et al., 1990a). Baker et al. (1990a) discussed 10 selected studies that documented this phenomenon, with sample sizes ranging from 12 to nearly 3,000 lakes and streams analyzed per study.

Lake and stream size can be an important complicating factor in interpreting species richness data. Larger lakes and streams in larger watersheds would generally be expected to contain more species than smaller lakes or streams in smaller watersheds, irrespective of acid-base chemistry. Nevertheless, when adjusted for lake size, lakes with pH less than approximately 6.0 contain significantly fewer species than lakes with pH above 6.0 (Figure B-16) (Frenette et al., 1986; Rago and Wiener, 1986; (Schofield and Driscoll, 1987); Matuszek and Beggs, 1988).

Studies in the Adirondack Mountains demonstrated the effect of acidification on species richness; of the 53 fish species recorded in Adirondack lakes by the ALSC, about half (26 species) were absent from lakes with pH below 6.0. Those 26 species included important recreational species, such as Atlantic salmon, tiger trout (*Salmo trutta* X *Salvelinus fontinalis*), redbreast sunfish (*Lepomis auritus*), bluegill (*Lepomis macrochirus*), tiger musky (*Esox masquinongy* X *lucius*), walleye (*Sander vitreus*), alewife (*Alosa pseudoharengus*), and kokanee (*Oncorhynchus nerka*) (Kretser et al., 1989), plus ecologically important minnows that serve as forage for sport fish. Fully 346 of 1,469 lakes surveyed by the ALSC supported no fish at all at the time of the survey. These lakes were significantly lower in pH, dissolved Ca^{2+}, and ANC, and had higher concentrations of Al_i than lakes hosting one or more species of fish (Gallagher and Baker, 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 > 6.5 (Kretser et al., 1989; Driscoll et al., 2001a). Figure B-17 shows the mean number of fish species for pH classes from 4.0 to 8.0 in lakes in the Adirondacks. It is important to note, however, that there are many possible causes of fish absence in addition to acidification. These include lack of suitable habitat (especially for spawning), winter kill, blocked access, etc.



Source: Matuszek and Beggs (1988).

Figure B-16. Mean residual number of species per lake for lakes in Ontario, by pH interval. The residual number of species for a lake is the deviation of the observed number from the number predicted by lake area.

Sullivan et al. (2006a) developed a relationship between fish species richness and ANC class for Adirondack lakes. Fish species richness observations, as a function of ANC (µeq/L) class, were fit to a logistic relationship by a non-linear regression analysis. Under chronically acidic conditions (summer index or annual average ANC < 0 µeq/L), Adirondack lakes are generally fishless. There was a marked increase in mean species richness with increases in ANC up to values of approximately 100 µeq/L. 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 100 µeq/L. It does not account, however, for the possibility that lakes having higher ANC are often larger, and therefore support more fish species because of increased habitat diversity and complexity.

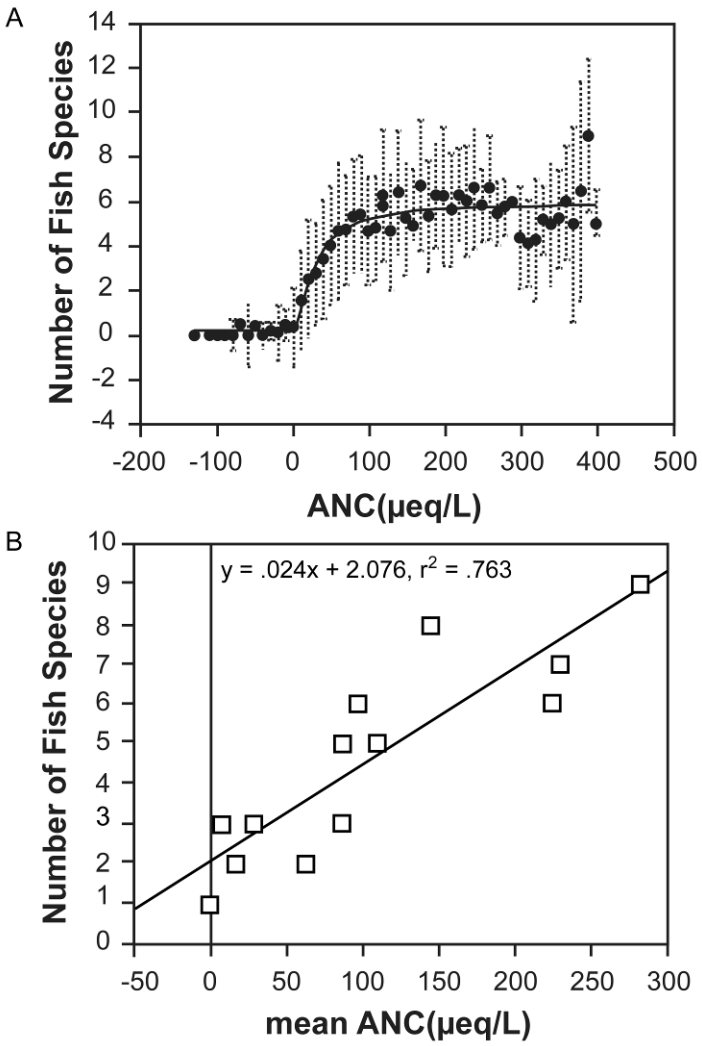
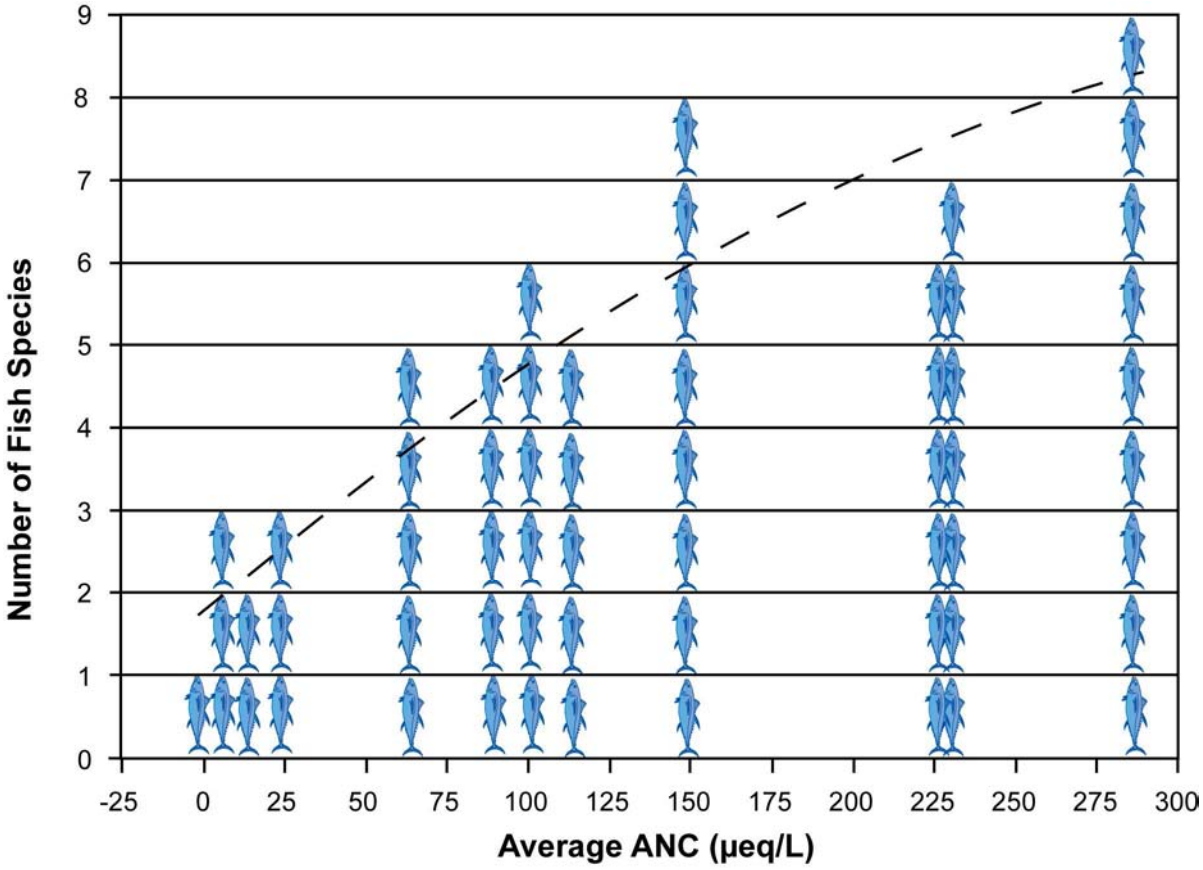


Figure B-17. Number of fish species per lake or stream versus acidity statues, expressed either as pH or ANC. (A) Adirondack lakes (Sullivan et al., 2006a).; (B) streams in Shenandoah National Park (Bulger, 1999). The data for the Adirondacks are presented as mean and range of species richness within 10 µeq/L ANC categories, based on data collected by the Adirondack Lakes Survey Corporation.

As an element of the FISH project (Bulger, 1999), 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 (see figure B-18).



Source: Redrawn from Bulger et al. (1999).

Figure B-18. Number of fish species among 13 streams in Shenandoah National Park. Values of ANC are means based on quarterly measurements, 1987–94. The regression analysis shoed a highly significant relationship ($p < 0.0001$) between mean stream ANC and number of fish species. Streams having ANC consistently <75 µeq/L had three or fewer species.

Median stream ANC values and watershed areas are shown in Table B-11 for the 14 streams used by Bulger et al. (1999) to develop the relationship between ANC and fish species richness shown in Figure B-18. Despite the overall similarities, these study streams vary in watershed area by a factor of 10. The streams that have larger watershed areas generally have more fish species than the streams having smaller watershed areas. All of the "rivers" have watersheds larger than 10 km^2 and ANC higher than 75 µeq/L. In contrast, the majority (but not all) of the "runs" have watershed area smaller than 10 km^2 and ANC less than 20 µeq/L. All of the streams that have watershed areas smaller than 10 km^2 have three or fewer known species of fish present. All of the streams having larger watersheds (>10 km^2) have three or more known fish species; seven of nine have five or more species; and the average number of fish species is six. There is no clear distinction between river and run, but it is clear that as small streams in Shenandoah National Park combine and flow into larger streams and eventually to rivers, two things

happen: acid-sensitivity generally declines, and habitat generally becomes suitable for additional fish species (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. Bugas et al. (1999) conducted electrofishing in the St. Marys River in 1976, and every 2 years from 1986 through 1998. Systemic stream acidification occurred during the study period. Sampling occurred at six sites between the downstream end of the St. Marys Wilderness and the headwaters over a distance of about 8 km. 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 Shenandoah National Park, which is also located in Virginia (Bulger et al., 1999). Bugas et al. (1999) reported that successful brook trout reproduction in the St. Marys River occurred only 1 year out of 4 during the period 1995 through 1998. Eight of the fish species recorded in one or more early years have not been observed in more recent years. Several, including blacknose dace, rainbow trout, and torrent sucker (*Thoburnia rhothoeca*), showed a pattern of being progressively restricted over time to lower river reaches, which generally have higher ANC. The number of fish species decreased with decreasing minimum ANC, from nine species at ANC of about 160 μeq/L to one to three species at ANC near 0. The best fit regression line suggested, on average, a loss of one species for every 21 μeq/L decline in annual minimum recorded ANC value.

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 data in Figure B-18 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 (RMSE) 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 RMSE of the coupled models, suggesting that the projections were reasonably robust.

It appears that fish species richness is controlled by multiple factors, of which both acidification and watershed area can be important. Watershed area might be important in this context because smaller watersheds may contain smaller streams having less diversity of habitat, more pronounced effects on fish from high-flow periods, or lower food availability. Such issues interact with other stresses, including acidification, to determine overall habitat suitability.

For Shenandoah National Park, Bulger et al. (1999) concluded that the most important cause of the observed decline in species richness with decreasing ANC was acid stress associated with acidification. However, an additional causal factor may have been the 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). The relative importance of this latter factor, compared with the importance of acid stress, in determining this relationship is unknown.

In the Adirondack region, Driscoll et al. (2001b) concluded that high-elevation lakes are more likely to be fishless than larger lakes at low elevation (Gallagher and Baker, 1990) because they have poor access for fish immigration, poor fish spawning substrate, or low pH, or they may be susceptible to periodic winter kills. Nevertheless, small, high-elevation Adirondack lakes with fish also had significantly higher pH compared with fishless lakes; acidity is likely to play an important role in the absences of fish from such lakes (Driscoll et al., 2001b).

B.4.1.4. Community Structure

Ecosystem response to pollutant deposition is a direct function of the ecosystem's ability to ameliorate resulting changes in individual species (Strickland et al., 1993). In order to determine ecosystem response and the possible effects on community structure, species responses must be scaled in both time and space and be propagated from the individual to the more complex levels of community interaction within an ecosystem.

Individuals within a population vary in their ability to withstand a stress. The response of each individual is based on its genetic constitution (genotype), its stage of growth at time of exposure to the stress, and the microhabitat in which it lives (Levlin, 1998). The range within which individuals in the population can exist and function determines the ability of the population to survive when exposed to a chronic stress. Those individuals that are able to cope with the stress survive and reproduce. The same kinds of pressures act on populations of different species. Competition among species results in community change over time and eventually produces ecosystems composed of populations of species

that have the capability to tolerate the stress (Guderian et al., 1985; Rapport and Whitford, 1999; U.S. Environmental Protection Agency, 2004).

Work conducted on the biological effects of acidification has largely been focused on the response of fish, especially salmonids (trout and salmon). This focus tends to be driven by the value people place on fish and fishing, rather than any ecological consideration. Other vertebrate, invertebrate, plant, and algal communities are also sensitive to acidification. In general, higher order trophic groups are more susceptible to acidification. Thus, in terms of changes in community structure in response to aquatic acidification, the general progression of sensitivity is as follows: fish > invertebrates (benthic and zooplankton) > algae > microbes (Baker et al., 1990a). 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). Al_i, pH, and Ca^{2+} have been identified as the variables most likely to have the greatest influence on fish community structure.

B.4.1.5. Indices of Ecological Effects

The most widely used index of acidification effect is the Acid Stress Index (ASI) developed by Baker et al. (1990a). This index uses fish bioassay survival data fitted to a maximum likelihood logistic regression model as a function of exposure to pH, Al, and Ca^{2+} to predict the probability of fish survival expressed as a percent mortality. This approach can aid in determination of effects on species composition by predicting the probability of occurrence of species of varying acid sensitivity. Separate ASI models were developed for tolerant, intermediate, and sensitive fish species. Approximate ASI reference levels were established for various 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*). They are presented in Table B-12.

The ASI was deemed a useful index of stress by Baker et al. (1990a), even though the relationships between ASIs and fish population status could not be quantified precisely because of confounding factors. Such factors included the abundance and types of food species, competitors and predators present, variations in habitat quality, and density-dependent effects on fecundity.

B.4.2. Timing of Effects

B.4.2.1. Life Stage Differences in Sensitivity

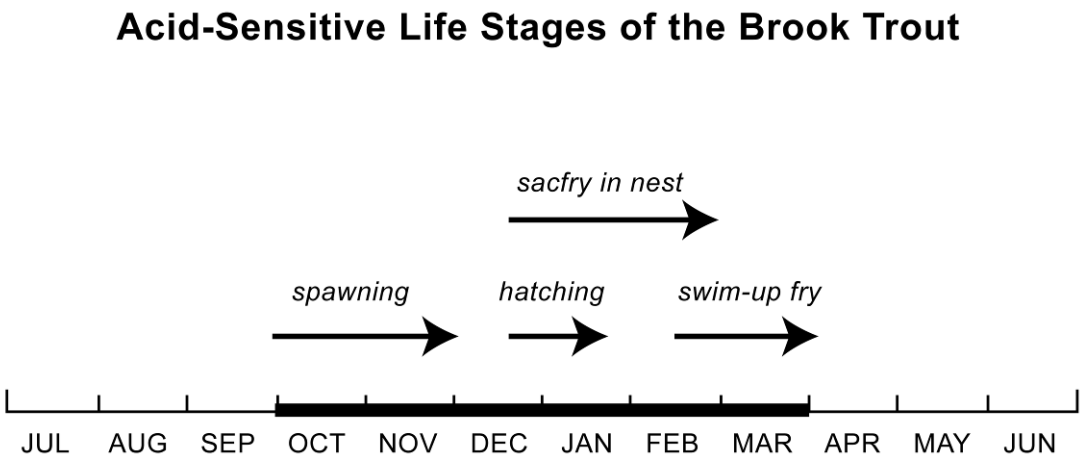
Episodic and chronic changes in the chemistry of surface waters can have different effects on aquatic organisms and populations depending on species and the life history stages present. More is known about the sensitivity to acidification of the life stages of fish than is known for other aquatic

organisms. In general, early life stages are more sensitive to acidic conditions than the young-of-the-year, yearlings, and adults (Baker and Schofield, 1985; Johnson et al., 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 et al., 1996).

There are a number of issues of acidification timing that are important to determination of the extent and magnitude of effects. One important issue concerns the timing of acidity exposure relative to life stage. For example, adult fish are generally more tolerant of acidity than early life stages such as eggs, fry and juveniles. There could be substantial differences in effect based on small differences in age or timing of exposure to acidity. No definite pattern was observed by Baker et al. (1990a) across all studies or species. This may reflect either differences in the test conditions or actual differences among species.

The presence of early life stages of brook trout, which are most sensitive to adverse effects from acidification (Bulger et al., 2000), varies with season. For example, the most acid-sensitive stages of brook trout development are present in Virginia streams throughout the cold season in general, and the winter in particular (Source: Sullivan et al. (Sullivan, 2003).

Figure B-19).



Source: Sullivan et al. (Sullivan, 2003).

Figure B-19. Life stages of brook trout.

The processes of oogenesis and fertilization in fish and aquatic invertebrates are especially sensitive to low pH (Muniz, 1991; Havas et al., 1995). In fish, this sensitivity is most likely due to adverse effects on the female spawner. For instance, Beamish et al. (1976) reported that reduced serum and plasma Ca^{2+} in female fish in acidified Canadian lakes lead to a higher probability for failure in

producing viable eggs. A depletion of Ca^{2+} from bone and increased numbers of females with unshed eggs have also been linked to sensitivity 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. The 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 H^+ concentrations and also to the toxic effects of Al_i at intermediate pH-values. Low pH in the surrounding water also results in pH-depression inside the egg, leading to either a prolongation of the hatching or to a 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, 1985b). Nevertheless they can experience high mortality during periods of acid runoff, such as snowmelt (Gunn and Keller, 1984a).

In fish, emergent alevins show susceptibility to the adverse effects of Al_i and H^+ that increases with age (Baker and Schofield, 1982; Wood and McDonald, 1982). Rosseland (1986) indicated that this increasing sensitivity results from changes that take place in the respiratory system. Shortly after hatch, 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 H^+ and Al_i 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. Fertilized egg, eyed embryo, alevin, and swim-up larval stages were exposed to low pH for a period of seven days. Each life stage was monitored for mortality, growth, and development for 40 days after hatching. Reductions in pH from 6.5 to 6.0 in low-Ca^{2+} water (70 µeq/L) did not affect survival, but reduced 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.

Woodward (1991) exposed greenback cutthroat trout (*Oncorhynchus clarki stomias*) in the laboratory to 7–day pH depressions. Low-Ca^{2+} (65 µeq/L) water at pH 6.5 was experimentally reduced to pH values of 6.0, 5.5, 5.0, and 4.5. Four life stages were exposed: freshly fertilized egg, eyed embryo, alevin, and swim-up larva. Alevin survival was reduced at pH 5.0, whereas survival of eggs, embryos, and swim-up larvae was reduced at pH 4.5. Swim-up larvae showed feeding inhibitions at pH 4.5. The authors concluded that the threshold for effects of acidity on greenback cutthroat trout in the absence of Al was pH 5.0 (Woodward, 1991).

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. Eyed embryos were not sensitive to any of the exposures.

According to Bulger et al. (1999), adult brook trout in Shenandoah National Park streams are more tolerant of acidity than are adult blacknose dace. For both species, the early life stages are more sensitive than the adults, and brook trout young are actually more sensitive than blacknose dace adults (Bulger et al., 1999). Blacknose dace spawn during summer and the eggs and very young fry are therefore somewhat protected from the most acidic episodes, which typically occur during cold-season, high-flow conditions.

B.4.2.2. Biological Effects of Episodes

Episodic decreases in pH and ANC can produce chemical conditions in lakes, and especially in streams, that are as harmful to biota as chronic acidification (Baker et al., 1996). Adverse effects on biota occur particularly when changes involve pH, Al_i, or Ca^{2+} (Baker et al., 1990a). Aquatic biota vary greatly in their sensitivity to episodic decreases in pH and increases in Al_i in waters having low Ca^{2+} concentration. However, 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.

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 Al_i levels during high flow, had substantially lower numbers and biomass of brook trout than in non-acidic streams (Wigington et al., 1996). Streams having acidic episodes showed significant mortality of fish.

Some brook trout avoided exposure to stressful chemical conditions during episodes by moving downstream or into areas with higher pH and lower Al_i. This movement of brook trout only partially mitigated the adverse effects of episodic acidification, however, and was not sufficient to sustain fish biomass or species composition at levels that would be expected in the absence of acidic episodes. Just as spatially heterogeneous environments or refugia enable some species to survive in otherwise unfavorable conditions, temporal heterogeneity often has the opposite effect. These findings suggest that stream assessments based solely on chemical measurements during low-flow conditions will not accurately predict the status of fish populations and communities in small mountain streams unless some adjustment is made for episodic processes (Baker et al., 1990a, 1996; Wigington et al., 1996; (Sullivan, 2000).

In Shenandoah National Park, 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. Acid episodes (with associated low pH and elevated Al_i

concentrations, and high streamwater discharge) induced rapid mortality in the low-ANC stream, while the test fish in the higher-ANC stream survived (Bulger et al., 1999).

In the West, it has also been shown that native trout are sensitive to short-term increases in acidity. For example, Woodward et al. (1989) exposed native western cutthroat trout to pH depressions (pH 4.5 to 6.5) in the laboratory. Reductions in pH from 6.5 to 6.0 in low-Ca^{2+} water (70 µeq/L) did not affect survival, but did reduce growth of swim-up larvae. Eggs, alevins, and swim-up larvae showed significantly higher mortality at pH 4.5 as compared to pH 6.5. Mortality was also somewhat higher at pH 5.0, but only statistically higher for eggs. Some species of aquatic biota in western aquatic ecosystems have been shown to be somewhat more sensitive to pH and ANC change than are cutthroat trout (Baker et al., 1990a).

Multiple logistic regression models were used by Van Sickle et al. (1996) to relate fish bioassay mortality rates to summary statistics of time-varying stream chemistry over the 20–day bioassay periods. Higher mortality of all three test fish species (brook trout, dace, sculpin [*Cottus* spp.]) during the in situ bioassays was clearly associated with increased Al_i. In addition, individual bioassays conducted during chronically or episodically acidified conditions had higher median mortality than did those during non acidic conditions, but no mortality differences were detected between chronically acidic and episodically acidic conditions. Time-weighted median Al_i was the best single predictor of 20–day mortality for both brook trout and sculpin, whereas the number of days with $Al_i > 200$ µg/L provided the best prediction of blacknose dace mortality.

In the Northeast, Baker et al. (1996) studied the effects of episodic acidification on fish in 13 small streams in the Adirondack and Catskill Mountains of New York and the Northern Appalachian Plateau in Pennsylvania. They conducted *in situ* bioassays with brook trout and blacknose dace, mottled sculpin (*Cottus bairdi*) or slimy sculpin (*Cottus cognatus*) depending on the region, to measure direct toxicity. Movements of brook trout individuals in relation to stream chemistry were tracked using radiotelemetry. Electrofishing surveys assessed fish community status and the abundance and biomass of brook trout in each stream. 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 abundance and biomass compared to nonacidic streams. These streams lacked the more acid-sensitive fish species (blacknose dace and sculpin). Movement of trout into refugia (areas with higher pH and lower Al) during episodes partially mitigated the adverse effects of episodes.

Chemical measurements by ERP during high flow correlated with fish community status. In general, reduced trout abundance occurred in ERP streams with median high flow pH < 5.0 and $Al_i > 100$ to 200 µg/L. Acid -sensitive fish species were absent from streams with median high flow pH < 5.2 and $Al_i > 100$ µg/L. More recently, Baldigo et al. (2007) found that mortality of brook trout young of the year

occurred at concentrations as low as 54 µg/L .Al_i was the single best predictor of fish mortality in ERP bioassays (Van Sickle et al., 1996) and has been identified as an important toxic factor in other bioassays and field studies (Mount et al., 1988; Ingersoll et al., 1990b; Rosseland et al., 1990). The relationships between pH and Al_i or ANC and Al_i vary among streams (Wigington et al., 1996), and therefore predictions of potential effects on fish based solely on pH or ANC may be misleading. High Al_i concentrations during episodes are probably the dominant cause of adverse effects on fish during episodic acidity events.

Biological Effects of Chronic Acidification

Changes in surface water acid-base chemistry, including pH, ANC, Al_i, and Ca^{2+}, can affect in-stream and in-lake biota. Adverse biological effects may be seen at pH less than about 6.0 to 6.5 and Al_i greater than about 30 to 50 µg/L (1 to 2 µM). It tends to increase with decreasing pH, and reaches potentially toxic concentrations (> ~2 µM) in surface drainage waters having pH less than about 5.5. Effects vary substantially by organism, life stage, and the concentration of DOC. Inorganic Al in solution is also toxic to plants.

Calcium can ameliorate the toxic effects of acidity and Al on biota. Most organisms can tolerate lower pH and higher Al_i at higher Ca^{2+} concentrations, but in natural environments, elevated concentrations of Al_i are only found in Ca^{2+}-depleted systems. This effect is most important at low Ca^{2+} levels. Overall biological effects noted with decreasing pH are described in Table B-13 (Baker et al., 1990a). The organisms most likely to respond to such changes in water chemistry include fish, aquatic insects, zooplankton, and diatoms. In some cases, amphibians are also important sensitive biological receptors. Most available data are for fish response.

In most stream or lake survey areas, direct quantification of biological responses to surface water acidification is not possible, given the scarcity or absence of biological long-term monitoring and dose-response data. Few biological long-term monitoring studies have been conducted. Much of the available *in situ* dose-response data have been generated from studies of streams in Virginia and Pennsylvania and lakes in New York. Data with which to evaluate acidification relationships have been scarce in most other regions.

Lakes

Fish status assessments for the eastern and upper midwestern U.S. were conducted by Baker et al. (1990a), by region, using a variety of assessment methods. For the northeast region, two water chemistry models were linked to fish response models: the Integrated Lake-Watershed Acidification Study (ILWAS) model and MAGIC. For the Adirondack subregion, three process models were used: ILWAS, MAGIC,

and Regional MAGIC. For other areas in the eastern U.S. and for the Upper Midwest, analysis of fish status was limited to application of the sensitive, intermediate, and tolerant toxicity models.

Assessment results reported by Baker et al. (1991a) for the Adirondack region are presented in Table B-14 showing results based on the ASI. Table B-15 shows the estimated percentage of Adirondack lakes with acid-base chemistry unsuitable for fish population survival according to various assessment models based on responses for brook trout, lake trout, and common shiner. Assessment results for the Northeast region are presented in Table 16 and Table 17.

In acid-sensitive lakes in the western U.S., the focus is often mainly on native cutthroat trout. It is important to note, however, that many high-elevation western lakes and streams were historically fishless. The top predators in such aquatic ecosystems were often amphibians or crustaceans. Thus, even though cutthroat trout might be considered native to the region, they are not necessarily native to a particular lake or stream.

Streams

In streams, the major organisms of concern with respect to water acidification are fish, amphibians, benthic macroinvertebrates, and periphyton (attached algae). All of these groups have shown adverse effects in response to acidification (see Annex B-6). Most available data are for fish and aquatic insects, mainly in the southeastern U.S. Streams affected by acidic deposition tend to occur at high elevation. They are often high-gradient and flow through base-poor geology.

Baker et al. (1991a) presented assessment results for the mid-Appalachian region as the distribution (percent) of NSS lower node, upper node, and total streams classified in various ASI values (Table B-18) (Baker et al., 1991a). Most of the streams were classified in the lowest ASI category (Table B-18). Assessment results for the interior Southeast region were similar (Table B-19).

Some fish response research has also been conducted for streams in the Catskill Mountains. Baker and Christensen (1991) estimated that the fish species found in the Neversink River Basin in the Catskill Mountains are typically lost when pH decreases to the range of 4.7 to 5.2 (brook trout), 5.5 to 5.9 (slimy sculpin), 4.7 to 5.7 (brown trout), 5.6 to 6.2 (blacknose dace), and 4.9 to 5.3 (Atlantic salmon).

The Shenandoah National Park FISH Project evaluated the effects of streamwater acidification on fish populations and communities in streams in Shenandoah National Park. Fish species richness, population density, condition factor, age distribution, size, and bioassay survival were all lower in streams having low-ANC compared to intermediate-ANC and high-ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and Bulger, 1995).

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 VTSSS and SWAS. 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 acidic 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 acidic deposition and would likely have been suitable for brook trout.

The model projections suggested that neither the 40% nor the 70% reductions in acidic deposition would be expected to 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.

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 cause, but an observed pattern of co-variation between variables does provide a context for analysis of a possible relationship. In this case, the projections did not require extrapolation and are, therefore, 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.

The geochemical and biological response models also differ in that MAGIC is a dynamic model and explicitly predicts the time course of changing water quality, whereas the empirical relationships used for estimating biological response were static. These relationships reflected a point in time (when the observations were made) and provided no information concerning the dynamics of biological response. That is, the empirical models predicted a new biological status for a new water chemistry, but gave no indication of the time required to achieve the biological status once the water quality change had occurred.

There are thus two considerations that must be kept in mind when interpreting the biological responses predicted using a combination of process-based and empirical modeling approaches: the causality of the relationship between water quality and response, and the dynamics of biological response.

With respect to the issue of causality, acidification is a disturbance and disturbance usually lowers species richness. In turn, loss of species usually lowers ecosystem stability. Biodiversity loss is a predictable and proven consequence of acidification, and there are abundant examples of this in North America and Europe (cf. Bulger et al., 2000). With respect to the timing of biological response, it can be variable and difficult to predict.

B.4.2.3. Timing of Recovery from Acidification

Lakes and streams show spatial and temporal variability in response to a host of biotic and abiotic factors. Against this background of variability, it is difficult to detect changes in biological communities in response to changes in an individual environmental stressor without long-term biological data (Schindler, 1990; Lancaster et al., 1996). Long-term data sets are rare, and there are few well-documented instances of temporal changes in biological communities in response to changes in water chemistry. Regardless, it is known that surface water acidification affects virtually all trophic levels (e.g., Flower and Battarbee, 1983; Økland and Økland, 1986; Rundle and Hildrew, 1990; St. Louis et al., 1990; Ormerod and Tyler, 1991; Siminon et al., 1993; Lancaster et al., 1996; (Sullivan, 2000).

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).

The timing of fish recovery is highly uncertain, and probably will depend heavily on dispersal opportunities. Stocking could accelerate fish population recovery (Driscoll et al., 2001b). Fish populations have recovered in acidified lakes when the pH and ANC have been raised through liming or reduction of acidic 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).

Studies in Canada have improved understanding of the feasibility and complexity of biological recovery in response to chemical recovery from acidification. Biological recovery of previously acidified lakes is expected to be a slower process than chemical recovery. Sometimes there are other environmental stresses in addition to acidity, such as metal contamination (Gundersen and Rasmussen, 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996b). Barriers can be imposed by water drainage patterns between lakes that hinder re-colonization by some fish species (Jackson and Harvey, 1995). Predation by non-acid-sensitive fish species can affect the recovery of zooplankton and macroinvertebrate communities (McNicol et al., 1995). Finally, tributary-spawned fish can be preyed

upon when they move downstream into lakes inhabited by predatory fish and birds (Schofield and Keleher, 1996).

Changes in surface water chemistry as a direct response to changes in S and N deposition are difficult to predict. Both chemical and biological effects of changing deposition can lag as the ecosystem comes into equilibrium with the modified deposition inputs. Soils or wetlands may continue to release S at a high rate for many years subsequent to a decrease in S deposition. As a result, surface water SO_4^{2-} concentrations may decrease in the future as a consequence of deposition changes that have already occurred. If soil base cations have become depleted, base cation concentrations in some surface waters could decrease in the future irrespective of any further changes in SO_4^{2-} concentrations. This would be expected to contribute to additional acidification.

Studies in the U.S., Canada, and Europe have illustrated the feasibility and complexity of biological recovery in response to decreased surface water acidity. There is currently no theoretical basis on which to predict the paths of biological recovery. At some scale, each stream or river is unique. The null hypothesis is that recovery will proceed in the same fashion as acidification, only backwards. Thus, for example, the last species lost (the most acid-tolerant) would be the first to return. However, time lags are expected to differ widely among species and among water bodies. Biological recovery of previously acidified lakes or streams can lag behind chemical recovery because of such factors as (a) limits on dispersal and recolonization; (b) barriers imposed by water drainage patterns (Jackson and Harvey, 1995); (c) the influence of predation (McNicol et al., 1995); and (d) other environmental stresses (Gunn et al., 1995; Havas et al., 1995; Jackson and Harvey, 1995; McNicol et al., 1995; Yan et al., 1996a,b).

Limitations on dispersal and recolonization can hamper biological recovery from chronic and episodic acidification. If fish move into refugia areas during low pH and then return, behavioral avoidance would reduce the overall effect of acidification on fish populations. However, if fish move out of the stream system in response to sublethal 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.

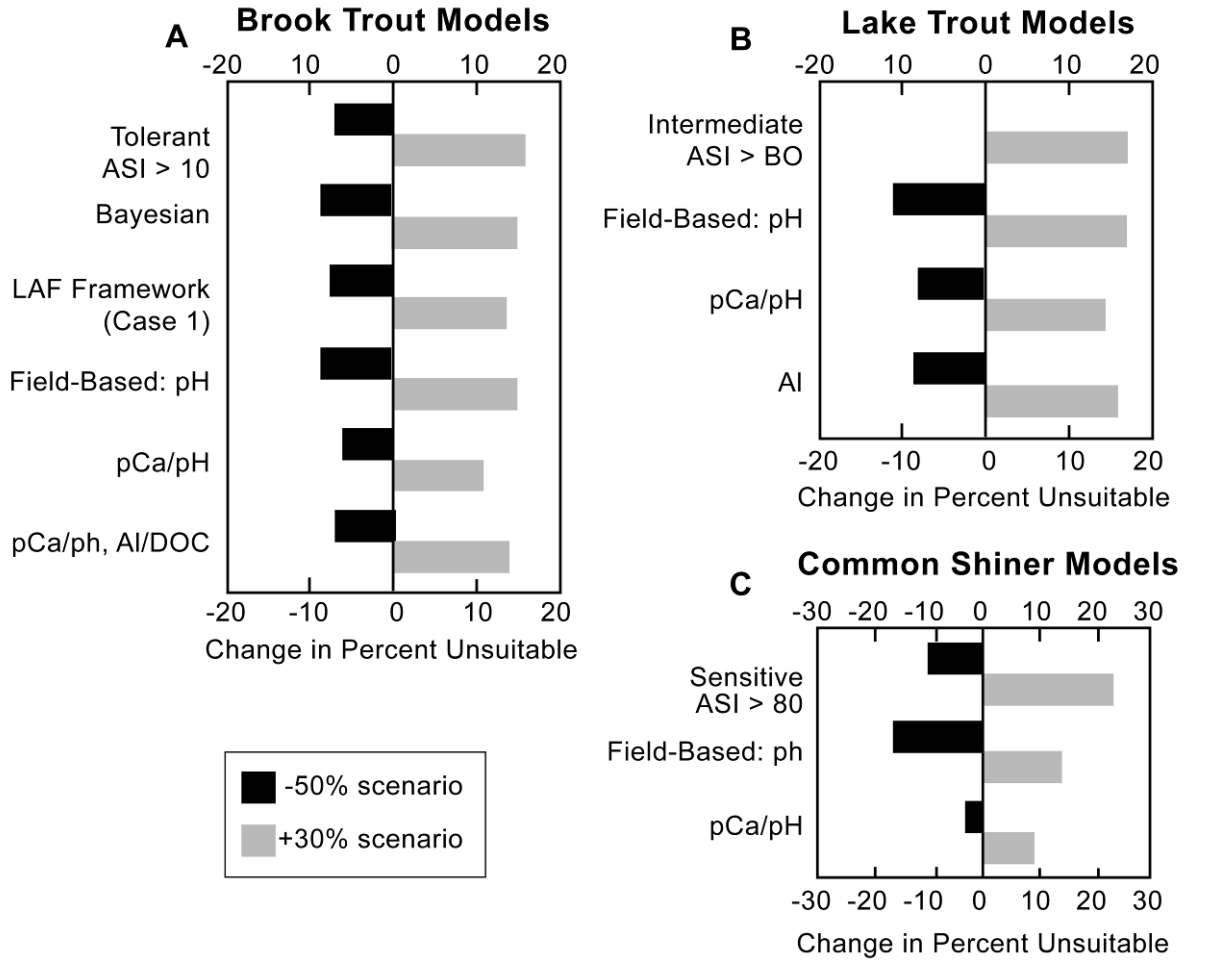
Stream macroinvertebrate communities are often dominated by immature life stages of flying insects, such as mayflies, dragonflies, and stoneflies. Such species have rather rapid colonization times, such that a functional stream macroinvertebrate community may return in only a few years in response to improved chemistry. However, fish community recovery is expected to be quite variable, depending on sources of colonists. In streams, fish could be introduced as soon as the water quality becomes suitable or the macroinvertebrate community becomes established. In streams that had simple fish communities in the past, a fish community might become rapidly established. It might take decades for complex communities without species introductions.

The Sudbury region of Ontario, Canada has been important for studying 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. This region has been the focus of extensive chemical and biological effects work since the 1980s (Keller, 1992). Sulfur 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).

Whitepine Lake, located 90 km north of Sudbury, had low pH (5.4) and ANC (1 µeq/L) in 1980 and its fish populations displayed symptoms of acid stress. Acid-tolerant yellow perch (*Perca flavescens*) were abundant, but the more acid-sensitive species lake trout and white sucker (*Catostomus commersoni*) were rare and not reproducing. Fish populations were studied by Gunn and Keller (1990) from 1978 through 1987, and zooplankton were sampled at least monthly during the open-water periods of 1980 through 1988. During the period between 1980 and 1988, pH increased to 5.9 and ANC increased to 11 µeq/L. Young lake trout first reappeared in 1982 and became increasingly abundant throughout the study. The number of benthic invertebrate taxa increased from 39 in 1982/83 to 72 in 1988, and the relative abundance of many of the invertebrates found in 1982 changed along with the changes in water chemistry (Gunn and Keller, 1990). 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, would soon follow.

Baker et al. (1990a) used field-based models to test the potential for biological recovery. The models were calibrated from the observed among-lake or among-stream associations between fish status and the chemical and physical characteristics measured in the surface water. The models were generally calibrated using chemistry data collected in conjunction with surveys of fish status. It was assumed that the systems surveyed were at steady state and that the observed status of the fish community was determined by the observed chemical and physical conditions in the lake or stream. 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^{2+}, ANC, and DOC) using maximum likelihood logistic regression (Reckhow et al., 1987). Models developed from data from the ELS and the ALSC were calibrated against data from Ontario lakes.

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. All the models provided similar results (Figure B-20) with the exception of those that relied on the pCa/pH term to predict fish status. Those models seemed to overestimate the effect of Ca^{2+}, and thus underestimate predicted fish response to changes in acidic deposition.



Source: Baker et al. (1990a).

Figure B-20. Example model application. Projected changes in the percentage of Adirondack lakes (Direct/Delayed Response project target population) with acid-base chemistry unsuitable for the survival of fish populations in the year 2034, versus current simulated conditions, based on projected changes in water chemistry from the Model of Acidification of Groundwater in Catchments (MAGIC) and using alternative models of fish response, given a 50% decrease in deposition or a 30% increase in deposition. (a) brook trout, (b) lake trout, (c) common shiner.

An important consideration for measuring the success of S and N emissions controls is the development of appropriate expectations for the magnitude of potential chemical recovery. Most lakes inferred to have been measurably acidified by atmospheric deposition were already marginally acidic, typically with pH less than about 6, before anthropogenic atmospheric pollution began prior to 1900. Therefore, full recovery of currently acidic lakes would not be expected to yield neutral pH. Nevertheless, increases in ANC may allow recovery of fish populations even if pH remains relatively low (Stoddard et al., 2003).

B.4.3. Effects by Ecosystem Type

B.4.3.1. Terrestrial Ecosystems

Due to a strong dependency on atmospheric deposition and exposure to gaseous compounds as the major sources of nutrients, lichens are affected by changes in these conditions. 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 nitrophilic lichen taxa are occurring in some areas (Fenn et al., 2003). In eastern North America and central Europe, areas experiencing relatively high levels of acidic deposition 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).

Fenn et al. (2007) speculated that large, pollution-sensitive macrolichens, including epiphytic cyanolichens, will be replaced by N-tolerant species in areas where development expands in western Oregon and Washington into N-limited Coast Range forests. Currently, in the Pacific Northwest, nitrophilic lichen species are common in and around Seattle, Portland, Spokane, the Tri-cities, Salem, Oregon's agricultural lands in the northeast and southwest, and the Willamette Valley (Fenn et al., 2007). The USDA Forest Service website contains information about lichen species pollution tolerance, diversity, and preferred habitat in relation to exposure to N (http://www.nacse.org/lichenair).

In London, epiphyte diversity, including a majority of the lichen taxa, declined in areas where NO_2 surpassed 40 $\mu g/m^3$ and NO_X surpassed 70 $\mu g/m^3$. Lichens remaining in areas affected by these levels of exposure contained almost exclusively families *Candelariaceae*, *Physciaceae* and *Teloschistaceae* (Davies et al., 2007).

Progressive decline in ectomycorrhizal fungal (EMF) community structure and species richness was observed at five Alaskan coniferous forest sites (white spruce [*Picea glauca*] dominant) along an N deposition gradient (1 to 20 kg N/ha/yr) downwind from a large industrial complex on the Kenai

Peninsula. The effects were attributed to both acidification and fertilization processes (Lilleskov et al., 2002). EMF communities are important in tree nutrition and C balance, and EMF trees tend to be dominant in N-limited forest ecosystems. A shift in EMF community structure could result in changes in tree species.

Westman et al. (1985) summarized the literature of negative effects of SO_2 on native plants, including decreased pollen germination and tube elongation in both angiosperms and gymnosperms. It is often difficult to separate the effects of SO_2 exposure on plants from the effects of S deposition. This is because areas that experience high SO_2 exposure generally also receive high S deposition. Kozlowski (1985) summarized relative susceptibility of different trees, lichens, and bryophytes to SO_2.

Available information is not sufficient to draw conclusions regarding the increased likelihood of future effects on the condition of hardwood forests in the Southern Appalachian Mountain region (Sullivan et al., 2002). Certainly, such effects are less likely for hardwood forests than for spruce-fir forests. Red oak seedlings grown in a greenhouse in deciduous forest soils exhibited no response to acidified soil (pH 4.0 from 9:1 H_2SO_4:HNO_3) or to high or low SO_4^{2-} inputs (12.8 to 24.8 mg/L). The lack of response suggested that red oak seedlings are not sensitive indicators of acidification effects from S deposition (McClenahen, 1987).

Grasslands and Alpine Tundra

Alpine communities are considered very sensitive to changes in N deposition, but documented effects in the scientific literature have been attributed to nutrient enrichment, rather than acidification (Seastedt et al., 2004; Bowman et al., 2006). Lower-elevation grasslands, especially those in semi-arid environments, would be expected to be even less sensitive to acidification because of low water leaching potential and the common presence of base-rich Mollisol and Aridisol soils. However, some effects of acidification may be manifested in mesic grasslands.

In a review of SO_2 effects on grasses in the United Kingdom, Bell (1985) suggested that damage can occur at levels as low as 150 µg/m^3. However, he asserted that any ubiquitous critical load value must be modified to include variations due to environmental conditions and combined effects with other pollutants. He also suggested that many grass species exhibit a tolerance to SO_2, resulting from more intraspecific competition in agricultural grasslands. Westman et al. (1985) also provided evidence of the evolution of a tolerant grass species, Bromus rubens, in southern California coastal sage scrub, influenced by an average of 3.7 µmol/m^3 of SO_2 over 25 years.

Studies of SO_2 effects on timothy grass (*Phleum pratense*) showed diminished leaf production and increased leaf senescence in seedlings exposed to 0.120 ppm SO_2 for 35 days (Mansfield and Jones, 1985). In another experiment, Mansfield and Jones (1985) reported that exposure to 0.120 ppm 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 (LAR) and specific leaf area (SLA) by the end of the experiment. They suggested that decreased growth and shifts in LAR and SLA could lead to decreased hardiness and increased susceptibility to water stress.

In a 5–year exposure of native mixed prairie grassland in Montana, Lauenroth and Milchunas (1985) exposed grasses to a control (~20 µg/m^3) and three elevated levels of SO_2 (~60, 106, 184 µg/m^3). 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*. However, lichen cover declined after 1–year of exposure at the low treatment level. Though no biomass or cover effects were observed at the community level, there were minor population changes. These results are consistent with the nature of semi-arid grasslands that typically adjust well to perturbations (Lauenroth and Milchunas, 1985).

Arid Lands

At the time of the previous AQCD, it was believed that arid and semi-arid ecosystems were not as susceptible to soil acidification and high NO_3^- leaching as are forested ecosystems. This is because of a scarcity of water for NO_3^- leaching, except on an episodic basis, and because arid soils tend to be more alkaline than soils in more humid environments. No new research has altered that conclusion. Arid lands in the U.S. generally receive low levels of S deposition. However, N deposition can be quite high, especially in southern California in the vicinity of the Los Angeles Basin. Little work has been done on the effects of acidification on arid land ecosystems. As reviewed by Fenn et al. (2003), acidification effects have not been demonstrated at the Central Arizona-Phoenix LTER site, despite the almost 30 kg N/ha/yr of deposition received. Nevertheless, N deposition has the potential to increase plant growth and denitrification and alter community composition in arid environments (Egerton-Warburton and Allen, 2000; Allen et al., 2005). Such changes could alter key ecosystem processes and, as such, merit consideration. There has been little research to examine these issues and, therefore, the state of knowledge is similar to what it was in 1993.

B.4.3.2. Aquatic Ecosystem

Chronic Effects

Sulfate

The study of Clow and Mast (1999) is unique in that SO_4^{2-} trends were evaluated with both raw data and data adjusted for existing trends in flow. From 1967 to 1983, Clow and Mast (1999) showed a decreasing trend in SO_4^{2-} concentrations in a Catskill river, no trend in three rivers in Maine, Pennsylvania, and Virginia, and an increasing trend in a river in Ohio. The Maine river did show a decreasing trend before flow adjustment of the data. From 1984 to 1996, however, Clow and Mast (1999) found decreasing trends in SO_4^{2-} concentrations in all five rivers, both with and without flow adjustment. The rivers in Pennsylvania, Ohio, and Virginia were south of the maximum southern extent of glaciation, and therefore were more likely to be subject to the effects of SO_4^{2-} adsorption in soils of their watersheds. In such streams, decreasing S-adsorption on soils would be expected to counteract the effects of decreasing S deposition in terms of effects on stream SO_4^{2-} concentration.

Surface waters in other unglaciated regions exhibited decreasing trends in SO_4^{2-} by the 1980s. Concentrations of SO_4^{2-} in 130 northeastern lakes in 1984 were compared to those in the same lakes in 2001 (Warby et al., 2005). Median concentrations in each subregion were lower in 2001 than 1984, and in the region as a whole, the overall median decrease was 1.53 µeq/L/yr. A decrease in SO_4^{2-} concentrations that averaged 2.16 µeq/L/yr was also observed in 47 of 48 Adirondack lakes from 1992 to 2004, and a similar decrease of 2.09 µeq/L/yr was observed in a subset of these lakes from 1982 to 2004 (Driscoll et al., 2007).

The pattern of increasing concentrations of SO_4^{2-} in surface waters before the year of peak S emissions in 1973, 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), provides convincing evidence of the link between S emissions and SO_4^{2-} concentrations in surface waters. A similar link has been shown in Europe (Stoddard et al., 1999). 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 uncertain due to an incomplete knowledge of S retention mechanisms in terrestrial systems. Also, in a detailed analysis of flow effects on SO_4^{2-} trends, Murdoch and Shanley (2006) found SO_4^{2-}that higher concentrations of SO_4^{2-} occurred at corresponding high, medium and low flows in 2000 to 2002 than in 1997 to 1999 in two of the rivers studied by Clow and Mast (1999), and at high and medium flows in a third river. Continued monitoring of surface waters will be needed to verify a future link between emissions and SO_4^{2-} concentrations in surface waters.

Nitrate

Driscoll et al. (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. (2000b) 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. Average concentrations of NO_3^- in most southeastern streams also tend to be considerably less than SO_4^{2-} concentrations (Webb et al., 2004).

High-frequency sampling in the study of 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. This study also reported increasing trends in NO_3^- concentrations during the period of 1970 to 1990 in all 16 Catskill streams for which data were available. A similar increase in NO_3^- concentrations was reported for Adirondack lakes in the 1980s (Stoddard et al., 1999). These increasing trends in NO_3^- concentrations were attributed to N saturation in response to atmospheric deposition (Aber et al., 1998).

The relationship between N deposition and surface water NO_3^- concentrations up through the 1980s suggested that continued N deposition would further the accumulation of N in terrestrial ecosystems and drive continued increases in surface water NO_3^- concentrations. However, more recent information on NO_3^- concentrations have been less consistent with the concept of N saturation. Goodale et al. (2003) resampled New Hampshire streams in 1996–97 that had been previously sampled in 1973−74 and found substantially lower NO_3^- concentrations in the more recent sampling, despite two decades of relatively stable levels of deposition to otherwise undisturbed forests. The lower NO_3^- concentrations could not be accounted for by differences in flow or forest succession, but interannual climate variation was proposed as a possible cause. The long-term record of dissolved inorganic N (which is largely NO_3^-) concentrations at the HBEF showed a similar pattern; high concentrations in the late 1960s and 1970s, followed by decreases to minimum values in the mid-1990s (Aber et al., 2002). These authors attributed this pattern to a combination of environmental factors, but did not identify a single most important control variable. A reversal from increasing trends in NO_3^- concentrations in the 1980s to decreasing trends in the 1990s was also observed in Adirondack lakes (Driscoll et al., 2003a). A small decrease in atmospheric deposition of N also occurred in this region through the 1990s, but was not considered sufficient by these authors to explain the decreasing trend in lakewater NO_3^- concentrations. Rather, they proposed that increased concentrations of atmospheric CO_2 may have resulted in a fertilization effect that increased N assimilation (Driscoll et al., 2007).

In general, trends in surface water NO_3^- concentrations during the 1990s were much smaller than trends in SO_4^{2-}, with the only ecologically significant changes occurring in the two regions with the highest ambient NO_3^- concentrations (Figure B-21). Lakes in the Adirondacks and streams in the Northern Appalachian Plateau both exhibited small but significant downward trends in NO_3^- in the 1990s

(Figure B-21). Both of these regions are central to the debate over whether N saturation is a legitimate threat to the health of forests and surface waters (Stoddard, 1994; Aber et al., 1998). While declining NO_3^- concentrations in these regions is a positive development for these ecosystems, we clearly do not know if these trends will continue, especially because they do not appear to reflect changes in N emissions or deposition. The presence of strong upward trends in NO_3^- in these same regions in the 1980s (Murdoch and Stoddard, 1992; Stoddard, 1994) suggests that trends measured on the scale of a single decade may reflect variability in long-term patterns of changing NO_3^- leakage from forested watersheds. Such patterns are controlled by factors that may take many years of additional research to determine. While great uncertainty exists and the time scales of N saturation may be longer than previously considered (e.g., centuries rather than decades), the long-term retention of N deposition in forested regions is unlikely to continue indefinitely (Aber et al., 2003).

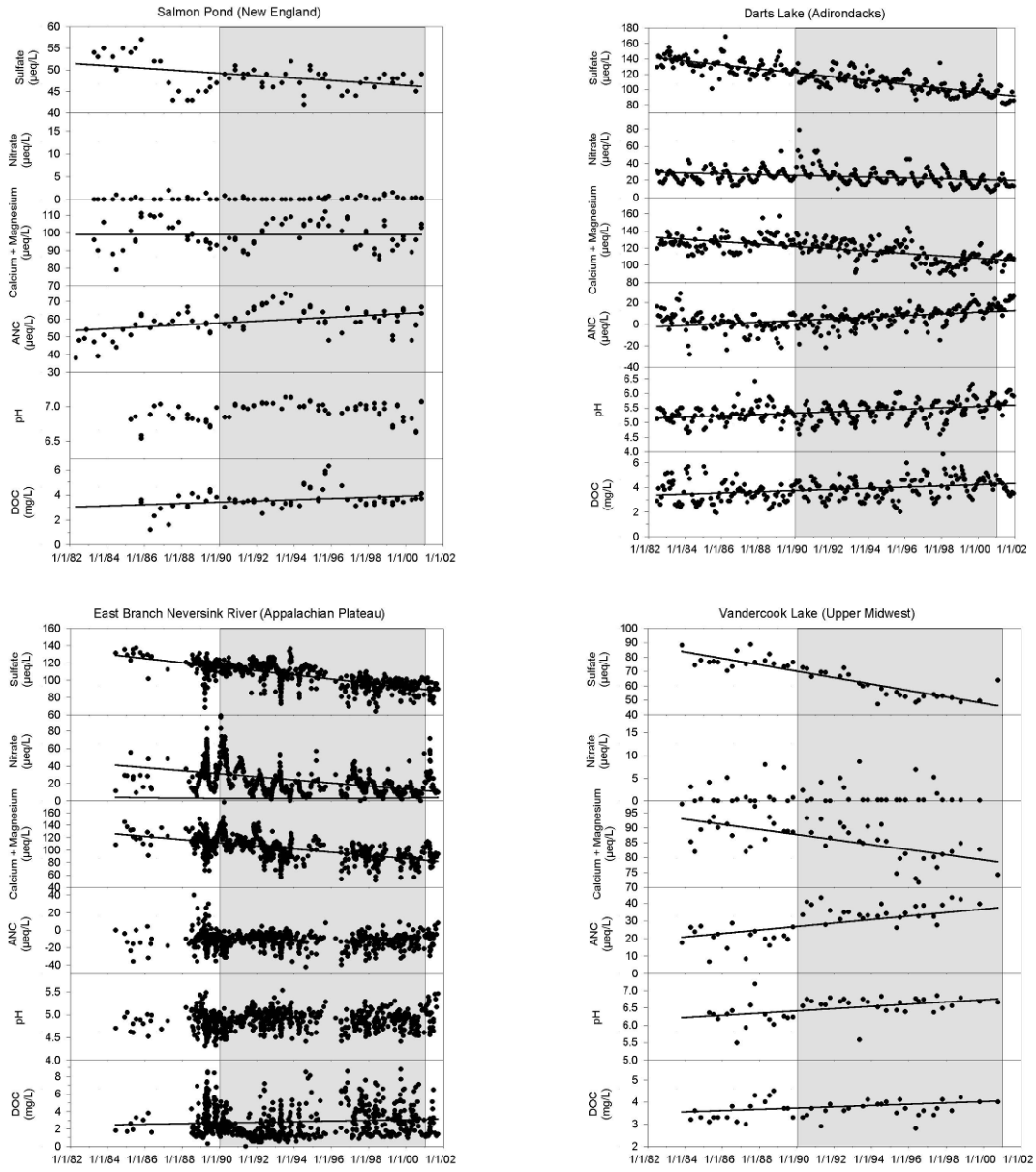
In New England and the Upper Midwest, where ambient NO_3^- concentrations are much lower than in the Adirondacks and Northern Appalachian Plateau (Source: Stoddard et al. (2003).

Figure B-21), 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^- during the 1990s, but interpretation of trends for NO_3^- in this region is complicated by an outbreak of gypsy moths that also occurred during this period. Forest defoliation by gypsy moths was the most likely cause of a pulse in NO_3^- export from many streams in this region in the mid-1990s (Eshleman et al., 1998).

Some evidence of climate effects on long-term trends in NO_3^- concentrations in surface waters was provided by studies of Mitchell et al. (1996) and Murdoch et al. (1998). A synchronous pattern in NO_3^- concentrations was observed from 1983 to 1993 in four small watersheds in New York, New Hampshire, and Maine, which included anomalously high concentrations during the snowmelt period of 1990. The region-wide spike in NO_3^- concentrations followed an unusually cold December that may have disrupted soil N cycling processes (Mitchell et al., 1996). Murdoch et al. (1998) also found that mean annual air temperatures were strongly related to average annual NO_3^- concentrations in most years in a Catskill watershed with elevated NO_3^- concentrations in stream water. Those relationships were explained by microbial control of N release in watersheds that were considered to be N-saturated.

Efforts to explain the decreasing trends in NO_3^- concentrations under conditions of reasonably stable atmospheric N deposition have focused on terrestrial N cycling and N-saturation theory. However, processes within lakes may have also played a role in the trends in Adirondack lakes. In a study of 30 of the 48 lakes studied by Driscoll et al. (2003a; 2007), Momen et al. (2006) found that concentrations of 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).

Thus, there is little or no apparent relationship between recent trends in N deposition and trends of NO_3^- concentrations in surface waters, in sharp contrast to S deposition and SO_4^{2-} concentrations. Rather than disprove the concept of N-saturation; however, these studies more likely reflect the complexities of N utilization within terrestrial and aquatic ecosystems. These complexities create considerable uncertainty with regard to how future trends in NO_3^- concentrations in surface waters will respond to changing levels of deposition.



Source: Stoddard et al. (2003).

Figure B-21. Time series data for SO_4^{2-}, NO_3^-, base cations [Ca^{2+} + Mg^{2+}], Gran ANC, pH, and DOC in example Long Term Monitoring Lakes and streams that have relatively low ANC. The example surface waters include Salmon Pond, Maine (New England region); Darts Lake, NY (Adirondack region); East Branch Neversink River (Appalachian Plateau region); and Vandercook Lake, Wisconsin (Upper Midwest region). Significant trends are indicated by trend lines. Shaded box indicates time period of analyses reported by Stoddard et al. (2003).

Base Cations

The earliest trends of base cation concentrations in acid-sensitive surface waters of the U.S. were presented by Stoddard (1991) for 12 streams in the Catskill region. In 5 of 12 streams, concentrations of (Ca^{2+} + Mg^{2+}) increased from 1915–22 to 1945, but decreased from 1945–46 to 1990. In the remaining seven streams, concentrations increased during both periods, but at a lower rate in the more recent period in five of the seven streams. In streams that showed an increase in concentrations during both periods, the average rate of increase from 1915 to 1922 was 2.8 μeq/L, whereas the average rate of increase from 1945 to 1990 was 1.2 μeq/L. Data on SO_4^{2-} trends were not available for the early period, but the trends in (Ca^{2+} + Mg^{2+}) concentrations were consistent with the expected pattern of high rates of cation leaching during the early stages of acidification from S deposition.

Clow and Mast (1999) observed trends in (Ca^{2+} + Mg^{2+}) concentrations that were generally consistent with SO_4^{2-} trends in five eastern rivers from 1968 to 1983. Decreasing trends in concentrations of (Ca^{2+} + Mg^{2+}) and SO_4^{2-} concentrations were observed in a Maine river, and increasing trends in (Ca^{2+} + Mg^{2+}) and SO_4^{2-} concentrations were observed in an Ohio river. None of the three other rivers showed a decrease in concentrations of (Ca^{2+} + Mg^{2+}), and only one showed a decreasing trend in SO_4^{2-} concentrations. For the period 1984 to 1996, the trend in SO_4^{2-} concentrations was negative in the Ohio River and the concentrations of (Ca^{2+} + Mg^{2+}) showed no trend. Also, a negative trend in (Ca^{2+} + Mg^{2+}) concentrations in a Virginia river was coupled with a negative trend in SO_4^{2-} concentrations. Relations for the other three rivers were similar to the earlier period of 1984 to 1996.

The study of Likens et al. (1996) evaluated trends in base cations in relation to trends in (SO_4^{2-} + NO_3^-) in the long-term record for the HBEF. This record showed an approximately linear, increasing relationship between concentrations of base cations and (SO_4^{2-} + NO_3^-) from 1964 to 1969, then a reversal in 1970 to a decreasing trend up to 1994. The slope of the phase with increasing anion concentrations was steeper than the slope for the phase with decreasing anion concentrations. This indicates lower base cation leaching per equivalent of mobile anion, and therefore suggests depletion of base cations stored in soil. The study of Lawrence et al. (1999b) showed decreased concentrations of base cations at a rate that exceeded decreases in (SO_4^{2-} + NO_3^-) in Catskill 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 on streamwater SO_4^{2-} concentrations.

Regional declines in base cation concentrations were measured in the LTM Program from 1990 to 2000 in New England lakes, Adirondack lakes, Appalachian streams, and upper Midwest lakes (Stoddard et al., 2003). These results were consistent with decreased Ca^{2+} concentrations measured by Warby et al. (2005) in 130 acid-sensitive lakes in the Northeast between 1984 and 2001. The rate of decrease identified by Warby et al. (2005) for base cations (1.73 μeq/L) was somewhat less than the rate of

decrease in SO_4^{2-} concentrations (1.53 µeq/L). Driscoll et al. (2007), also documented decreasing trends in base cation concentrations in 16 Adirondack Lakes from 1982 to 2004, and similar rates of decrease in 48 lakes (including the 16) from 1992 to 2004.

In summary, decreases in base cation concentrations over the past two to three decades are ubiquitous and closely tied to trends in SO_4^{2-} concentrations in acid-sensitive regions of the U.S. Reports of increases in concentrations of base cations in acid-sensitive regions were not found in the literature. In most regions, rates of decrease for base cations have been similar to those for SO_4^{2-} and NO_3^-, with the exception of streams in Shenandoah National Park. Decreasing trends of base cation concentrations do not necessarily indicate further acidification or recovery of surface waters, but do indicate lower leaching rates in soils, a prerequisite for recovery of soil base saturation. However, decreased concentrations of base cations, particularly Ca^{2+}, would also be expected to lower productivity in oligotrophic surface waters.

Acid Cations

Measurements of pH (sometimes expressed as H^+) have been routinely collected in surface waters in the U.S. where effects of acidic deposition have been monitored, but a long-standing reliance on titrated ANC rather than pH as the primary chemical measurement has limited the amount of pH data published. The longest continuous record of pH in surface waters dates back to 1963 at the HBEF (Driscoll et al., 2001b). This record shows an overall increasing trend from 1963 to 1994, although most of the increase occurred after 1980. In Adirondack lakes, 12 of 16 monitored from 1982 to 2004 showed an increase in pH, but the rates of change among lakes were highly variable, and one lake showed a decrease in pH (Driscoll et al., 2007). When expressed as H^+ concentration, the average increase for the 12 lakes was 0.18 µeq/L/yr. In this same region, pH also increased in 31 of 48 lakes (including the 16 lakes monitored from 1982) from 1992 to 2004. Two lakes showed increases in pH over the 12 years.

Comparison of pH measurements of 130 lakes in 1984 and in 2001, in the northeastern U.S., showed an overall average increase in pH of 0.002 units (Warby et al., 2005). However, in this assessment, lakes in the Adirondack region did not show a significant increase, nor did lakes in central New England, or Maine. The Catskill/Poconos region of New York and Pennsylvania showed an average increase of 0.008 pH units per year, and southern New England showed an average increase of 0.002 pH units per year. Through continuous monitoring from 1990 to 2000, Stoddard et al. (2003) found a decrease in H^+ (0.19 µeq/L/yr) similar to that observed in the same Adirondack lakes by Driscoll et al. (2007) from 1992 to 2004 (0.18 µeq/L), and an increase in Appalachian streams (0.08 µeq/L/yr) and Midwest lakes (0.01 µeq/L/yr). No trends were found in New England lakes or Blue Ridge streams in Virginia in this study. Stream monitoring in the Adirondack region from 1991 to 2001 showed an increase in H^+ in one stream, no trend in a second stream, and also an increase in a third stream near the outlet of a lake

(Lawrence et al., 2004). In summary, decreasing trends in pH in surface waters are common through the 1990s up to 2004, but many exceptions occur, and overall, the rates of change have been small.

The discovery that Al_i was toxic to aquatic life resulted in 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 (Johnson et al., 1981; Driscoll and Newton, 1985; Driscoll et al., 1987; Lawrence et al., 1987; Cronan et al., 1990). Monitoring of Al_i concentrations was begun in 16 Adirondack lakes in 1982 and expanded to 48 lakes in 1990. From 1982 to 2004, 5 of the original 16 Adirondack monitoring lakes showed decreasing trends in Al_i concentrations at rates that ranged from 0.02 µM/yr to 0.18 µM/yr (Driscoll et al., 2007). From 1992 to 2004, 24 of the 48 lakes showed decreasing trends in Al_i concentrations (Driscoll et al., 2007). The analysis of Stoddard et al. (2003) also observed an average decrease in Al_i concentrations from 1990 to 2000 in the same group of Adirondack lakes reported on by Driscoll et al. (2007), but observed no trend for this period in New England lakes, Appalachian streams, or Midwest lakes.

Monthly stream chemistry monitoring at the HBEF showed decreases in Al_i 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 et al., 2004). These data also showed a surprising decrease in pH at two of the locations where Al_i decreased, and no pH trend at the other two locations where Al_i decreased (Palmer et al., 2004). Comparison of total Al concentrations in 130 lakes in the northeastern U.S. in 1984 with those measured in 2001 showed lower average concentrations in 2001 in the Adirondack region, the Catskill/Pocono region, central New England, southern New England, and Maine (Warby et al., 2005). Because these measurements are of total Al, they are not directly comparable to Al_i. Most recently, Lawrence et al. (in review) found that 49 of 195 streams (25%) during August base flow in the western Adirondack region had Al_i concentrations above 2.0 µM, the level above which toxic effects on biota have been shown (Driscoll et al., 2001b; Baldigo et al., 2007).

Acid Neutralizing Capacity

In response to reduced levels of acidic deposition required by the CAA and other emissions control legislation, Stoddard et al. (2003) found trends during the 1990s toward increasing Gran ANC (Figure B-21) in all of the 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. Changes were relatively modest compared with observed reductions in SO_4^{2-} concentrations. Only the regional increases in the Adirondacks, Northern Appalachian Plateau, and Upper Midwest were statistically significant (Figure B-21). Median increases of about +1 µeq/L/yr in the Northern Appalachian Plateau, Adirondacks and Upper Midwest represent significant movement towards ecological recovery from acidification (Stoddard et al., 2003).

It has been hypothesized that decreases in acidic deposition will yield the most chemical recovery in lakes and streams that have experienced the most severe acidification. Using data from all of the sites in regions where decreases in surface water SO_4^{2-} and NO_3^- have occurred, Stoddard et al. (2003) found that acidic lakes and streams exhibited a highly significant median increase in Gran ANC of +1.3 µeq/L/yr during the 1990s. Low-ANC sites (0 to 25 µeq/L) showed a smaller significant median ANC increase of +0.8 µeq/L/yr. Moderate ANC sites, those with mean ANC values greater than 25 µeq/L, showed no significant change in Gran ANC (Figure B-21).

All of the glaciated regions in the eastern U.S. showed declines in base cation (Ca^{2+} + Mg^{2+}) concentrations during the 1990s, with the average changes in the range of −1.5 to −3.4 µeq/L/yr. All of the regional trends were highly significant (Figure B-21). Across the eastern U.S., surface water SO_4^{2-} has decreased at a rate of about −2.5 µeq/L/yr (the mean of regional median slopes), and NO_3^- at a rate of −0.5 µeq/L/yr, in surface waters on glaciated terrain during the 1990s. These rates of change set an upper limit to our expectation of ANC recovery of +3 µeq/L/yr (i.e., the sum of SO_4^{2-} and NO_3^- trend magnitudes). The Gran ANC increase reported by Stoddard et al. (2003) was actually about one-third of this maximum, +1 µeq/L/yr. The difference between the observed Gran ANC trend and the maximum trend estimated from rates of acid anion change can largely be explained by the average regional median decline in (Ca^{2+} + Mg^{2+} concentrations, which was about −2.0 µeq/L/yr (Stoddard et al., 2003).

Episodic Effects

Episodic acidification can result naturally from the mobilization of organic acids and from dilution of base cation concentrations, but decreases in pH and ANC associated with increases in SO_4^{2-} and NO_3^- are largely attributable to acidic deposition (Wigington et al., 1996). Episodic acidification is most common in the early spring and late fall as a result of snowmelt and rainstorms, and is least common in summer, when high flows tend to be infrequent. Seasonal variations in stream flow also result in seasonal patterns of surface water chemistry at base flow. Lakes and streams at base flow tend to be more acidic in early spring than at other times of the year and low flows in late summer tend to be least acidic (Lawrence et al., 2007).

The transient nature of high flows makes episodic acidification difficult to measure. Therefore, assessments have generally estimated the number of lakes and streams prone to episodic acidification by combining episode information from a few sites with base flow values of ANC determined in large surveys (Eshleman et al., 1995; Bulger et al., 2000; Driscoll et al., 2001b). 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 TIME Program indicated that 10% of the 1,812 lakes (>1 ha surface area) in the Adirondack region of New York could be considered chronically acidic on the basis of ANC values less than 0 µeq/L, but that an

additional 31% of these lakes had baseflow ANC values less than 50 μeq/L and were, therefore, estimated to be susceptible to episodic acidification (Driscoll et al., 2001b). Lawrence (2002) also estimated the extent of episodically acidified stream reaches in a Catskill, NY watershed (area = 85 km^2) through the use of 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 were chronically acidified (ANC < 10 μeq/L), but that 66% of the stream reaches became episodically acidified.

Stoddard et al. (2003) compared seasonal data from New England lakes, Adirondack lakes and Northern Appalachian streams, collected monthly to quarterly, to evaluate the difference between the chemistry of surface waters in the summer and in the spring. Results indicated that spring values of ANC were an average of 30 μeq/L lower than summer ANC. This study referred to samples collected in spring as "episodic samples," although sampling was done independent of flow. Therefore, the 30 μeq/L difference should be considered a seasonal effect rather than an episodic effect.

The most thorough characterization of episodic variations in stream chemistry 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 et al., 1996). Acid episodes with chemical concentrations within the 90th percentile involved decreases in ANC of up to 200 μeq/L, decreases in pH of up to one unit, and increases in concentrations of Al_i of up to 15 μM (Wigington et al., 1996). Results also 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 Al_i concentrations exceeded 3.7 μM, despite the relatively short duration of episodes (Baker et al., 1996). Baker et al. (1996) concluded that effect on biota from episodic acidification were likely to be similar to those from chronic acidification. Elimination of an annual age class can result from an episode that occurred in the presence of a sensitive life stage. Largely on the basis of this study, the EPA concluded that reversal of effects from episodic acidification could be used as a key ecological endpoint for an acid deposition standard for protection of the environment (U.S. Environmental Protection Agency, 1995).

Despite the significance of the findings of ERP, little assessment or monitoring of episodes was done in the 1990s. One exception was the work of Hyer et al. (1995) in three watersheds of differing geology in Shenandoah National Park. Results suggested that episodic acidification was occurring throughout the park on all bedrock types, although acidification was not sufficient to cause elevated Al concentrations. Lawrence (2002) also documented severe episodic acidification in August 1998 in a tributary of an ERP stream, where Al_i concentrations increased from 1.6 to 7.3 μM in 6.5 h.

In the first large-scale study designed to sample streams during high-flow conditions, Lawrence et al. (2007) found that 124 out of 188 (66%) western Adirondack streams were prone to acidification to the level at which Al_i becomes mobilized. Only streams accessible with less than a 60–min hike were sampled in this study. The March, 2004 survey was chosen to represent episodic conditions, and a survey conducted August 16–18, 2004 was chosen to represent base flow conditions. Based on this comparison, 35% of the streams were chronically acidified, 30% of the streams were episodically acidified, and 34% were not acidified. Survey results were also used to estimate that 718 km of stream reaches were prone to acidification, although 3085 km of stream reaches within the study region could not be assessed because of inaccessibility.

There have been no studies in the U.S. that determine if either the severity or frequency of episodic acidification has lessened. In a study of two streams in Nova Scotia (Laudon et al., 2002), trends in ANC in four phases of storm hydrographs from 1983 to 1998, were not detected other than in the peak-flow phase of one stream (an increase of 0.87 μeq/L). In Sweden, the anthropogenic contribution to episodic decreases in ANC were estimated to range from 40 to 80% in five streams from 1990 to 1999 (Laudon et al., 2002).

B.5. Effects on Watersheds and Landscapes

B.5.1. Interactions among Terrestrial, Transitional, and Aquatic Ecosystems

Acidification has pronounced effects on nutrient cycling in terrestrial, transitional, and aquatic ecosystems. Of particular importance in this regard is the role of N deposition in influencing N cycling. This topic is discussed in detail in Section 5. Also important are the influences of acidification on the availability of Ca^{2+} and other nutrient base cations (Mg^{2+}, K^{+}).

In general, decomposition, nutrient cycling, productivity, and other system-level processes in surface waters are not as sensitive as species composition and richness to relatively small amounts of acidification. Such effects only seem to occur at high levels of acidification (e.g., pH < 5). This is because acid-sensitive species are often replaced by more acid-tolerant species that perform the same function until acidification becomes severe. For example, whereas changes in microbial composition and abundance have been observed with acidification, they appear to have minimal effect on overall microbial respiration and nutrient cycling. At extreme levels of acidity, however, these system-level functions may also decrease. Thus, system-level functions are not generally good indicators of light to moderate levels of acidification.

Integrating the effects of atmospheric deposition across spatial scales is difficult. The response of a single plant, or small group of plants, cannot be easily scaled up to examine effects on plant communities, ecosystems, watersheds, or geographic regions. Integration typically requires a combination of approaches, including ecosystem modeling, experimental manipulation studies, surveys across pollution deposition gradients, and long-term monitoring studies. Similarly, aquatic effects at the population level can be readily quantified, but extrapolation to the community or aquatic ecosystem level is problematic. Linking research results across scales will be an important component of future research. Measurements that correlate with ecosystem processes, such as foliar N concentration, leaf area index, or spectral reflectance, can in some cases be remotely sensed. They offer great promise for future assessment of terrestrial effects across spatial scales.

Effects of atmospheric deposition of acidifying substances on soil, vegetation, and surface water are manifested in specific processes, affecting energy, water and nutrient flow, intra- and inter-species competitive interactions, and ecosystem primary production. Therefore, effects on sensitive species (only some of which have been documented) have the potential to cascade throughout the ecosystem and become manifested at a variety of scales. Such ecosystem- to landscape-scale effects from atmospheric deposition of acidifying substances are known to occur, but the results of these interacting processes have not been conclusively demonstrated.

It is also evident that acidification from natural and human-caused disturbances, including climatic stressors (temperature, moisture availability, wind), insect infestation, disease, fire, and timber harvest, can affect the severity of effect of atmospheric deposition of SO_X and NO_Y. Although it is clear that such interactions can occur, there are no studies that have clearly documented that acidic deposition at levels that commonly occur across broad landscapes in the U.S. has conclusively altered ecosystem structure or function. Similarly, although it is widely believed that acidic atmospheric deposition can make plants more susceptible to the adverse effects of other natural and human-caused stressors, such effects have not been conclusively demonstrated in more than a few cases. The data demonstrating and quantifying the extent to which SO_X and NO_Y deposition are altering natural terrestrial ecosystems via acidification pathways are sparse. In particular, effects of soil and soil water acidification on soil ecosystem processes and nutrient cycling are poorly known. Even less is known about effects on soil microorganisms and food webs, or how such effects interact with the above-ground vegetation community.

B.5.2. Interactions with Land Use and Disturbance

The prevailing scientific consensus during the 1980s held that the majority of lakes in eastern North America that had pH less than about 5.5 to 6.0 had been acidified by acidic deposition. Reports that acidic lakes and streams were rare or absent in similar areas not receiving acidic deposition were used as

evidence of acidification by acidic deposition in many regions (e.g., Neary and Dillon, 1988; Sullivan et al., 1988; Baker et al., 1991a). An alternative hypothesis had been advanced by Rosenquist (1978), Krug (1989, 1991), and Krug and Frink (1983) that land use changes could explain recent lake acidification in southern Norway and the northeastern U.S. According to this hypothesis, natural soil processes and changes in vegetation can generate more acidity than is received from atmospheric deposition. For example, an increase in acidic humus formation in response to decreased upland agriculture was suggested as being responsible for regional acidification in southern Norway, rather than acidic deposition (Rosenqvist, 1978). Subsequent acidic deposition effects research in some cases seemed to be designed to refute this hypothesis rather than to explore the relationships between land use and acid-base chemistry (cf. Havas et al., 1984; Birks et al., 1990). Research intended to discriminate between acidic deposition and land use as the major cause of acidification generally concluded that acidic deposition was the principal cause of regional acidification in certain areas of North America and Europe. Perhaps more appropriate research questions might have focused on quantifying the relative importance of land use activities or landscape change in exacerbating or ameliorating acidic deposition effects. The importance of acidic deposition as an agent of acidification does not preclude the importance of land use and landscape changes which, in some cases, may actually be more important than acidic deposition (Sullivan et al., 1996b).

There has not been a regional evaluation of land use changes in areas of the U.S. susceptible to surface water acidification from acidic deposition. It has therefore not been possible to quantify the extent or magnitude of land use effects on acidification. It is clear, however, that such changes can have important effects on acid-base status (Sullivan, 2000), especially as influenced by N deposition (Goodale and Aber, 2001).

Changes in human land use activity, and associated changes in vegetative structure, influence ecosystem response to external stressors such as acidic deposition, exposure to O_3, natural disturbance factors such as wind and fire, and climatic changes. Some activities contribute to the acidification of soil and surface waters; other activities decrease acidity (Sullivan et al., 1996b) (Table B-21).

Forest management practices, especially those that have occurred over many generations of trees, can have important effects on soil erosion, nutrient supplies, and organic material. Such effects can influence the availability of base cations for acid neutralization and/or aspects of N cycling.

Forests are efficient at scavenging S and N from the atmosphere. Differences in forest canopy, particularly between deciduous and coniferous trees, can cause large differences in dry deposition, and therefore total deposition of S and N. In regions that receive high levels of acidic deposition, the presence of forest vegetation, especially coniferous trees, enhances total deposition of acid-forming precursors (Rustad et al., 1994). In addition to the enhanced deposition caused by the presence of large trees, there are also differences in nutrient uptake. In particular, younger trees take up larger quantities of N and other

nutrients than do trees in older forests. Therefore, changes in the occurrence and age or species composition of the forest can influence the rates of atmospheric deposition to the site as well as the fate of atmospherically deposited substances.

Landscape processes and watershed disturbance can influence soil and water acidification in many ways. Land use practices and vegetation patterns have been changing in various parts of the U.S. for decades to centuries. These changes in human activity can influence the response of forested ecosystems to external stressors, including atmospheric deposition of S or N, natural disturbance factors such as wind and fire, and climatic changes. Some processes contribute to the acidification of soil and surface waters or reduce the base saturation of the soils thereby increasing their sensitivity to acidic deposition. Other processes cause decreased acidity (Sullivan et al., 1996b; (Sullivan, 2000).

Watershed disturbance from logging, blowdown, and fire disrupts the normal flow of water and can cause increased contact between runoff water and soil surfaces, leading to increased base cation concentration and ANC in drainage water. Recovery from disturbance can cause a decrease in drainage water ANC as the system returns to pre-disturbance conditions. In particular, soil loss through erosion can reduce the base cation pool size, thereby limiting the capacity of soils to neutralize atmospheric acidity. In addition, forest harvesting has an important effect on forest N-demand, thereby reducing the likelihood of future N-saturation in response to high N deposition. Forest management practices, especially those that have occurred over many generations, have had important effects on soil chemistry, nutrient supplies, and organic material.

Watershed disturbances, including road building, agriculture, mining, urbanization, logging, blowdown, and fire can alter various aspects of ecosystems biogeochemistry. Such disturbances can influence the water budget, base cation mobilization, routing of drainage water, nutrient input, and S and N cycling in ways that affect the acid-base chemistry and nutrient dynamics of soils and drainage waters (Sullivan et al., 1996b). The effects of such disturbances can greatly modify the response of a given watershed to atmospheric inputs of S and N.

B.5.2.1. Timber Harvest

Removal of the forest affects drainage water quality in several ways. Deposition of S and N are reduced; leaching of NO_3^- increases and, in some cases, causes a pulse of surface water acidification. Base cations tied up in wood are lost when wood is transported off-site. Regrowth of the forest may further affect drainage water quality through vegetative uptake of N and base cations. Trees accumulate base cations to a greater degree than anions. To balance the charge discrepancy, roots release an equivalent amount of protons and acidify the soil. Base cation accumulation by trees is age-dependent. Young forests grow faster and are therefore more acidifying than older forests (Nilsson et al., 1982; Nilsson, 1993). They also retain greater amounts of N.

Most forests in the northeastern U.S. are recovering from extensive human disturbance that occurred over a period of about 200 years. Landscapes were mainly forested during pre-colonial times, logged or cleared for agriculture in the mid to late 19th century, and are now largely early to mid-seral stage regenerating forests (Niering, 1998).

In some areas that experience relatively high levels of acidic deposition, there is growing concern about sustainable timber productivity (cf. Adams, 1999). Harvest-induced leaching losses have been estimated to range from 6 to 60 kg/ha/yr of N, 28 to 48 kg/ha/yr of Ca^{2+}, and 7 to 16 kg/ha/yr of Mg^{2+} (Federer et al., 1989). Timber harvesting also increases leaching losses from the site because of the reduction in transpirational water loss. The increased water flux after tree removal increases the opportunity to leach base cations from the soil.

If base cations sequestered in tree wood are removed from the site by tree harvesting, the result is a decrease in the available base cation pool on the site. Physical disturbances to forest soils during logging operations and increased soil temperature that results from exposure of the forest floor to sunlight may also cause a short-term increase in the rates of N mineralization and nitrification (Joslin et al., 1992). The resulting increase in NO_3^- production and leaching further depletes base cations from the soil pool.

Johnson et al. (1991a) measured short-term (3 years) effects of logging at HBEF in New Hampshire on soil acid-base chemistry. Base saturation of the mineral soil Bh horizon decreased from 14 to 11% and pH decreased by 0.24 pH units.

Likens et al. (2002) reported results of a 34–year study of the biogeochemistry of forest ecosystems at HBEF. Part of the study evaluated the effects of tree removal on S cycling and related biogeochemical processes. Vegetation removal resulted in increased decomposition of organic matter and nitrification. These changes, in turn, lowered soil water pH, enhanced SO_4^{2-} adsorption on mineral soil, and therefore decreased the flux of SO_4^{2-} in stream water. With subsequent vegetation regrowth, the adsorbed SO_4^{2-} was released from the soil to drainage water, and streamwater SO_4^{2-} concentrations increased.

Baldigo et al. (2005) compared the effects of clear-cut and timber-stand improvement (TSI) harvests on water chemistry and mortality of caged brook trout in three Catskill Mountain streams. Harvests removed 73% of tree basal area from a clearcut subbasin, 5% basal area from a TSI subbasin, and 14% basal area at a site below the confluence of both streams (the combined effect of the two harvest methods). Water quality and trout mortality were affected only in the clearcut stream. Acidity and concentrations of NO_3^- and Al_i increased sharply during high flows after the first growing season (1997). Acid-Al_i episodes were severe during this period and decreased steadily in magnitude and duration thereafter. All trout at the clearcut site died within 7 days during spring 1998, and 85% died during spring 1999. Only background mortality was observed in other years at this site and at the other three sites during all tests. The effects of tree harvests on fish communities are of concern because they might

interact with effects of acidic deposition and produce more substantial effects on biota than either stress factor on its own.

B.5.2.2. Insect Infestation

Effects of insect-caused defoliation on the N cycle can be pronounced. The foliar N consumed by insects is deposited on the forest floor as insect feces (frass), greenfall, and insect biomass. Some of this deposited N is subsequently taken up by tree roots and soil microbes, with little effect on the nutritional condition of the trees or the site. Where a sizable component of this N is leached in drainage water, the nutritional consequences can be more significant. There are also various feedback mechanisms. For example, low N supply can slow the population growth of defoliating insects (Mason et al., 1992) and enhance the tree's chemical defenses against insects (Hunter and Schultz, 1995). The amount of N leaching loss is generally small, relative to atmospheric deposition inputs and relative to the amount of N transferred to the forest floor with the defoliation (Lovett and Ruesink, 1995; Lovett et al., 2002). Nevertheless, it can be high enough to contribute to base cation depletion of soils and effects on downstream receiving waters. The extent of NO_3^- leaching may be partly related to the extent of defoliation and tree mortality that occurs and also the amount of precipitation that occurs immediately after the defoliation (Lovett et al., 2002).

Forest insect infestation can have profound effects on the acid-base and nutrient chemistry of soils and drainage waters. Effects of a gypsy moth infestation in Shenandoah National Park provide a good example. Between the mid-1980s and the early 1990s, the southward expanding range of the European gypsy moth traversed Shenandoah National Park and affected all of the University of Virginia's SWAS study watersheds (Webb, 1999). Some areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. This insect infestation of forest ecosystems in Shenandoah National Park resulted in substantial effects on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over 6 years before returning to predefoliation levels. The very low levels of pre-disturbance NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (Aber et al., 1989; Stoddard, 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (Likens et al., 1970; Swank, 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in Shenandoah National Park forests.

Although N is thought to play an important role in the chronic acidification of surface waters in some areas (cf. Sullivan et al., 1997), the elevated concentrations of NO_3^- in Shenandoah National Park streams following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation concentrations increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^-. Episodic acidification following defoliation thus became more frequent and more extreme in terms of observed minimum ANC (Webb et al., 1995).

The full effect of the gypsy moth on aquatic resources in Shenandoah National Park is not well understood. One consequence may be a reduction in the supply of available soil base cations and associated effects on streamwater ANC. Repeated periods of defoliation would probably increase the effect of episodic acidification on sensitive aquatic fauna and may determine the conditions under which some species are lost. Ultimately such effects may depend upon both the severity of future gypsy moth or other insect outbreaks and possibly on the amount of atmospheric N deposition. Gypsy moth populations typically display a pattern of periodic outbreaks and collapse (Cambell, 1981). It remains to be seen what the long-term pattern will be (Sullivan et al., 2003).

Webb et al. (1994) compared pre- and post-defoliation streamwater chemistry for 23 VTSSS watersheds. Nitrate concentrations, measured quarterly, increased in most of the streams in response to defoliation, typically by 10 to 20 µeq/L or more. The increased streamwater NO_3^- concentration was probably derived from the N content of the foliage that had been consumed by the gypsy moth larvae and converted to feces on the forest floor. Sulfate concentrations and ANC also decreased in streamwater. Although the mechanism for decreased SO_4^{2-} was not totally clear, Webb et al. (1994) hypothesized that increased nitrification in response to the increased soil N pool may have caused soil acidification, which would be expected to have increased soil S adsorption (cf. Johnson and Cole, 1980). Decreased S deposition during the comparison period may also have contributed to the SO_4^{2-} response.

Eshleman et al. (1998) reported NO_3^- outputs from five small (<15 km^2) forested watersheds in Virginia and Maryland from 1988 to 1995. The study watersheds varied in geology, vegetation, and acid sensitivity, with baseflow ANC typically in the range of 0 to 10 µeq/L in Paine Run to the range of 150 to 350 µeq/L in Piney River. Oak species (*Quercus* spp.), which are a preferred food source of gypsy moth larvae, occupied about 60% to 100% of the study watersheds. Nitrate concentrations increased in at least three of the watersheds in association with intense defoliation by the gypsy moth larva during the late 1980s to early 1990s, to peak annual average NO_3^- concentrations of about 30 to 55 µeq/L. Most of the increased NO_3^- leaching occurred during storm flow conditions.

A number of other studies have been conducted that examined the effects of gypsy moth, or other forest insect pests, on watershed biogeochemistry. Defoliation of poplars (*Populus* sp.) by gypsy moth larvae in southwestern Michigan did not result in appreciable NO_3^- leaching (Russell et al., 2004).

Other pest species can have similar effects. For example, spruce-fir forests throughout the southern Appalachian Mountains have been subjected to significant disturbance, especially from the balsam wooly adelgid, a European pest which has infested Fraser fir since about the 1960s. Severe fir mortality has occurred in many areas. This disturbance factor has the potential to interact with acidic deposition and other ecosystem stresses, and contribute to multiple-stress tree mortality and to changes in biogeochemical cycling.

Defoliation by the elm spanworm (*Ennomos subsignarius* Hübner) larvae in old-growth hemlock-hardwood forests on the Allegheny High Plateau of northwestern Pennsylvania increased streamwater NO_3^- concentrations from pre-defoliation levels of about 29 µeq/L to peak values the summer after defoliation of about 100 µeq/L (Lewis and Likens, 2007).

B.5.3. Wind or Ice Storm Damage

Forest blowdown might affect surface water acid-base chemistry by changing the pathway followed by drainage water through watershed soils (Dobson et al., 1990). Pipes formed in the soil by decaying tree roots can alter hydrologic flow so that less water enters the soil matrix, where neutralization processes buffer the acidity of rainwater and snowmelt. Pipes tend to occur most commonly in near-surface soil horizons where most tree rooting occurs. Contact between drainage water and mineral soil is reduced when runoff is routed through them. If enhanced pipeflow, resulting from sudden extensive tree mortality, affects a large portion of a watershed, runoff water may have less opportunity for acid neutralization than would be the case in the absence of such pipeflow.

Severe canopy damage occurred in 1998 in response to an ice storm at HBEF and surrounding areas in the White Mountains. Houlton et al. (2003) reported effects of this disturbance on N cycling and leaching losses. Subsequent to the ice storm, drainage water NO_3^- concentrations increased sevenfold to tenfold. Peak streamwater NO_3^- concentrations during spring months reached or exceeded 50 µeq/L at many sites. There were no significant differences, however, in N mineralization, nitrification, or denitrification rates between damaged and undamaged areas. Houlton et al. (2003) interpreted these results as an indication that increased NO_3^- leaching was probably due to decreased root uptake rather than accelerated N cycling by soil microbes. The amount of NO_3^- leaching loss was estimated to be more than half of the entire year's worth of atmospheric N deposition.

B.5.3.1. Fire

Fire can increase concentrations of NO_3^- and SO_4^{2-} in soils and drainage water (cf. Chorover et al., 1994; Riggan et al., 1994). Fenn and Poth (1998) hypothesized that successful fire suppression efforts may have contributed to the development of N-saturation in fire-adapted ecosystems in southern California by allowing N to accumulate in soil and in the forest floor, and by maintaining dense mature stands with reduced N demand.

The effects of fire on NO_3^- leaching in chaparral stands in the San Gabriel Mountains, CA that received high atmospheric N deposition were investigated by Riggan et al. (1994). Study watersheds were burned with fires of different intensity and, after rainfall, NO_3^- and NH_4^+ were measured in watershed streams. Nitrogen release was up to 40 times greater in burned watersheds than in unburned watersheds, and the amount and concentration of N release were found to be related to fire intensity.

Chorover et al. (1994) evaluated the effects of fire on soil and stream water chemistry in Sequoia National Park, CA. Burning increased concentrations of NO_3^- and SO_4^{2-} in soil water and stream water. Sulfate concentrations increased 100 fold. Nitrate concentrations also increased and remained higher in soils and stream water for about 3 years. These results suggest that successful fire suppression may have contributed to the development of N saturation in fire-adapted ecosystems in southern California by allowing N to accumulate in the soil and forest floor, and by maintaining dense mature stands with reduced N demand (Fenn and Poth, 1998).

B.5.3.2. Multiple Stress Response

Acidification-related effects of S and N deposition do not occur in isolation; they interact with disturbances of various types, both natural and human-caused. They also influence a range of biogeochemical processes that may be difficult to predict. Overall, the interactions between disturbance and ecosystem acidification as a consequence of acidic deposition are not well understood.

It is believed that high rates of N deposition cause increased susceptibility of forests to other stressors, including reducing the resistance of some tree species to frost, insect damage, or drought. The effects of acidic deposition can interact with a variety of stressors, both natural and human-caused. The end result might include adverse effects that would not occur solely in response to acidic deposition, or in response to any one of the other stressors.

Watershed disturbance might also effect Hg cycling and its relationship to S deposition. For example, Garcia and Carignan (2000), in a study of 20 watersheds in Quebec, Canada, found that the average Hg concentration in 560–mm northern pike (*Esox lucius*) was significantly higher in lakes whose watersheds had recently (1995) been logged (3.4 µg/g), as compared with reference lake watersheds

(1.9 µg/g), that had remained undisturbed for at least 40 years. Fish tissue Hg concentration also increased with increasing DOC and lakewater SO_4^{2-} concentration, and with decreasing pH.

B.6. Ecological indicators of acidification

B.6.1. Biological Indicators

Surface water acidification from acidic deposition causes effects on organisms at all trophic levels. Early studies focused on the loss of fish populations, especially salmonids. Later studies also reported that many species of phytoplankton, zooplankton, insect larvae, crayfish, snails, and freshwater mussels are sensitive and are often reduced or absent from acidified lakes and streams (Havas, 1986; Baker et al., 1990a). Similarly, many species of microrhizal fungi and lichens have been reported to be particularly sensitive to acidic deposition in terrestrial ecosystems.

Effects of acidification on aquatic biota have been demonstrated in laboratory and field bioassays (e.g., Baker et al., 1996), whole-ecosystem acidification experiments (e.g., Schindler et al., 1985), and field surveys (e.g., Baker and Schofield, 1982; Gallagher and Baker, 1990). Many of the species that commonly occur in acid-sensitive surface waters susceptible to acidic deposition cannot reproduce or survive if the water is acidic. Some sensitive species of fish, invertebrates, and algae cannot survive at moderate levels of acidity. For example, some zooplankton predators, sensitive mayfly species, and sensitive fish species are affected at pH values below the range of 5.6 to 6.0 (Baker and Christensen, 1991). Such pH values generally equate to ANC below about 25 to 50 µeq/L.

There are few published examples of long-term monitoring data for biological assemblages in acid-sensitive surface waters, and none in the U.S. Therefore, conclusions about the effect of acidic deposition on the distribution of sensitive species are based on other kinds of data (Stoddard et al., 2003). For example, the number of fish species increases with increasing pH and ANC when evaluated for multiple water bodies across the landscape. This result has been shown for streams in Virginia, lakes in the Adirondacks, and both high-elevation and seepage lakes in Maine (Figure B-17).

Given the available data, it is clear that acidification from acidic deposition limits the distribution of acid-sensitive fish, benthic invertebrate, phytoplankton, and zooplankton species, but a lack of adequate data makes it difficult to quantify the magnitude of change in biota from historical condition or in response to recent (past two to three decades) decreases in acidic deposition in individual lakes or streams. Studies in Canada and Europe have illustrated the feasibility and complexity of biological recovery in response to decreased acidity.

Threshold pH levels for adverse biological effects have been summarized for a variety of aquatic organisms (Haines and Baker, 1986; Baker et al., 1990a). The effects of low pH are specific to the organism, and perhaps region, under consideration and depend also upon the concentrations of other chemical constituents in the water, notably Al_i and Ca^{2+}. 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 5.2 to 5.5 (Haines and Baker, 1986). A number of synoptic surveys indicate loss of species diversity and absence of many other fish species in the pH range of 5.0 to 5.5 (Haines and Baker, 1986). Levels of pH less than 6.0 to 6.5 have been associated with adverse effects on populations of dace, minnows, and shiners (family Cyprinidae), and bioassays suggest that given sufficient Al concentrations, pH less than 6.5 can lead to increased egg and larval mortality in blueback herring (*Alosa aestivalis*) and striped bass (*Morone saxatilis*) (Hall, 1987; Klauda et al., 1987).

Mycorrhizal fungi have been suggested as possible biological indicators of atmospheric deposition effects by Løkke et al. (1996) because they are intimately associated with tree roots, depend on plant assimilates, and play essential roles in plant nutrient uptake. Thus, mycorrhizal fungi can influence the ability of their host plants to tolerate different anthropogenically generated stresses. Mycorrhizae and associated fine roots have short lifespans and their turnover appears to be controlled by environmental factors. Changes in mycorrhizal species composition, or the loss of dominant mycorrhizal species in areas where diversity is already low, may cause increased susceptibility of plants to stress (Løkke et al., 1996).

Mycorrhizal fungi are dependent for their nutrition on the supply of assimilates from the host plant. Stresses that shift the allocation of C reserves to the production of new leaves at the expense of supporting tissues will be reflected rapidly in decreased fine root and mycorrhizal biomass (Winner and Atkinson, 1986). Decreased C allocation to roots could also affect soil carbon and rhizosphere organisms. For example, earthworms are believed to decrease in abundance, and in species number, in acidified soils (Løkke et al., 1996). Soil dwelling animals, including earthworms, are important for decomposition, soil aeration, and nutrient redistribution in the soil. They contribute to decomposition and nutrient availability, mainly by increasing the accessibility of dead plant material to microorganisms.

B.6.1.1. Phytoplankton

Phytoplankton are the small microscopic plants or plant-like organisms that live suspended in the water column of lakes and large rivers. Acidification results in decreased species richness and diversity of phytoplankton communities. There is also a shift in the composition of dominant taxa, but species composition shifts cannot be accurately predicted (though it is clear that community restructuring occurs with acidification). This effect is most prevalent in the pH 5 to 6 range (Baker et al., 1990a). Acidification has also been found to cause decreases in food web complexity (indicated by the number of trophic links or species) in the Adirondack Mountains (Havens and Carlson, 1998). Both Al toxicity and P limitation

may also be responsible for shifts in phytoplankton community composition. Neither grazing pressure nor changes in water clarity associated with acidification seem to have a major effect on phytoplankton community structure. There is no consistent pattern of acidification effects on phytoplankton biomass. Various lakes have shown increases, decreases, or no change in phytoplankton biomass with acidification (Baker et al., 1990a). Leavitt et al. (1999) suggested that the complex interactions between pH, DOC, and light explain the high variability in the algal biomass-acidification relationship. In most lakes, acidification has a negligible effect on primary productivity.

Diatoms, which comprise an important component of the phytoplankton, are excellent indicators of environmental change in aquatic ecosystems, including acidity, nutrient status, salinity, and climatic features (Sullivan and Charles, 1994; Stoermer and Smol, 1999). There are thousands of different species, many of which have rather narrow ecological tolerance ranges. Diatoms have been widely used as indicators of past lake acidification. Inference based on diatom fossil remains preserved in lake sediments is an excellent approach for quantifying historical chemical change (Charles and Norton, 1986).

Paleolimnological reconstructions of past lakewater chemistry are based on transfer functions derived from relationships between current lakewater chemistry and diatom (or, in some cases, chrysophyte) algal remains in surface sediments. Predictive relationships are developed using regional lake datasets, and are then applied to diatom assemblage data collected from horizontal slices of lake sediment cores to infer past lakewater conditions (Charles et al., 1989; Husar and Sullivan, 1991).

Periphyton are the small microscopic plants (or plant-like organisms) that live on submerged substrates in aquatic systems (e.g., stream or lake bottoms). As seen in phytoplankton communities, acidification results in decreased species richness, community alteration, and emergence of new dominant species in periphyton communities. Many diatom and blue-green bacterial periphyton species cannot tolerate acidic conditions. On the other hand, green algae, particularly the filamentous Zygnemataceae, increase in relative abundance at lower pH (Baker et al., 1990a). Unlike for phytoplankton, there is evidence that the biomass of attached periphyton increases at lower pH.

Studies of phytoplankton recovery from acidification indicate that there is an increase in phytoplankton species richness and diversity as pH increases. In the Experimental Lakes area of Ontario, previously acidified lakes have been experimentally de-acidified. In Lake 223, 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. Cyanobacteria were among the first to recover at pH 5.5 to 5.8 (Findlay et al., 1999). In the Killarney Park area of Ontario, Findlay (2003) reported that lakes that were previously low in pH (5.0 to 5.5) and are now above pH 6 have shifted towards phytoplankton assemblages typical of circumneutral environments.

B.6.1.2. Zooplankton

Field survey and experimental lake studies both indicate that acidification reduces zooplankton species richness. Effects of acidification on community biomass and abundance, however, were not definitive. Some studies indicated a lower biomass under low pH conditions, whereas other studies showed no consistent pattern in the biomass-pH relationship. Limited data indicated that acidification does not alter zooplankton community grazing rates. Zooplankton species that have been shown to be sensitive to low pH include *Diaptomus sicilis, Epischura lacustris, Tropocyclops parsinus mexicanus, Daphnia galeata mendotae, Daphnia rosea*, *Diaphanosoma birgei*, *Leptodora kindtii*, *Asplanchna priodonta*, and *Conochilus unicornis*. In North America, species reported to have increased dominance in acidic lakes (acid-tolerants) include *Keratella taurocephala, Bosmina longirostris,* and *Diaptomus minutus*. Possible mechanisms for zooplankton sensitivity to low pH include ion regulation failure, reduced oxygen uptake, inability to reproduce, and Al toxicity. Indirect effects of acidification on zooplankton communities are also possible due to pH-induced shifts in higher trophic level zooplankton predators. This mechanism is probably of less importance than the direct effects of low pH. It is also probable that under acidic conditions, zooplankton communities are less able to ameliorate nutrient additions or control algal densities (Baker et al., 1990a).

Reported pH thresholds for zooplankton community alteration range from 5 to 6. Holt and Yan (2003) reported a threshold of community change at pH 6 for lakes in southern Ontario. Locke and Sprules (1994) reported that acidification below pH 5 in the 1970s overcame the resistance stability of the zooplankton community in Ontario Precambrian Shield lakes. The subset of study lakes that showed pH recovery from acidification 20 years later in 1990 also showed recovery in the stability of the zooplankton community. Holt and Yan (2003) also noted recovery in zooplankton community composition (based on similarity to neutral lakes) in the subset of Killarney Park (Ontario) lakes in which the pH increased to over 6 during the 1971 to 2000 study period. They did not, however, note any time trend of increasing species richness between recovering lakes and non-recovering lakes.

Recovery in experimentally acidified Lake 223 back to pH 6.1 was studied by Malley and Chang (1995). They reported that the zooplankton community was still in a state of flux. Species diversity that had been reduced during the acidification phase had partially returned to preacidification 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 noted in the neutral reference basin.

In situ enclosure studies were conducted for 35 days at Emerald Lake in the Sierra Nevada by Barmuta et al. (1990). The lake sediments were included within the experimental enclosures. This allowed

the investigators to document the response of zoobenthos as well as zooplankton. Treatments included a control (pH 6.3) and acid addition to reach pH levels of 5.8, 5.4, 5.3, 5.0, and 4.7. Results indicated that zooplankton were sensitive to acidification but zoobenthos were unaffected by the experimental treatment. *Daphnia rosea* and *Diaptomus signicauda* decreased in abundance below the range of pH 5.5 to 5.8 and were eliminated below about pH 5.0. *Bosnia longirostris* and *Keratella taurocephala* generally became more abundant with decreasing pH. Barmuta et al. (1990) concluded that even slight acidification of high-elevation lakes in the Sierra Nevada might alter the structure of the zooplankton community.

Sullivan et al. (2006a) found that zooplankton taxonomic richness varied with ANC in Adirondack lakes (Table B-22). Taxonomic richness expressed as number of species of crustaceans, rotifers, and total zooplankton, increased with increasing ANC. In general, lakewater ANC explained nearly half of the variation in total zooplankton and crustacean taxonomic richness, but less for rotifer richness. These results (Table B-22) provided the basis for estimating changes in zooplankton richness in response to past or future changes in lakewater ANC. Several zooplankton species found in lakes in the Sierra Nevada are also known to be sensitive to acidity status (Gerritsen et al., 1998).

B.6.1.3. Benthic Invertebrates

Within stream systems, macroinvertebrate communities are among the most sensitive life forms to disturbances, including those associated with atmospheric deposition (Cairns and Pratt, 1993). In addition, they are relatively easy to sample in the field (Plafkin et al., 1989; Resh et al., 1995; Karr and Chu, 1999).

Acidification results in the loss of acid-sensitive benthic invertebrates and decreases in pH of one unit or more typically result in species loss. Invertebrate taxa that are most sensitive to acidification are mayflies, amphipods, snails, and clams. At low levels of acidification (pH 5.5 to 6.0), acid-sensitive species are replaced by more acid-tolerant species, yielding little or no change in total community species richness, diversity, density, or biomass. If pH decreases are larger, more species will be lost without replacement, resulting in decreased richness and diversity. Many sites also note decreases in invertebrate biomass and productivity (more so in streams than lakes). High levels of acidification ($pH < 5$) were found to virtually eliminate all mayflies, crustaceans and mollusks from French streams (Guerold et al., 2000). Examples of sensitive benthic invertebrate species include *Baetis rhodani, Gammarus lacustris, Hyalella azteca, Asellus aquaticus, Orconectes rusticus*, and *O. propinquous*. Stoneflies are generally more acid-tolerant than mayflies and caddisflies.

Possible mechanisms for acidification effects on invertebrates include direct toxicity of H^+ and Al, disruption of ion regulation, and reproductive failure. Indirect effects due to acidification-induced changes to invertebrate predator populations are also possible (Baker et al., 1990a). Acidic episodes in streams can

cause increased downstream drift of acid-sensitive species, particularly *Baetis* (Kratz et al., 1994; Smock and Gazzera, 1996).

It has been well documented that low streamwater pH can be associated with reductions in invertebrate species richness or diversity (Townsend et al., 1983; Raddum and Fjellheim, 1984; Burton et al., 1985; Kimmel et al., 1985; Hall and Ide, 1987; Peterson and Van Eechhaute, 1992; Rosemond et al., 1992; Sullivan et al., 2003), and sometimes density (Hall et al., 1980; Townsend et al., 1983; Burton et al., 1985; Kimmel et al., 1985). Effects on invertebrate density are not universal; a number of studies have found no density effects (Harriman and Morrison, 1982; Simpson et al., 1985; Ormerod and Tyler, 1987; Winterbourn and Collier, 1987). However, a decrease in species richness with decreasing pH has been found in almost all such studies (Rosemond et al., 1992), and this finding has been especially pronounced in streams for order Ephemeroptera (mayflies).

The Ephemeroptera-Plecoptera-Tricoptera (EPT) Index is a common measure of stream macroinvertebrate community integrity. The EPT metric is the total number of families present in those three insect orders (mayflies, stoneflies, and caddisflies, respectively). The total number of families is generally lower at acidified sites because species within those families tend to exhibit varying acid sensitivity (cf. SAMAB, 1996). Mayflies tend to be most sensitive of the three, and stoneflies tend to be least sensitive (Peterson and Van Eechhaute, 1992).

There has been some recovery in 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 acidic deposition reductions and sufficient time for reversal of soil acidification may be required before biotic recovery can occur. Tipping et al. (2002) noted increases of invertebrate richness and diversity in the English Lake District in their study streams that had pH increases of 0.3 to 0.5 units since about 1970.

Responses of aquatic macroinvertebrates to acidification were evaluated by Kratz et al. (1994) in 12 streamside channels in Sequoia National Park, CA. Replicated treatments included a control (pH 6.5 to 6.7) and experimental exposure at pH levels of 5.1 to 5.2 and 4.4 to 4.6. Invertebrate drift was monitored continuously and benthic densities were determined before and after acidification. Single 8–hr acid pulses increased the drift of sensitive taxa, and benthic densities were reduced. *Baetis* showed reduced density post-treatment to less than 25% of control densities in both pH reduction treatments (5.2, 4.6) and two different experimental exposures. Densities of *Paraleptophlebia* appeared to be reduced by the acidification, but most treatment effects were not statistically significant. Kratz et al. (1994) suggested that the effects of acid inputs on benthic species densities depended on microhabitat preferences. *Baetis* nymphs are epibenthic and active. They are often found on the upper surfaces of rocks where they are

directly exposed to acidified water. This may have been responsible for their greater response to acidification.

B.6.1.4. Fish

By 1990 it was well established that pH in the range of 4.0–6.5 could cause significant adverse biological effects on fish. Low pH was one of the most important factors resulting in adverse effects. The toxicity of pH was, in most cases, the result of impaired body salt regulation. Decreased pH in the water inhibited the active uptake of Na^+ and Cl^- and stimulated the passive loss of these ions (Baker et al., 1990a).

The response to acidification was not uniform, however. Some species and life stages experienced significant mortality in bioassays at relatively high pH (e.g., pH 6.0–6.5 for eggs and fry of striped bass and fathead minnow) (Buckler et al., 1987; McCormick et al., 1989), whereas others were able to persist at quite low pH without adverse effect (Mudminnow; [Umbra spp.] at pH 4.0 and Umbra pygmaea at pH 3.5) (Dederen, 1987). Many minnows and dace (Cyprinidae) are sensitive to acidity (threshold effects at pH < 5.5 to 6.0), but some common game species such as brook trout, largemouth bass, and small mouth bass are relatively insensitive (threshold effects at pH < 5.0 to 5.5). A summary of studies that demonstrated the difference among species is shown in Table B-23. Table B-24 summarizes the results from a variety of studies that determined the threshold values of pH for various taxa and kinds of effects.

The effect of acidification on aquatic organisms, especially fish, is due in large part to the toxic effect of Al_i that is released from watershed soils. A number of studies reviewed by Baker et al. (1990a) reported threshold values of Al_i for various species and effects. Those results are presented in Table B-25. The effects of low pH and high Al_i can be ameliorated to an extent in the presence of increased Ca^{2+} concentration. A summary of the effect of increasing Ca^{2+} concentration is presented in Table B-26.

Fish populations in acidified streams and lakes of Europe and North America have declined, and some have become extinct as a result of atmospheric deposition of acids and the resulting changes in water quality (Baker et al., 1990a). A variety of factors, including Al_i, DOC, and Ca^{2+}, along with the timing and magnitude of episodic fluctuations in toxic acid and Al_i concentrations, are related to the degree to which surface water acidification influences fish survival in natural systems (Baker et al., 1990a; Gagen et al., 1993; Siminon et al., 1993; Van Sickle et al., 1996; Baldigo and Murdoch, 1997). Aluminum fractionation and Al_i concentration are directly dependent upon pH levels (Driscoll et al., 1985).

Fish communities of acid-sensitive streams and lakes may contain a variety of species, but are often dominated by trout. Across the eastern U.S., brook trout is often selected as an indicator of acidification effects on aquatic biota because it is native to many eastern streams and lakes and because residents place great recreational and aesthetic value on this species. It must be emphasized, however, that

brook trout is a relatively acid-tolerant species. Many other fish species, including rainbow and brown trout, as well as a variety of other fish species, are more acid-sensitive than brook trout. In many Appalachian Mountain streams that have been acidified by acidic deposition, brook trout is the last species to disappear; it is generally lost at pH near 5.0 (MacAvoy and Bulger, 1995), which usually corresponds in these streams with ANC near 0 (Sullivan et al., 2003).

Although there are known differences in acid sensitivity among fish species, experimentally determined acid sensitivities are available for only a minority of freshwater fish species. Baker and Christensen (1991) reported critical pH values for 25 species of fish. They defined critical pH as the threshold for significant adverse effects on fish populations. The reported range of pH values represents the authors' estimate of the uncertainty of this threshold. The range of response within species depends on differences in sensitivity among life stages, and on different exposure concentrations of Ca^{2+} and Al. To cite a few examples, blacknose dace is regarded as very sensitive to acid stress, because population loss due to acidification has been documented in this species at pH values as high as 6.1; in field bioassays, embryo mortality has been attributed to acid stress at pH values as high as 5.9. Embryo mortality has occurred in common shiner at pH values as high as 6.0. Although the critical pH range for rainbow trout is designated as 4.9–5.6, adult and juvenile mortality have occurred at pH values as high as 5.9. Brown trout population loss has occurred over the pH range of 4.8–6.0, and brook trout fry mortality has occurred over the range of 4.8–5.9 (Baker and Christensen, 1991). Relative sensitivities can be suggested by regional surveys as well, although interpretation of such data is complicated by factors that correlate with elevation. Such factors, including habitat complexity and refugia from high-flow conditions, often vary with elevation in parallel with acid sensitivity. It is noteworthy, however that about half of the 53 fish species found in Adirondack Mountain waters in New York never occur at pH values below 6.0 (Kretser et al., 1989; Driscoll et al., 2001b); for those species whose acid tolerances are unknown, it is probable that acid sensitivity is responsible for at least some of these absences. It is the difference in acid tolerance among species that produces a gradual decline in species richness as acidification progresses, with the most sensitive species lost first.

Effects on biota can be assessed as effects on a particular sensitive species or species perceived to be important, or as effects on the richness or diversity of fish or other potentially sensitive life form. For example, Bulger et al. (2000) developed ANC thresholds for brook trout in Virginia, which are presented in (Table B-27). These values were based on annual average stream water chemistry, and therefore represent chronic exposure conditions. The likelihood of additional episodic stress is incorporated into the response categories in the manner in which they are interpreted. For example, the episodically acidic response category, which has chronic ANC in the range of 0 to 20 µeq/L, represents streams that are expected to acidify to ANC near or below 0 during rainfall or snowmelt episodes. In such streams, sublethal and/or lethal effects on brook trout are possible (Bulger et al., 2000; Sullivan et al., 2003).

Fish species richness, population density, condition factor, age distribution, size, and bioassay survival have all been shown to be reduced in low-ANC streams as compared to intermediate-ANC and high-ANC streams (Bulger et al., 1995; Dennis et al., 1995; Dennis and Bulger, 1995; MacAvoy and Bulger, 1995). Fish species richness is a good indicator of acidification response. Lakes or streams having pH below about 5.0 or ANC below about 0 generally do not support fish. Depending on the region, waters having pH above about 6.5 and ANC above about 50 µeq/L support large, but variable, numbers of species. 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 et al., 1999; 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 one of the most useful indicators of biological effects of surface water acidification.

Acidification and the associated elevated concentrations of Al_i in surface waters have adversely affected fish populations and communities in parts of the Adirondack Mountains of northern New York (Baker and Schofield, 1982; Johnson et al., 1987; (Schofield and Driscoll, 1987)Kretser et al., 1989; Siminon et al., 1993) and in acid-sensitive streams of the Catskill Mountains of southeastern New York (Stoddard and Murdoch, 1991) and the Appalachian Mountains from Pennsylvania to Tennessee and South Carolina (SAMAB, 1996; Bulger et al., 1999, 2000).

Adverse effects of low pH and high Al_i concentration on fish include increased mortality, decreased growth, decreased reproductive potential, and ionoregulatory impairment. A partial list of studies demonstrating such effects is provided in Table B-28 from Baker et al. (1990a). It has been shown, however, that there is marked variability among species and among life stages within species in the specific levels of pH and Al_i that produce measurable responses.

Surface-water acidification can affect fish populations by a number of mechanisms ranging from increased morality and emigration to decreased food supplies (Baker et al., 1990a). The primary reason for population decline and extinction, however, is usually the failure of a species to successfully recruit young-of-the-year fish (Mills et al., 1987; Brezonik et al., 1993). The response of aquatic communities to acidification, therefore, should appear first as changes in age distribution and decreased health of individual fish (growth and condition), then as decreased biomass and density in populations of acid-intolerant fish species, and finally as elimination of sensitive species (Baker et al., 1990a).

The primary mechanism for the toxic effects of low pH and elevated 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 disruption of Ca^{2+} metabolism (Peterson and Martin-Robichaud,

1986; Gunn and Noakes, 1987; Reader et al., 1988), and decreased hatching success (Runn et al., 1977; Peterson et al., 1980; Haya and Waiwood, 1981; Waiwood and Haya, 1983).

Prominent physiological disturbance for 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^{2+} 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).

The energy costs to fish for active iono-osmoregulation can be substantial (Farmer and Beamish, 1969; Bulger, 1986). The concentrations of serum electrolytes (such as Na^+ and Cl^-) are many times higher (often 100–fold higher) in fish blood than in the fresh waters in which they live. The active uptake of these ions occurs at the gills. Because of the steep gradient in Na^+ and Cl^- concentrations between the blood and fresh water, there is constant diffusional loss of these ions, which must be replaced by energy-requiring active transport. Low pH increases the rate of passive loss of blood electrolytes (especially Na^+ and Cl^-); and Al elevates losses of Na^+ and Cl^- above the levels due to acid stress alone (Wood, 1989). For example, dace in an acidified stream maintain whole-body Na^+ at levels similar to dace in a high-ANC stream (Dennis and Bulger, 1995), despite probable higher gill losses of electrolytes due to acid/Al stress. Therefore, the homeostatic mechanisms at the gill responsible for maintaining blood electrolyte levels must work harder and use more energy to maintain these levels for dace in the acidified stream.

Whole lake experiments and artificial stream channel experiments have shown that acidification can lead to loss of fish species. A summary of the work on Lake 223 in the Experimental Lakes Area in Canada is provided in Table B-29. Work at Little Rock Lake in Wisconsin suggested that rock bass suffered recruitment failure at pH 5.6 or below. Artificial channel studies showed poor survival and reproductive success for fathead minnow at pH 5.9 to 6.0.

ANC criteria have been used for evaluation of potential acidification effects on fish communities. The utility of these criteria lies in the association between ANC and the surface water constituents that directly contribute to or ameliorate acidity-related stress, in particular pH, Ca^{2+}, and Al. Bulger et al. (2000) developed ANC thresholds for brook trout response to acidification in forested headwater catchments in western Virginia (See Table B-27). Note that because brook trout are comparatively acid tolerant, adverse effects on many other fish species should be expected at relatively higher ANC values.

Streams with chronic ANC greater than about 50 µeq/L are generally considered suitable for brook trout in southeastern U.S. streams because they have a large enough buffering capacity that persistent acidification poses no threat to this species, and there is little likelihood of storm-induced acidic episodes lethal to brook trout. In such streams, reproducing brook trout populations are expected if the habitat is otherwise suitable (Bulger et al., 2000), although some streams may periodically experience episodic chemistry that affects species more sensitive than brook trout. Streams having annual average ANC from

20 to 50 µeq/L may or may not experience episodic acidification during storms that can be lethal to juvenile brook trout, as well as other fish. Streams that are designated as episodically acidic (chronic ANC from 0 to 20 µeq/L) are considered marginal for brook trout because acidic episodes are likely (Hyer et al., 1995), although the frequency and magnitude of episodes vary. Streams that are chronically acidic (chronic ANC less than 0 µeq/L) are not expected to support healthy brook trout populations (Bulger et al., 2000).

Field surveys provided a regional context for fish response to acidification. Although there were some variations, the results of field surveys generally confirmed the results of bioassays, field experiments, and other intensive field studies. The results of many field surveys were summarized in Baker et al. (1990a) and are compiled in (Table B-30).

It is important to note, however, that 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), and some of the currently fishless acidic lakes probably never supported fish.

Many of the data for the assessment of fish status in the Adirondack region of New York come from the reports by Kretser et al. (1989) and Baker et al. (1990a). The status of fish and of the presence of individual species were related to a variety of lake characteristics. Of the lakes without fish, 42% had high organic acid content that may have caused the observed low pH, 13% were bog lakes of high acidity and naturally poor fish habitat, 9% had pH > 5.5 suggesting other factors were likely responsible for the lack of fish, and 3% were small high-elevation lakes that were unlikely to have fish regardless of acid-base chemistry. However, 34% of the lakes surveyed (112 lakes) that had no fish at the time of survey had low pH that was most likely the result of acid deposition and no other obvious explanation for the lack of fish.

Multivariate regression of the presence/absence of brook trout in Adirondack waters produced a ranking of factors that appeared to influence the presence of brook trout when biological factors were excluded from the analysis (stocking, presence of associated species, and presence of competitors). Among contributing factors, including SiO_2, ANC, DOC, substrate, 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 hypothesis that 1990 levels of pH and related variables restricted the distribution of some fish in Adirondack waters.

Fish toxicity models have been developed as mathematical regression functions fit to observations of fish mortality when exposed to constant levels of pH, Al_i, and Ca^{2+} in laboratory toxicity tests. These models had the advantage that they dealt directly with the interaction effects of pH, Al, and Ca^{2+}, but they did not account for the effects of variations in other aspects of surface water quality, and they could not be directly interpreted in terms of population-level response.

The many bioassays conducted of pH effects were screened by Baker et al. (1990a) to provide data most suitable for model development. Bioassays selected for inclusion were those that measured the mortality of early life stages, those that incorporated different combinations of pH, Al, and Ca^{2+}, and those that used fish of varying sensitivity (Bergman et al., 1988).

Acidity and Al toxicity are not the only stress factors that influence the distribution of fish in acid-sensitive streams. Other habitat characteristics, including water temperature and stream channel morphology, can be important (Sullivan et al., 2003). In addition, it is probable that some trout populations have been affected by competition with other introduced species (cf. Larson and Moore, 1985).

B.6.1.5. Amphibians

Some species of amphibians are considered to be highly sensitive to changes in environmental conditions and some species have probably been adversely effected by acidic deposition in some areas. Furthermore, several species of amphibian have exhibited marked declines in abundance throughout the western U.S. in recent decades and there has been much speculation concerning the cause(s) of these declines in abundance.

Populations of many species of amphibians have declined or become eradicated throughout the world in recent decades (Barinaga, 1990; Wake, 1991). The causes have not been evident and some of the declines have occurred in remote pristine areas. For example, in the Sierra Nevada, at least two of five species of aquatic-breeding amphibians, *Rana muscosa* (mountain yellow-legged frog) and *Bufo canorus* (Yosemite toad) have been declining (Phillips, 1990). A number of hypotheses have been proposed for amphibian decline, including acidic deposition. In the western U.S., however, acidic deposition has been discounted as the primary cause of the decline of *R. muscosa* and *B. canorus* in the Sierra Nevada and of *R. pipiens* and *B. boreas* in the Rocky Mountains (Corn et al., 1989; Bradford et al., 1992). Grant et al. (2005) reported little relationship between streamwater ANC and the adjacent salamander community in Shenandoah National Park.

In some cases, population fragmentation as a consequence of fish predation may be a more likely cause (Bradford et al., 1993). It is generally recognized that *R. muscosa* was eliminated by introduced fish early in the 20th century in many lakes and streams in Sequoia and Kings Canyon National Parks. The amphibians have been eliminated from nearly all waters inhabited by fish, presumably by predation on tadpoles. Prior to 1870, virtually all of the high-elevation (>2500 m) lakes in the Sierra Nevada were barren of fish, but have since been stocked with fish. Fish introductions may have contributed to recent amphibian declines because amphibian populations are now more isolated from each other than formerly. The role of atmospheric deposition as an additional stressor is not clear.

The acidification sensitivity of temporary ponds, where many amphibians live or reproduce, have not been well studied. These ponds tend to fill directly from rain or snowmelt and thus can be more acidic than surrounding lakes and streams. There is a correlation between pond acidity and amphibian abundance.

There are both acid-sensitive and acid-tolerant amphibians. Examples of acid-sensitive amphibians include the spotted salamander (Ambystoma maculatum) and Jefferson salamander (*Ambystoma jeffersonianum*). Embryos of acid-sensitive species are killed by water with pH less than about 4.5. Acid-tolerant embryos may survive at a pH of 3.7. Toxicity is not solely a matter of pH, but is also influenced by Ca^{2+}, Al_i, and DOC concentrations. It is also dependent on the life stages present and water temperature (Baker et al., 1990a). Large-scale amphibian extinctions in any geographic region due to acidic deposition have not been detected.

Although acidic deposition may play a role in some areas, there is no evidence to suggest that it is a primary factor. Other issues, including fish introductions, are probably more important as stressors on amphibian populations across broad regional to national scales.

B.6.1.6. Fish-Eating Birds

Relative to other trophic groups, there are few studies assessing acidification effects on fish-eating birds. Limited data suggest that fish-eating birds are adversely affected by acidification. Acidification effects on birds may be indirect, related to changes in the quantity and quality of food. Other potential causal pathways include delayed egg laying, lighter/thinner egg shells, and reduced chick growth in acidic waters (Tyler and Ormerod, 1992). There is also concern about increased metal and Hg concentrations in fish-eating birds associated with bioaccumulation from contaminated fish in known areas of acidification (Baker et al., 1990a).

Fish-eating birds can serve as biological indicators of lakes affected by acidic deposition (McNicol, 2002). Lack of prey resources, decreased food quality, and elevated lake water methylmercury (MeHg) concentrations that could be associated with acidification may negatively effect foraging, breeding, and/or reproduction for the common loon (*Gavia immer*), common merganser (*Mergus merganser*), belted kingfisher (*Ceryle alcyon*), osprey (*Pandion haliatus*), American black duck (*Anas rubripes*), ring-necked duck (*Aythya collaris*), eastern kingbird (*Tyrannus tyrannus*), and tree swallow (*Tachycineta bicolor*) (Table B-31) (Longcore and Gill, 1993). Breeding distribution for the common goldeneye (*Bucephala clangula*), an insectivorous bird, may be positively effected by acidic deposition (Longcore and Gill, 1993). 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).

Since the mid 1980s, a statistically significant increase in fish-eating birds has been observed in the Sudbury region of Ontario, Canada, which has corresponded with a decreasing abundance of common

goldeneye (McNicol, 2002). This interaction has been attributed to an increase in prey for pisciverous birds and a decrease in available prey for insectivorous birds as a result of stricter S emissions controls in the U.S. and Canada (McNicol, 2002). Logistic regression modeling with measured pH and species occurrence data for acid-sensitive lakes in the Algoma region of Ontario showed that the occurrence of fish, common loons, and common mergansers is 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 modeled emissions scenarios include:

- S1: sulfate emissions equal to those in the early 1980's (base case)
- S2: sulfate emissions equal to that in 1994 (full Canadian emissions reductions based on the 1991 Canada/U.S. Air Quality Agreement)
- S3: expected sulfate emissions in 2010 (full implementation of U.S. emissions reductions based on the 1991 agreement)
- S4: a hypothetical 50% reduction in expected 2010 sulfate emissions
- S5: a hypothetical 75% reduction in expected 2010 sulfate emissions

The number of lakes projected to be suitable for supporting breeding pairs and broods increased with lake pH and stricter emissions controls (Table B-32) (McNicol, 2002).

Marginal improvements to fish-eating bird habitat were predicted to occur by 2010 (S3), with more significant improvements expected under hypothetical S emissions reductions of 50% and 75% (S4 and S5) 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.

Elevated MeHg accumulation in fish-eating birds in Wisconsin and the northeastern U.S. has been linked to lake acidification (Meyer et al., 1995; Hrabik and Watras, 2002; Evers et al., 2007). This form of Hg is toxic, bioavailable, and accumulates in top predators to levels of concern for both human health and the environment (Table B-33) (Evers et al., 2007).

Acidic deposition might contribute to Hg toxicity in fish-eating birds because SO_4^{2-} addition to wetland environments could stimulate the production of MeHg, thereby increasing lake water concentrations of MeHg (Jeremiason et al., 2006). Kramar et al. (2005) determined that the extent of wetland located in close proximity (less than150 m) to loon territory was positively correlated with Hg concentrations in loon blood. Wetland MeHg production is discussed in greater detail in Section 6.3.

Accumulation of MeHg in fish-eating birds can result in damage to nervous, excretory, and reproductive systems (Wolfe et al., 1998). Table B-34 (Wolfe et al., 1998) lists several studies indicating

effects related to mercury bioaccumulation in avian eggs and tissues. Reproduction is considered one of the most sensitive endpoints to chronic low-level MeHg exposure for fish-eating birds (Wolfe et al., 1998). Reduced clutch size, increased number of eggs laid outside the nest, eggshell thinning, and increased embryo mortality have all been documented (Wolfe et al., 1998).

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Table B-1. N-saturated forests in North America, including estimated N inputs and outputs.

Location	Forest Type	Elevation (m)	N Input (kg/ha/yr)	N Output (kg/ha/yr)	Reference
Adirondack Mts., northeastern New York	Northern hardwoods or hardwood/conifer mix	396–661	9.3[a]	Stage 1 N loss[b]	Driscoll and Van Dreason (1993)
Catskill Mts., southeastern New York	Mainly hardwood; some eastern hemlock	335–675	10.2[a]	Stage 1 and 2 N loss[b]	Stoddard (Stoddard, 1994)
Turkey Lakes Watershed, Ontario, Canada	Sugar maple and yellow birch	350–400	7.0–7.7 (as throughfall)	17.9–23.6	Foster et al. (1989); Johnson and Lindberg (1992)
Whitetop Mt., southwestern, Virginia	Red spruce	1,650	32[c]	47[c]	Joslin and Wolfe (1992); Joslin et al. (1992)
Fernow, West Virginia	Mixed hardwood	735–870	15–20	6.1	Gilliam et al. (1996); Peterjohn et al. (1996)
Great Smoky Mts. National Park, Tennessee	American beech	1,600	3.1[d]	2.9	Johnson and Lindberg (1992)
Great Smoky Mts. National Park, Becking Site, North Carolina	Red spruce	1,800	10.3[d]	19.2	Johnson et al. (1991c)
Great Smoky Mts. National Park, Tower Site, North Carolina	Red spruce	1,740	26.6	20.3	Johnson et al. (1991c)
Front Range, Colorado	Alpine tundra, subalpine conifer	3,000–4,000	7.5–8.0	7.5	Williams et al. (1996)
San Dimas, San Gabriel Mts., southern California	Chaparral and grasslands	580–1,080	23.3[e]	0.04–19.4	Riggan et al. (1985)
Camp Paivika, San Bernardino Mts., southern California	Mixed conifer	1,600	30	7–26	Fenn et al. (1996)
Location	Forest Type	Elevation (m)	N Input (kg/ha/yr)	N Output (kg/ha/yr)	Reference
Klamath Mts., northern California	Western coniferous	NA	Mainly geologicg	NAg	Dahlgren (1994)
Thompson Forest, Cascade Mts., Washington	Red alder	220	4.7 plus > 100 as N_2 fixation	38.9	Johnson and Lindberg (1992)

[a] Estimated total N deposition from wet deposition data is from Driscoll et al. (1991) for the Adirondacks, and from Stoddard and Murdoch (1991) for the Catskills. Total deposition was estimated based on the wet deposition: total N deposition ratio (0.56) at Huntington Forest in the Adirondacks (1992). N deposition can be higher in some areas, especially at high-elevation sites such as Whiteface Mountain (15.9 kg/ha/yr); Johnson, 1992).

[b] Stage 1 and 2 of N loss according to the watershed conceptual model of Stoddard (Stoddard, 1994). N discharge (kg/ha/yr) data are not available, only stream water NO_3^- concentration trend data were collected.

[c] Values appear high compared to other sites, especially N leaching losses. Joslin and Wolfe (1992) concede that "there is considerable uncertainty associated with the estimates of atmospheric deposition and leaching fluxes." However, elevated NO_3^- concentrations in soil solution and lack of a growth response to N fertilization ratio (Joslin and Wolfe, 1994) support the hypothesis that the forest at Whitetop Mountain is N -saturated.

[d] Estimated total N deposition from throughfall data. Total deposition was estimated based on the throughfall/total N deposition ratio from the nearby Smokes Tower site (Johnson, 1992).

[e] Annual throughfall deposition to the chaparral ecosystem.

[f] N output is from unpublished stream water data (Fenn and Poth, 1999). The low value represents a year of average precipitation, and the high value is for 1995, when precipitation was nearly double the long-term average. N output includes N export in stream water and to groundwater.

[g] Annual input and output data are not known, although N deposition in this forest is probably typical for much of the rural western U.S. (2–3 kg N/ha/yr; Young et al., 1988). Excess N is from weathering of ammonium in mica schist bedrock. The ammonium was rapidly nitrified, leading to high NO_3^- concentrations in soil solution (Dahlgren, 1994).

Table B-2. Summary of measured ANC, pH, and Al concentrations compared with reference values in the six high-interest areas.

Area	n*	N*	Percent of Population with		
			ANC ≥ 0	pH ≥ 5.5	Ali > 100 µg/L
ADIRONDACKS					
Southwest lakes	52	450	38	51	36
Other lakes	84	707	0	3	0
NEW ENGLAND					
Seaboard Lowlands lakes	94	848	8	11	0
Highland lakes	354	3,574	2	5	2
MID-ATLANTIC HIGHLANDS					
Forested lakes	91	433	10	9	1
Other lakes	52	791	0	0	0
Forested streams	78	11,631	12	17	8
Other streams	69	10,172	0	2	0
ATLANTIC COASTAL PLAIN					
Northeast lakes	22	187	11	15	7
Pine Barrens streams	12	675	56	92	56
Other streams	31	7,452	10	24	15
FLORIDA					
Northern Highland lakes	32	522	63	53	10
Northern Highland streams	18	669	28	55	0
EASTERN UPPER MIDWEST					
Low silica lakes	155	1,254	16	19	1
High silica lakes	125	1,673	3	4	2

* n = sample size, N = estimated number of lakes or upstream reach ends in population.
Source: Baker et al. (1990b).

Table B-3. Sources of data and sample sizes for datasets analyzed by Stoddard et al. (2003), along with estimates of the condition of surface waters in each region in the 1980s.

Source of Data and Region	No. of Sites[1]	Size of Population[2]	Percent Acidic in 1980s[3]
Statistical Surveys			
New England Lakes[4]	30	4,327 lakes	5%
Adirondack Lakes[4]	43	1,290 lakes	14%
Appalachian Plateau Streams	31	72,000 stream miles	6%
Sensitive Surface Waters			
New England Lakes	24	N.A.	5%
Adirondack Lakes	48	N.A.	14%
Northern Appalachian Streams	9	N.A.	6%
Upper Midwest Lakes	38	N.A.	3%
Ridge/Blue Ridge Streams	69	N.A.	5%

[1] Number of monitoring sites with monitoring data available (1990–2000)

[2] Total number of lakes, or stream length, for which statistical survey results can be inferred. Site selection for LTM (sensitive surface waters) is not statistically based, and results cannot be expanded to population level.

[3] Estimates of extent of acidification, based on National Surface Water Survey results (Linthurst et al., 1986; Kaufmann et al., 1988).

[4] Estimates are for lakes with surface areas > 4 ha; estimates based on populations including smaller lakes are likely to be higher, due to the increased incidence of acidification in small lakes.

Statistical survey data are from the EMAP and TIME projects. Sensitive surface water data are from the LTM project, as well as other contributed studies.

Source: Stoddard et al. (2003).

Table B-4. 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.

Region	Results of Regional Survey				Results of Monitoring during 1990s			
	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%
No. Appalachians	42,426 km	5014 km	11.8%	1993–94	+0.7	3600 km	8.5%	−28%
Ridge/Blue Ridge	32,687 km	1634 km	5.0%	1987	−0.0	1634 km	5.0%	0%
Upper Midwest	8,574 lakes	251 lakes	2.9%	1984	+1.0	80 lakes	0.9%	−68%

Source: Stoddard et al. (2003)

Table B-5. Regional trend results for long-term monitoring sites for the period 1990 through 2000.

Region	SO_4^{2-} (µeq/L/yr)	NO_3^- (µeq/L/yr)	Base Cations [Ca2+ + Mg2+] (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

Note: Values are median slopes for the group of sites in each region.

Source: Stoddard et al. (2003).

Table B-6. Slopes of trends in Gran ANC in acidic, low ANC and moderate ANC lakes and streams for the period 1990–2000.

ANC Class	Number of Sites	Change in Gran ANC (µeq/L/yr)
Acidic (ANC < 0 µeq/L)	26	+1.29**
Low ANC (0 < ANC < 25 µeq/L)	51	+0.84**
Moderate ANC (25 < ANC < 200 µeq/L)	43	+0.32 ns

ns trend not significant ($p > 0.05$)

** $p < 0.01$

Note: Analysis includes all sites in New England, Adirondacks, Appalachian Plateau, and Upper Midwest; Ridge and Blue Ridge sites excluded.

Source: Stoddard et al. (2003)

Table B-7. Changes in key chemical characteristics during periods of record in aquatic systems in Maine.

	Years	Change in (all in µeq/L)					
		Sulfate	Nitrate	Base Cations	Calculated ANC[a]	ANC	DOC[b]
Acadia NP lakes (22)	17	−10	0	−17	−7	0	−2
LTM lakes @ Tunk Mtn (6) – spring	17	−9	0	−10	−1	1	1
LTM lakes @ Tunk Mtn (6) – fall	17	−7	0	−9	−2	−2	1
LTM lakes since 1990 – fall only	8	−9	0	−10	−1	−1	0
High elevation lakes (90)	12	−16	1	−23	−8	−2	4
Seepage lakes (120)	12	−9	1	−1	7	7	4
East Bear Brook at BBWM	11	−22	−16	−44	−6	−4	1
RLTM lakes (16)	7	−6	1	−17	−12	−4	2

[A] Calculated ANC = [change in base cations] minus [change in (sulfate + nitrate)]

[B] DOC (µeq/L) = DOC in mg/l * 4 (e.g., Kahl et al., 1999).

Source: Kahl et al. (1999)

Table B-8. Projected changes (µeq/L) in median values of streamwater chemistry at the regional modeling sites from 1995 to 2040 in each of the three emissions control strategies, stratified into two segments of the SAMI region (northeast and southwest) and by physiographic province.

Physiographic Province	Number of Sites	Δ Sulfate	Δ Nitrate	Δ SBC	ΔANC
A2 STRATEGY[1]					
Virginia and West Virginia					
Blue Ridge	16	1.8	0.03	−2.2	−4.0
Valley and Ridge	41	−0.45	0.02	−6.8	−6.6
Appalachian Plateau	34	−31.2	−3.5	−33.8	−4.4
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					
Blue Ridge	33	8.8	0.15	1.0	−8.0
Appalachian Plateau	6	15.3	0.15	−1.2	−15.9
Virginia and West Virginia					
Blue Ridge	16	−2.7	−0.04	−3.0	−1.0
Valley and Ridge	41	−5.6	−0.37	−8.2	−4.7
Appalachian Plateau	34	−36.3	−4.9	−38.4	−1.4
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					
Blue Ridge	33	5.6	−0.48	−0.60	−5.4
Appalachian Plateau	6	11.6	−0.23	−1.9	−13.3
B3 STRATEGY[1]					
Virginia and West Virginia					
Blue Ridge	16	−7.4	−0.09	−5.1	2.9
Valley and Ridge	41	−13.8	−0.36	−10.3	−0.83
Appalachian Plateau	34	−40.4	−5.8	−39.3	2.6
North Carolina, Tennessee, South Carolina, Georgia, and Alabama					

Physiographic Province	Number of Sites	Δ Sulfate	Δ Nitrate	Δ SBC	ΔANC
Blue Ridge	33	3.2	−1.0	−2.3	−3.2
Appalachian Plateau	6	7.2	−0.53	−3.1	−10.4

[1] Emissions control strategies were based on existing regulations (A2), moderate additional controls (B1), and more aggressive additional controls (B3)
Source: Sullivan et al. (2004)

Table B-9. Population estimates of water chemistry percentiles for selected lake populations in the western U.S.[a]

Population	n	N	pH		ANC (μeq/L)		SBC (μeq/L)		SO_4^{2-} (μeq/L)		NO_3^- (μeq/L)		DOC (mg/L)	
			P1	P5	P1	P5	P1	P5	P95	P99	P95	P99	P50	P99
Sierra Nevada	114	2,119	5.84	6.31	15	16	21	26	90	386	8	10	0.8	2.7
Cascades	146	1,473	5.95	6.25	11	18	20	31	60	97	3	6	1.3	2.6
Idaho Batholith	88	937	6.34	6.42	21	33	30	45	30	43	3	4	1.2	2.4
NW Wyoming	38	648	6.56	6.56	38	38	64	66	41	2,909	13	32	1.0	4.8
Colorado Rockies	121	1,173	6.02	6.65	25	42	58	80	915	2,212	10	13	1.3	5.7

[a]Data from Landers et al. (1987).

[b]Excluding Fern Lake (4D3−017) which is naturally acidic

Note: The 1st and 5th percentiles (P1, P5) are presented for pH, ANC (μeq/L), and SBC (μeq/L) and the 95th and 99th (P95, P99) percentiles are shown for SO_4^{2-} (μeq/L) and NO_3^- (μeq/L). The median (P50) and 90th percentiles are shown for DOC (mg/L).

Table B-10. Population estimates of the percentage of lakes in selected subregions of the West with ANC and NO_3^- within defined ranges.

	ANC (μeq/L)			NO_3- (μeq/L)	
	<0	<25	<50	>5	>10
Sierra Nevada	0	8.7	39.3	10.6	1.5
Cascades	0	10.2	22.4	1.5	0.0
Idaho Batholith	0	2.0	23.6	4.6	3.9
NY Wyominga	0	2.3	12.8	22.8	8.9
Colorado Rockies	0	0.9	5.5	9.8	1.8

a Excluding Fern Lake (4D3−017) which is a naturally acidic lake
Source: Landers et al. (1987)

Table B-11. Median streamwater ANC and watershed area of streams in Shenandoah National Park that have water chemistry and fish species richness data.

Site ID	Watershed Area (km^2)	Median ANC (µeq/L)	Number of Fish Species
Smaller Watersheds (<10 km^2)			
North Fork Dry Run	2.3	48.7	2
Deep Run	3.6	0.3	N.D.[a]
White Oak Run	4.9	16.2	3
Two Mile Run	5.4	10.0	2
Meadow Run	8.8	−3.1	1
Larger Watersheds (>10 km^2)			
Brokenback Run	10.1	74.4	3
Staunton River	10.6	76.8	5
Piney River	12.4	191.9	7
Paine Run	12.7	3.7	3
Hazel River	13.2	86.8	6
White Oak Canyon	14.0	119.3	7
N. Fork Thornton River	18.9	249.1	9
Jeremy's Run	22.0	158.5	6
Rose River	23.6	133.6	8

[a] No data were available regarding the number of fish species in Deep Run

Source: Sullivan (2003)

Table B-12. Reference levels for the Acidic Stress Index (ASI) based on logistic regression of fish presence as a function of the sensitive intermediate and tolerant ASI values for brown bullhead, brook trout, lake trout, and common shiner.

Reference Acid Stress Index		Fish Response
Lakes	Streams	
Tolerant ASI > 30	Intermediate ASI > 30	Loss of all fish species
Tolerant ASI > 10	Sensitive ASI > 30	Loss of brook trout
Intermediate ASI > 80		Loss of other sport fish, such as smallmouth bass and lake trout
Sensitive ASI > 80	Sensitive ASI > 10	Loss of acid-sensitive species, such as minnows.

Source: Baker et al. (1990a)

Table B-13. 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.
5.0 to 4.5 (cont'd)	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.

Source: Baker et al. (1990a)

Table B-14. Estimated percentage of Adirondack lakes with and Acidic Stress Index exceeding the reference levels for effects on fish populations, based on diatom-inferred historical (pre-industrial) chemistry and present-day measured and inferred acid-base chemistry.

ASI Reference Level	DDRP Target Population				ELS/NSWS Target Population Measured
	Diatom Inferred			Measured	
	Historical	Current	Net Change		
Tolerant ASI > 30	0.0	3.6	+3.6	1.8	2.2
Tolerant ASI > 10	0.0	9.1	+9.1	10.9	6.5
Intermediate ASI > 80	7.3	21.8	+14.5	21.8	15.2
Sensitive ASI > 80	28.5	41.2	+12.7	32.7	20.0

Source: Baker et al. (1990a)

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Table B-15. Estimated percentage of Adirondack lakes with acid-base chemistry unsuitable for fish population survival, based on diatom-inferred historical (pre-industrial) chemistry and present-day measured and inferred acid-base chemistry.

Fish Species Model[a]	DDRP Target Population[b]				ELS/NWS Target Population[b]	ALSC
	Diatom-Inferredc					
	Historical	Current	Net Change	Measured	Measured	Measured
Brook Trout						
Bayesian	2.7	13.0	+10.3	14.2	10.1	21.8
LAF framework	-	-	-	-	15.8	24.6
pH	2.3	11.3	+9.0	12.8	9.3	22.2
pCa/pH	16.0	13.3	−2.6	14.5	10.3	23.0
pCa/pH, Al/DO[C]	16.6	15.6	−1.0	19.2	13.9	23.5
Lake Trout						
pH	6.4	18.1	+11.2	21.4	14.4	30.9
pCa/pH	31.7	25.1	−6.6	29.0	18.9	-
Inorg. Al	23.9	38.6	+14.7	26.2	17.1	-
Common Shiner						
pH	19.2	29.6	+10.5	33.5	21.3	42.3
pCa/pH	45.8	37.7	−8.1	40.2	29.1	-

[a] All models, except the brook trout Bayesian model (Section 3.5) and LAF framework (Section 3.4), are field-based acidification response models as defined in Section 3.3.3.
[b] ELS/NSWS target population in Subregion 1A, defined in Section 3.1 (N = 1,290 lakes); a subset of these lakes was considered for the DDRP and sediment diatom analyses, for example, excluding lakes with ANC > 400 µeq/L and with site depths < 1.5 m (N = 675 lakes). See Sullivan (1990) for further details.
[c] Estimates of acid-base chemistry inferred from sediment diatom analysis; methods and water chemistry described in Sullivan (1990).
- Analysis not conducted.
Source: Baker et al. (1990a)

Table B-16. Estimated percentage of the lakes in the Northeast and Upper Midwest, ELS/NSWS target population with an Acidic Stress Index exceeding the reference levels for fish populations defined in Table C-12.

ASI Reference Level	Subregion 1A	Northeast Region	Upper Midwest Region
Tolerant ASI > 30	2.2	1.0	0.5
Tolerant ASI > 10	6.5	2.4	1.0
Intermediate ASI > 80	15.2	5.7	2.0
Sensitive ASI > 80	20.0	8.6	3.1

Source: Baker et al. (1990a)

Table B-17. Estimated percentage of lakes in the Northeast, ELS/NSWS target populations with acid-base chemistry unsuitable for fish population survival.

Fish Species/Model	Subregion 1A	Entire Northeast
Brook trout		
Bayesian	10.1	3.7
LAF Framework	15.8	8.9
pH	9.3	3.5
pCa/pH	10.3	4.4
pCa/pH, Al/DOC	13.9	7.0
Lake trout		
pH	14.4	5.8
pCa/pH	18.9	8.9
Inorganic Al	17.1	6.3
Common shiner		
pH	21.3	9.5
pCa/pH	29.1	19.7

Source: Baker et al. (1990a)

Table B-18. Distribution of acidic stress index values among the NSS-1 Target populations for the mid-Appalachian region.

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
Sensitive ASI			
≥ 10	84.6	66.7	76.1
10–30	10.1	18.9	14.0
30–50	1.4	1.9	1.9
50–80	1.8	2.6	1.6
>80	2.0	9.8	6.4
Intermediate ASI			
≥ 10	97.8	89.3	88.9
10–30	0.2	2.5	0.7
30–50	0.6	1.3	0.4
50–80	0.1	1.4	0.4
>80	1.3	5.4	1.9
Tolerant ASI			
≥ 10	99.4	97.1	98.1
10–30	0.6	1.4	0.9
30–50	0.0	0.6	0.3
50–80	0.0	0.9	0.7
>80	0.0	0.0	0.0

Source: Baker et al. (Baker, 1990)

Table B-19. Distribution of acidic stress index values among the NSS-1 target populations for the interior Southeast region.

	Number (%)		Total Length (%)
	Lower Node	Upper Node	
Sensitive ASI			
≥ 10	79.4	70.1	75.9
10–30	18.8	21.1	18.8
30–50	0.0	1.7	2.0
50–80	1.7	5.2	2.5
>80	0.0	1.7	0.7
Intermediate ASI			
≥ 10	100.0	98.3	99.3
10–30	0.0	0.0	0.0
30–50	0.0	0.0	0.0
50–80	0.0	0.0	0.0
>80	0.0	1.7	0.7
Tolerant ASI			
≥ 10	100.0	100.0	100.0
10–30	0.0	0.0	0.0
30–50	0.0	0.0	0.0
50–80	0.0	0.0	0.0
>80	0.0	0.0	0.0

Source: Baker et al. (Baker, 1990)

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Table B-20. Comparison of solution and tissue chemistries at threshold treatment levels where significant impacts on tree growth or nutrient content were first observed. In many cases, adverse impacts were observed at the lowest Al treatment level. Hence, the actual threshold Ca/Al ratio may be higher than that reported. Results are from a variety of studies reported in the literature.

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al (M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
Norway spruce											
Godbold et al. (1988)	100	1.3							H	N	Ali
Matzner et al. (1989)	100+	0.3 to 1.8							F	N	Alt
Stienen and Bauch (1988)	1500	0.66	1470	32	31	770	1890	0.28	H	N,B	Alt
Schroder et al. (1988)	2000	1							H	N	Ali

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al (M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
Red spruce											
Thornton et al. (1987)	250	1	1100	65	11.4	650	6000	0.07	H	B	Ali
Hutchinson et al. (1986)	185	2.2							S	B	Alt
Joslin and Wolfe (1988)	200	nd	~3000			~2000			S	B	Ali
Schier (1985)	1850	1.35			12.9			0.43	H	B,N	Ali
Ohno et al. (1988)	250	0.8			14				S	N	Ala in soil paste
Joslin and Wolfe (1992)		0.45							F	B	Alt
White spruce											
Nosko et al. (1988)	50	0.2							H	B	Alt
Red oak											
Joslin and Wolfe (1989)	300	4.05			11.9			0.06	S	B	Alt in SrCl2
DeWald et al. (1990)	115	4.48	3630	75	32.4	3630	6415	0.38	S	B	Alt
McCormick and Steiner (1978)	7405	0.54							H	B	Alt
Honeylocust											
Thornton et al. (1986b,c)	50	1.1			8.4			0.21 to 0.32	H	B	Ali
Sucoff et al. (1990)	100	1.4						0.35	S	B	Ali
Wolfe and Joslin (1989)	100	4.3						0.71	S	B	Ali
Sugar maple											
Thornton et al. (1986a)	100–600	0.42 to 2.5	~2000	~190	9.9	~1500	~2700	0.4	H	B,N	Ali
Loblolly pine											
Cronan et al. (1989) Thornton (unpubl.)	500–3000	0.5	900	260	2.3	3700	7770	0.32	H	N	Ali
American beech											
Cronan et al. (1989)	500–3000	0.5	2670	69	26.1	1140	7930	0.1	H	N	Ali
European beech											
Asp and Berggren (1990)	300	0.35			3.8			0.2	H	N	Ali
Cronan et al. (1989)	500	0.5							H	N	Ali
Peach											
Edwards and Horton (1977)	222				10.8			0.008	H	N	Ali
Scotch pine											

Study	Solution Al (µmol/L)	Solution Ca/Al (M)	Foliar Ca (mg/km)	Foliar Al (mg/km)	Foliar Ca/Al (M)	Root Ca (mg/km)	Root Al (mg/kg)	Root Ca/Al (M)	Type of Study or Experiment[a]	Response Variable[b]	Al Analysis Used in Ratio[c]
Ilvesniemi (1992)	185	nd	400	300	0.9		2300		S	N,B	Alt
McCormick and Steiner (1978)	2960	1.35							H	B	Alt
Virginia pine											
McCormick and Steiner (1978)	2960	1.35							H	B	Alt
Pitch pine											
McCormick and Steiner (1978)	2960	1.35							H	B	Alt
Cumming and Weinstein (1990)	50	20							S	N,B	Alt
Birches: gray, paper and yellow											
McCormick and Steiner (1978)	4444	0.9							H	B	Alt
European birch											
Goransson and Eldhuset (1987)	1000	0.02						0.17	H	N	Ali
Radiata pine											
Truman et al. (1986)	17	10.5	2120	800	1.8	1320	1850	0.48	H	N	Alt
Douglas-fir											
Keltjens and Van Loenen (1989)	370	0.54	2300	300	5.2				H	B	Alt
Larch											
Keltjens and Van Loenen (1989)	555	0.36	1800	250	4.9				H	B	Alt

[a] Types of study include hydroponic (H), soil or sand culture (S), or existing forest (F).
[b] Response variables include biomass (B), or nutrient content (N).
[c] Aluminum measurements include Ali (Ali), monomeric Al (Ala), and total Al (Alt). Since most of the lab studies were conducted under conditions of low pH and minimal DOC, measurements of total Al, Ali, and labile Al are very comparable.
Source: Cronan and Grigal (Cronan, 1995)

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Table B-21. Overview of selected major processes by which landscape change can alter drainage water acid-base chemistry

Landscape Change	Effect on Acid-Base Chemistry
Logging, blowdown	Dilution Lower deposition, less acidity Pulse of NO_3– acidity initially Less base cation neutralization, more acidity Less water contact with mineral soils, less neutralization of acidic deposition inputs
Road building and construction	More base cation neutralization, less acidity initially Depletion of base cation reserves in soils, more acidity long-term
Drainage of wetlands	Re-oxidation of stored S, pulses of acidity with increased discharge
Drought	Reduced groundwater inputs to seepage lakes with consequent increased acidity Increased relative baseflow to drainage waters with consequent decreased acidity
Lake shore development	Decreased acidity
Insect damage	Pulse of NO_3– acidity initially

Source: Sullivan (2000)

Table B-22. Observed relationships between zooplankton species richness (R) and lakewater ANC.

Taxonomic Group	Equation	r^2	p
Total Zooplankton	R = 15.65 + 0.089ANC	0.46	0.001
Crustaceans	R = 6.35 + 0.028ANC	0.47	0.001
Rotifers	R = 9.04 + 0.053ANC	0.30	0.001

Source: Sullivan et al. (2006a)

Table B-23. Threshold response of increased mortality of fish to low pH listed from least sensitive to most sensitive.

Study	Species	Increased Mortality Threshold, pH	Study Conditions
Johnson et al. (1987)	Blacknose dace, creek chub	5.9 - 6.0	In situ bioassay with early life stages in Adirondack surface waters
	Brook trout	4.8 - 5.1	
Holtze and Hutchinson (1989)	Common shiner	5.4 - 6.0	Laboratory exposure of early life stages to pH and Al.
	Lake whitefish, white sucker, walleye	5.1 - 5.2	
	Smallmouth bass	4.8	
Johansson et al. (1977)	Atlantic salmon	5.0	Laboratory tests with eggs exposed to low pH, no Al.
	Brown trout	4.5 - 5.0	
	Brook Trout	4.5	
Swenson et al. (1989)	Black crappie	5.5	Laboratory tests with early life stages exposed to pH and Al.
	Rock bass	5.0	
	Yellow perch, largemouth bass	4.5	
Mills et al. (1987)	Fathead minnow	5.9	Whole-lake treatment (fish population recruitment failure)
	Slimy sculpin	5.6 - 5.9	
	Lake Trout	5.6	
	Pearl dace	5.1	
	White sucker	5.0 - 5.1	

Source: Baker et al. (1990a)

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Table B-24. Threshold values of pH for various taxa and effects.

Reference	Type of Study	Taxa	pH	Observed Effects
Buckler et al. (1987)	Lab bioassay	Striped bass	6.5	>50% larval mortality
McCormick et al. (1989)	Lab bioassay	Fathead minnow	6.0	Significant decrease in embryo survival
Mills et al. (1987)	Whole-lake experiment	Fathead minnow	5.9	Population recruitment failure
Klauda et al. (1987)	Lab bioassay	Blueback herring	5.7	>50% mortality of larvae
Holtze and Hutchinson (1989)	Lab bioassay	Common shiner	5.4	>50% embryo mortality
Baker and Schofield (1980)	Lab bioassay	White sucker	5.2	Substantial reduction in embryo survival
Kane and Rabeni (1987)	Lab bioassay	Smallmouth bass	5.1	>50% mortality of larvae after 30–day exposure
Leino et al. (1987)	Whole-Lake experiment	Adult fathead minnow	5.2–5.8	Increased numbers of chloride (ionoregulatory) cells on the gills
Lacroix (1985a)	Field survey	Atlantic salmon parr (age 1+)	4.9–5.3	Significantly lower blood Cl levels; high K levels
McDonald and Milligan (1988)	Lab bioassay	Adult brook trout	5.2	Reduced Na transport activity
McWilliams and Potts (1978)	Lab bioassay	Adult brown trout	5.0	Net Na loss; major shift in the gill tansepithelial potential
Tietge et al. (1988)	Lab bioassay	Adult brook trout	4.9	Increased volume density of lamellar chloride cells on gills
Booth et al. (1988)	Lab bioassay	Adult brook trout	4.8	Net loss of Na and Cl
Audet and Wood (1988)	Lab bioassay	Adult rainbow trout	4.8	Decreased plasma Na and Cl levels
Peterson and Martin-Robichaud (1986)	Lab experiment	Atlantic salmon larvae	4.5	Reduced accumulation of Na, K, and Ca
Powell and McKeown (1986)	Lab bioassay	Coho salmon parr and smolts	4.4	Net decrease in plasma Na

Source: Baker et al. (1990a).

Table B-25. Threshold values of Al for various species and effects (form of A not specified for most studies).

Reference	Type of Study	Taxa	pH	Al (µg/L)	Observed Effect (at similar pH without added Al)
Sadler and Lynam (Sadler, 1988)	LB	Brown trout	5.2	30	Significant reduction in fish growth
Turnpenny et al. (Turnpenny, 1987)	Field survey	Broen trout	—-	40	Fish absent or rare in streams in Wales and England
Holtze and Hutchinson (1989)	LB	Walleye	4.9	50	>50% mortality of embryos to 4–d post-hatch
Skogheim and Roseland (1986)	Field mesocosm experiment	Atlantic salmon	5.1	75	>50% mortality of smolts
Klauda and Palmer (1987)	LB	Blueback herring	5.5–5.6	100	>50% larval mortality
Rosseland and Skogheim (1984)	LB	Atlantic salmon	4.9–5.0	130	Significant increase in mortality of presmolts
Baker and Schofield (Baker, 1982)	LB	White sucker	5.2	200	>50% larval mortality
Fjellheim et al. (1985)	LB	Eel	5.1	230	Significant increase in elver mortality
Brown (1983)	LB	Brown trout	4.5–5.4	250	>50% fry mortality
Schofield and Trojnar (1980)	Field study	Brook trout	4.9	286	No survival of trout stocked into lakes with higher total Al (even after accounting for pH effects).
Ormerod et al. (1987)	Whole-stream experiment	Atlantic salmon and brown trout	5.0	350	>50% mortality of young-of-the-year.

Source: Baker et al. (1990a)

Table B-26. The effects of increasing Ca^{2+} to ameliorate low pH and high Al.

Reference	Type of Study	Taxa	pH	Al Range (µg/L)	Ca^{2+} Range (µeq/L)	Observed Response to Increasing Ca^{2+}
Brown (1982, 1983)	LB	Brown trout	4.5–5.1	—-	12–400	Increased embryo survival and hatch
Wright and Snekvik (1978)	Field survey	Brown trout	4.5–7.5	—-	20–200	Trouot status significantly correlated with log Ca^{2+} and pH.
Brown (1983)	LB	Brown trout	4.5–5.4	0–500	12–100	Increased fry survival in low pH or high Al waters
McDonald (1983)	LB	Rainbow trout	4.3	—-	69–223	Decreased adult mortality and net loss of Na and Cl
Edwards et al. (1987)	LB	Brown trout	4.2	—-	100–5600	Lower loss of plasma Na and Cl ions
Freda and McDonald (1988)	LB	Common shiner, rainbow trout	4.0	—-	70–1000	Significant decrease in Na loss
Mount et al. (1988)	LB	Brook trout	5.0–6.3	0–500	25–400	Increased survival and growth of adults; increased progeny survival with adult exposure to low and high Al
Sadler and Lynam (Sadler, 1988)	LB	Brown trout	5.2	0–80	8–800	Increased yearling survival and growth in waters with elevated Al.

Source: Baker et al. (1990a)

Table B-27. Brook trout acidification response categories developed by Bulger et al. (XXXXXXXXXX) for streams in Virginia (2000).

Response Category	Chronic ANC Range (µeq/L)	Expected Response
Suitable	>50	Reproducing brook trout expected if other habitat features are also suitable
Indeterminate	20 to 50	Brook trout response expected to be variable
Episodically acidic	0 to 20	Sub-lethal and/or lethal effects on brook trout are possible
Chronically acidic	<0	Lethal effects on brook trout probable

Table B-28. Partial listing of bioassays demonstrating decreased fish survival in waters with low pH and (or) elevated aluminum.

Reference	Species	Life Stage	Lab/Field
Johansson and Kihlström (1975)	Northern pike	Fry	Lab
Johansson and Milbrink (1976)	Roach European perch	Egg	Lab, field
Johansson et al. (1977)	Brown trout Brook trout	Egg and fry	Lab
Trojnar (1977)	White sucker	Egg and fry	Lab
Peterson et al. (1980)	Atlantic salmon	Egg	Lab
Schofield and Trojnar (1980)	Brook trout	Fry	Lab
Baker and Schofield (Baker, 1982)	Brook trout White sucker	Egg and fry	Lab
Brown (1983)	Brown trout	Fry	Lab
Hulsman et al. (1983)	Walleye Rainbow trout	Egg Fry	Field
Sharpe et al. (1983)	Brook trout Brown trout Rainbow trout Mottled sculpin	Fry and adult	Field
Jagoe et al. (1984)	Arctic char	Egg and fry	Lab
Lacroix (1985b)	Atlantic salmon	Egg and fry	Field
Ingersoll (1986)	Brook trout	Egg and fry	Lab
Buckler et al. (1987)	Striped bass	Fry	Lab
Johnson et al. (Johnson, 1987)	Brook trout Lake trout Creek chub Blacknose dace	Egg, fry, and young-of-year	Field
Klauda and Palmer (1987)	Blueback herring	Egg and fry	Lab
Lacroix and Townsend (1987)	Atlantic salmon	Juvenile	Lab
Wales and Liimatainen (1987)	Walleye	Egg	Field
Palmer et al. (1988)	Bluegill Fathead minnow	Juvenile	Lab
Gunn (1989)	Lake trout	Egg and fry	Lab, field
Holtze and Hutchinson (1989)	Common shiner Lake whitefish White sucker Walleye Smallmouth bass Largemouth bass	Egg and fry	Lab
Hutchinson et al. (1989)	Lake trout Brook trout	Egg and fry	Lab

Table B-29. Mills et al., 1987. Shows effect of various pH on fish forage fish and lake trout.

Biota	1977 pH 6.13	1978 pH 5.93	1979 pH 5.64	1980 pH 5.59	1981 pH 5.02	1982 pH 5.09	1983 pH 5.13
Forage fish		Fathead minnow experience recruitment failure	Fathead minnow near extinction; slimy sculpin decline in abundance	Increase in abundance of pearl dace, Suckers very abundant.	White sucker recruitment failure; no effect on adult growth and survival	Recruitment failure for all species	Recruitment failure for all species
Lake trout	Increase in condition i.e., "fatter"		Increased abundance of young-of-the-year	Lake trout recruitment failure; condition similar to preacidification	Recruitment failure; no effect on adult growth and survival	Lake trout condition poor; recruitment failure; reduced adult survival	Lake trout condition very poor; recruitment failure; reduced adult survival

Source: (Baker, 1990)

Table B-30. Range of minimum pH of fish species occurrence in 11 lake surveys.

Family and Species	High Minimum pH	Low Minimum pH
Cyprinidae		
Bluntnose minnow	6.6	5.6
Fathead minnow	6.3	5.1
Blacknose dace	6.8	5.6
Pearl dace	5.9	4.7
Northern redbelly dace	5.9	4.7
Common shiner	6.2	4.9
Golden shiner	5.5	4.5
Creek chub	5.9	4.6
Salmonidae		
Brook trout	5.6	4.6
Lake trout	5.2	4.9
Brown trout	5.0	4.6
Atlantic salmon	6.3	5.3
Centrarchidae		
Smallmouth bass	7.0	4.9
Largemouth bass	5.0	4.6
Pumpkinseed	6.6	4.6
Bluegill	4.5	4.5
Rock bass	6.2	4.6
Black crappie	5.6	5.6
Percidae		
Yellow perch	5.8	4.4
Walleye	6.9	5.2

Family and Species	High Minimum pH	Low Minimum pH
Johnny darter	6.2	4.9
Iowa darter	6.2	4.6
Esocidae		
Northern pike	5.9	4.0
Catastomidae		
White sucker	5.5	4.6
Ictaluridae		
Brown bullhead	5.6	4.5
Umbridae		
Central mudminnow	4.5	4.2
Gasterosteidae		
Brook stickleback	5.4	4.6

Source: Baker et al. (1990a)

Table B-31. Studies[a] that either did (yes) or did not (no) yield evidence that acidic deposition affected certain species of birds

Species	Diet/ Foraging		Breeding Distribution		Reproductive Measures		Reference[a]
	Yes	No	Yes	No	Yes	No	
Common loon	x		x	x	x	x	1–3, 19,20
Common merganser			x		x		19
Belted kingfisher			x				4
Osprey	x		x		x		5,6
Black duck	x		X		x[b]		7–9
Common goldeneye			x[b]				8
Ring-necked duck	x				x		10,11
Eurasian dipper	x		x		x		12–14
Eastern kingbird				x	x		15
Tree swallow	x			x	x		16–18

[a]1= Alvo et al. (1988); 2 = Parker (1988); 3 = Wayland and McNicol (1990); 4 = Goriup (1989); 5 = Eriksson (1983); 6 = Eriksson (1986); 7 = Hunter et al. (1986); 8 = DesGranges and Darveau (1985); 9 = Rattner et al. (1987); 10,11 = McAuley and Longcore (1988a,b) 12,13 = Ormerod et al. (1985, 1986); 14 = Ormerod and Tyler (1987); 15 = Glooschenko et al. (1986); 16,17 = Blancher and McNicol (1988, 1991); 18 = St. Louis et al. (1990); 19 = Blancher and McNicol (1991); 20 = Blair (1990).

[b]The effect was beneficial

Source: Longcore and Gill (1993)

Table B-32. Predicted habitat suitability for lakes in the Algona Model Dataset

Group	Total Model Lakes	Current Suitable Lakes	Number of Lakes with Suitable Habitat Under Each Emission Scenario													
			Current pH < 6					Current pH 6–6.5					Current pH > 6.5			
			S1	S2	S3	S4	S5	S1	S2	S3	S4	S5	S1	S2	S3	S4	S5
Fish	526	338	29	34	40	77	100	97	100	107	124	133	196	196	197	197	197
Common loon pairs	433	100	12	14	14	16	17	22	22	23	24	24	66	66	66	67	67
Common loon broods	433	36	2	2	2	2	2	6	6	7	7	7	28	28	28	28	28
Common merganser pairs	433	52	6	12	27	68	86	14	17	20	33	44	31	31	32	34	35
Common merganser broods	433	31	6	10	18	69	89	14	15	16	21	29	12	11	10	10	10

Results are expressed as the number of lakes with suitable habitat for fish, common loons (pairs and broods) and common mergansers (pairs and broods) under each emission scenario (S1, S2, S3, S4, S5) according to current pH classes (<6, 6–6.5, >6.5). Habitat suitability is calculated by probability of presence at time t from WARMS output (# of suitable lakes at time t/total number of lakes), for fish [n = 526], and for loons and mergansers [n = 433].

Table B-33. Summary statistics of biological data layers for mercury (Hg) concentrations in fish and wildlife (µg/g) in the northeastern U.S. and southeastern Canada.

Hg Concentrations						
Category/Species	Sample Size	Data layer Designation	Mean ± Standard Deviation	Range	Hg Level of Concern (Tissue Type)	Percentage of Samples with Concentration > Level of Concern
Human health						
Yellow perch[a]	4089	Primary	0.39 ± 0.49	< 0.05–5.24	0.30 (fillet)	50
Largemouth bass[b]	934	Secondary	0.54 ± 0.35	<0.05–2.66	0.30 (fillet)	75
Ecological health						
Brook trout	319	Secondary	0.31 ± 0.28	<0.05–2.07	0.16 (whole fish)	75
Yellow perch[c]	(841)[d]	Secondary	0.23 ± 0.35	<0.05–3.18	0.16 (whole fish)	48
Common loon[e]	1546	Primary	1.74 ± 1.20	0.11–14.20	3.0 (blood)	11
Bald eagle	217	Secondary	0.52 ± 0.20	0.08–1.27	1.0 (blood)	6
Mink	126	Secondary	19.50 ± 12.1	2.80–68.50	30.0 (fur)	11
River otter	80	Secondary	20.20 ± 9.30	1.14–37.80	30.0 (fur)	15

Note: All data are in wet weight except for fur, which is on a fresh-weight basis
[a]Fillet Hg in yellow perch is based on individuals with a standardized length of 20 cm.
[b]Fillet Hg in largemouth bass is based on individuals with a standardized length of 36 cm.
[c]Whole-fish Hg in yellow perch is based on individuals with a standardized length of 13 cm. Whole-fish Hg for yellow perch was converted to fillet Hg.
[d]The sample population of 841 yellow perch examined for whole-fish Hg is included with the 4089 fillets (i.e., the total number of all biotic data layers does not double-count yellow perch).
[e]Egg Hg for the common loon was converted to the adult blood equivalent

Table B-34. Mercury concentrations in avian eggs and tissues and related effects.

Tissue	Concen. (ppm)	Wet (w) or Dry (d)	Endpoint	Species	Reference
Liver	1.06	w	No effect	Common tern	Gochfeld (1980)
Liver	22.2	w	Abnormal feather loss in juveniles	Common tern	Gochfeld (1980)
Liver	5	w	Conservative threshold for major toxic effects	Water birds	Zillioux et al. (1993)
Liver	7.2	w	Increased disease and emaciation	Common tern	Spalding and Forrester (1991)
Liver	9.08	w	Nesting success	Common tern	Finley and Stendall (1978)
Liver	20.7	w	Hatching success	Common tern	Finley and Stendall (1978)
Liver	30	w	Neurologic effects	Osprey	Heinz (1974)
Liver	35	w	Death	Common loon	Wiemeyer et al. (1987)
Liver	54.5	w	LD33[a]	European starling	Finley et al. (1979)
Liver	97.7	w	Death	Gannet	
Liver	103.6	w	LD33	European starling	Finley et al. (1979)
Liver	126.5	w	LD33	Red-winged blackbird	Finley et al. (1979)
Liver	306 total/ 20.4 MeHg	d	No adverse effects observed	Black-footed albatross	Gochfeld (1980)
Brain	4–6	w	Failure to hatch	Black duck	Hoffman and Moore (1979)
Brain	20	w	25% mortality	Zebra finch	Scheuhammer (1988)
Egg	1–5/0.2–1.0	d	Reduced productivity in one half of the population	Merlin	Newton and Hass (1988)
Egg	0.5–1.5	w	Decreased hatchability	Pheasant	Heinz (1979)
Egg	0.86	w	Aberrant nesting behavior	Common loon	Heinz (1979)
Egg	1.0	w	Successful reproduction	Common tern	Finley and Stendall (1978)
Egg	1.0–3.6	w	Residue threshold for significant toxic effects	Variety of water birds	Zillioux et al. (1993)
Egg	2–16	w	No decreased hatchability	Herring gull	Finley and Stendall (1978)
Egg	3.65	w	27% hatching, 10–12% fledging	Common tern	Finley and Stendall (1978)
Kidney	37.4 total/ 6.2 MeHg	d	No adverse effect observed	Black-footed albatross	Kim et al. (1996)
Kidney	40.4	w	LD33	Grackle	Finley et al. (1979)
Kidney	74.3	w	LD33	Red-winged blackbird	Finley et al. (1979)
Kidney	86.4	w	LD33	European starling	Finley et al. (1979)

[a]LD33 = lethal dose, 33%
Source: Wolfe et al. (1998)

ANNEX B - References

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Annex C. Nutrient Enrichment Effects from N

C.1. Effects on Biogeochemical Pathways and Cycles

C.1.1. N Cycling in Terrestrial Ecosystems

C.1.1.1. N Deposition Effects on DON Leaching

Some N fertilization experiments suggest that increasing N deposition drives an increase in production of dissolved organic nitrogen (DON) in soil (e.g., Seely and Lajtha, 1997; McDowell et al., 2004), but there is little evidence that elevated N deposition increases the export and loss of DON from terrestrial ecosystems. Essentially all of the increase in N export across gradients of N deposition occurs as an increase in NO_3^- rather than DON export. The latter is typically less than 2 kg N/ha/yr from most northeastern-forested watersheds (Campbell et al., 2000; Goodale et al., 2000; Lovett et al., 2000; Aber et al., 2003).

C.1.1.2. Interactions between snow melt and nitrate leaching

Changes in other environmental parameters can also be important. Measurement of nutrient concentrations in Emerald Lake (Sierra Nevadas) over a period of 19 years suggested that NO_3^- concentration declined between 1983 and 1995. This was likely caused by changes in the snow regime induced by a drought during the period 1987 to 1992 (Sickman et al., 2003a). Years that had shallow and early melting snowpacks generally had lower snowmelt NO_3^- concentration. In addition, declines in NO_3^- concentration during the growing season even in the wet years of 1993 through 2000 were likely the result of increased P loading to Emerald Lake and the consequent release of phytoplankton from P limitation (Sickman et al., 2003a).

C.1.1.3. Denitrification: NO and N_2O Flux

Davidson et al. (2000) described N gas loss from terrestrial ecosystems using a conceptual model called "hole-in-the-pipe." In this model, production of NO, N_2O, and N_2 gas are functions of the general rate of N cycling processes through soil (i.e., the N flux "flowing through the pipe"), combined with information on soil water content, a key determinant of the ratio of NO:N_2O (relative "hole size" for NO

and N_2O gas "leakage"). The model formulation has been supported by a range of field measurements in temperate and especially tropical ecosystems (Davidson et al., 2000), and suggests that processes that increase the rate of N cycling through soils should also increase the rate of N gas loss from these systems. Production of NO and N_2O tend to be lower in temperate than in tropical ecosystems, largely because of colder temperatures and slower rates of N cycling in temperate systems, and the frequency of P rather than N limitation in tropical systems. However, increased availability of N through fertilization can increase the rate of NO and N_2O gas loss from temperate forests.

Early studies of N gas emission in response to N fertilization experiments at the Harvard Forest, MA, found small increases in N_2O production in response to the highest N treatment (150 kg N/ha/yr) to a red pine (Pinus resinosa) stand, but N_2O losses accounted for <0.4% of N additions (Magill et al., 2000). However, later studies found that NO emission rates can be more than an order of magnitude greater than N_2O emissions, with NO emissions amounting to 3-4% to 8% (4 to 5 kg N/ha/yr) of the N additions to the fertilized pine stands (Venterea et al., 2003, 2004). Emissions of NO and N_2O increased with fertilization rate (0, 50, and 150 kg N/ha/yr) in both the red pine and a nearby red oak (Quercus rubra)/red maple (Acer rubrum) stand (Venterea et al., 2003, 2004). A study of the response of Scots pine (Pinus sylvestris) stands across a gradient of N deposition in Germany found a threefold to fourfold increase in the rate of NO and N_2O production as N deposition increased from 15 to 22 kg N/ha/yr. In these forests, both gases were produced in roughly equal amounts, although as N deposition increased, the rate of NO production increased more steeply than did the rate of N_2O production (Butterbach-Bahl et al., 2002a).

At Höglwald, a German site receiving 20 to 30 kg N/ha/yr in throughfall, Butterbach-Bahl et al. (2002b) reported higher emissions of NO than N_2O in both a spruce and a beech stand, with N oxide emissions totaling 4.5 to 6.8 kg N/ha/yr. Intensive laboratory studies suggested additional emissions of N_2 gas amounting to 7.2 and 12.4 kg N/ha/yr in the spruce and beech stands, respectively. This is the only known forest site for which a complete (NO, NO_2, N_2O, and N_2) N gas budget has been estimated, and in total, these measurements suggest that soil emissions may balance 46% to 78% of the N received in throughfall at this site. This result suggests somewhat higher rates of N gas loss than might be inferred from a series of ^{15}N tracer studies in conifer stands across Europe, which spanned a range of rates of N input from atmospheric and experimental sources of 3 to 91 kg N/ha/yr. Across all sites, total recovery of added ^{15}N in soil, vegetation, and lysimeter leachate after 9 to 21 months amounted to 65% to 105% of added ^{15}N (Tietema et al., 1998), providing a broad constraint on N gas emissions of no more than 35% of added ^{15}N. The lowest rates of ^{15}N recovery (65% to 67%) occurred at Speuld and Ysselsteyn, two sites in The Netherlands with the highest rates of chronic throughfall N input (35 to 53 kg N/ha/yr). Although much more work is needed on complete N gas budgets, several lines of evidence suggest that trace gas emissions of N may constitute an increasing pathway of N loss with increasing rates of N deposition.

C.1.1.4. Climate and N_2O Interactions

Rainfall events are an important feature controlling N_2O produced via denitrification. Rainfall increases soil moisture. This inhibits oxygen diffusion creating anoxic conditions, which increases rates of denitrification. A study of a spruce forest sites under ambient and elevated N deposition (20 and 30 kg N/ha/yr, respectively) indicated through most of the study period N_2O emission was equivalent between the sites (Mohn et al., 2000). However, after rainfall events the maximum rate of N_2O emission was much higher for the +N plots, especially when rainfall caused low soil redox potential (an indicator of anoxic conditions). Another study of mixed spruce, pine and birch forest (100 yrs old) under well- and poorly drained soil moisture conditions indicated poorly drained soils produced 1/3 more N_2O (118 g N_2O N ha/yr) than well drained soils. In this study, N deposition was increased in the poorly drained soil from ambient (12 kg N/ha/yr) to elevated (42 kg N/ha/yr), N_2O emissions increased by a factor of more than 2 (254 kg N/ha/yr) (Klemedtsson et al., 1997).

In addition to soil moisture, temperature also influences denitrification. The PnET model (Photosynthesis-Evapotranspiartion-Model) is coupled with Denitrification-Decomposition (DNDC) model, and an N module that are further described in Li et al. (1992, 1996, 2000), Li (2000), and Stange et al. (2000) to form the PnET-N-DNDC model. The PnET-N-DNDC model is designed to simulate and predict soil C and N biogeochemistry in temperate forest ecosystems and to simulate the emissions of N_2O and NO from forest soils. Denitrification is described in the model as a series of sequential reductions driven by microorganisms using N oxides as electron acceptors under anaerobic conditions. As intermediates of the processes, NO and N_2O are tightly controlled by the kinetics of each step in the sequential reactions. The capacity of this model to simulate N trace gas emissions from forest soils was tested by comparing model results with results form field measurements at 19 different field sites across Europe and 1 site in the United States (Kesik et al., 2005). Possible feedbacks of temperature and precipitationchange on forest soil NO and N_2O emissions in Europe were investigated using PnET-N-DNDC (Kesik et al., 2006). The model results indicated decreasing precipitation and increasing temperature in areas with light texture soils (below 15%) resulted in decreased soil moisture values; in turn, N_2O production by denitrification decreases. Under these same environmental conditions, NO production by nitrification increases. Most laboratory studies show increasing temperature increases N_2O production, however if water filled pore space (WFPS) increases to 70-80%, then N_2 rather than N_2O is the main product of denitrification and N_2O emissions go down. This illustrates how N_2O emissions increase with increasing soil moisture until soil moisture become more conducive to N_2 emission.

C.1.2. N Cycling in Transitional Ecosystems

C.1.2.1. Denitrification: Measurement Techniques

There are a variety of methods for measuring denitrification rates in wetland, freshwater and marine sediments, including measurements of NO_3^- loss, N_2 production, N_2O accumulation in response to acetylene inhibition of N_2O reduction, isotopic methods, and N_2:argon (Ar) measurement by membrane inlet mass spectrometry (MIMS) (Smith et al., 2006). The majority of direct measurements of denitrification have measured only rates of production of N_2O, or used the "acetylene block" technique of inhibiting transformation of N_2O to N_2 and monitoring the accumulation of N_2O as a surrogate of the sum of N_2O and N_2. The acetylene block method is highly problematic, however, as it also inhibits rates of nitrification, and so denitrification rates are strongly underestimated where nitrification and denitrification processes are coupled closely in space or time (Groffman et al., 2006).

Techniques can be based on laboratory incubation of sediment cores or in situ studies. Each method has advantages and disadvantages and many studies have been conducted to compare results among the various methods (e.g., Seitzinger, 1988; Seitzinger et al., 1993, 2002; Bernot et al., 2003; Groffman et al., 2006; Smith et al., 2006). Kana et al. (1998) described the MIMS method to measure small changes in dissolved N_2 caused by denitrification in sediments. This technique allows measurement of N_2 flux in unperturbed sediment cores with high temporal resolution (Kana et al., 1998). This is especially useful during summer conditions when NO_3^- concentration in the water is typically low, but the high temperature can support high rates of denitrification. Under such conditions, it is likely that a coupled sequence of nitrification and denitrification accounts for substantial N loss from estuarine sediments (Kemp et al., 1990). Constraints regarding field and analytical methods have seriously limited understanding of the magnitude and controls on denitrification (Groffman et al., 2006).

C.1.2.2. N Deposition Effects on Methane

Increased N loading to transitional ecosystems can affect both methane (CH_4)-producing and CH_4-oxidizing microbial activity. The difference between the CH_4 production and oxidation determines the magnitude of CH_4 emission from soils. There is evidence to support that ammonium compounds reduce CH_4 oxidation (Steudler et al., 1989; King and Schnell, 1994; Gulledge et al., 1997), but ammonium compounds have also been observed to increase methanotropic bacterial activity (Bodelier et al., 2000). In general CH_4 emissions from saturated soils have been observed to increase with N addition (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007). The prevailing hypothesis for explaining this effect

is that increases in vegetative cover caused by N addition increase C availability through root exudates, which in turn stimulates methanogenic bacteria and CH_4 emissions (Granberg et al., 2001; Saarnio et al., 2003; Zhang et al., 2007).

Saarnio et al. (2003) observed moderate increases in CH_4 emissions from boreal wetland soils with N fertilization rates of 30 kg N/ha/yr as ammonium nitrate (NH_4NO_3). Comparable N application rates and effects on CH_4 emissions were also observed by Granberg et al. (2001) in a similar ecosystem type. Zhang et al. (2007) observed elevated CH_4 emissions from freshwater wetland soils with experimental N additions of 240 kg N/ha/yr. They postulated that additional N increased abundance of *Deyeucia angustifolia* which increased CH_4 emissions by supplying methanogenic bacteria with additional substrate in the form of root exudates. Other studies have shown that N addition had little or no effect on CH_4 emissions across a variety of ecosystem types (Saarnio et al., 2000; Silvola et al., 2003; Ambus and Robertson, 2006). Note that the N enrichment rates employed in all of the above reported studies related to N effects on soil CH_4 emissions were greater (30 to 240 kg N/ha/yr) than atmospheric N inputs in most areas of the United States that are heavily effected by elevated atmospheric N deposition. See ISA section 3.3 for a discussion of methane flux from terrestrial, transition and aquatic ecosystems.

C.1.3. N Cycling in Estuarine Ecosystems

C.1.3.1. Denitrification and Anammox in Estuarine Ecosystems

Denitrification is a major factor governing the loss of N from estuarine ecosystems. Denitrification by microbes found in estuarine and marine sediments releases much of the added N inputs back into the atmosphere (Vitousek et al., 1997a; Arrigo, 2005). Collection of quantitative data on this process has been hampered, however, by the complexity of environmental controls on the denitrification process and difficulties in measuring denitrification rates (Kana et al., 1998). Major environmental controls include temperature and the availability of NO_3^-, O_2, and organic materials (Seitzinger, 1988; Rysgaard et al., 1994).

Marine microbial ecology is highly complex and poorly understood. Relatively new knowledge about anammox bacteria has completely altered scientific understanding of N cycling in the oceans. Although it was previously believed that denitrification was responsible for virtually all of the transfer of Nr in the ocean to the atmosphere as N_2 gas, it now appears that anaerobic ammonium oxidation (anammox) may account for up to 50% of the N_2 production in the oceans (Devol, 2003; Ward, 2003; Dalsgaard et al., 2005; Kuypers et al., 2005). This reaction uses NO_2^- as the primary electron acceptor and is catalyzed by planctomycete bacteria of the genera Brocadia, Kuenenia, and Scalindua. That NH_4^+

could be oxidized under anoxic conditions was theorized several decades ago based on calculations of the ratios among N, P, and C in marine ecosystems. Nevertheless, the process was not experimentally documented until the 1990s (van de Graaf et al., 1995). More recently, anammox has been detected in a variety of freshwater, estuarine, and marine waters and sediments (Devol, 2003; Jetten et al., 2003; Ward, 2003; Rysgaard et al., 2004; Dalsgaard et al., 2005; Engstrom et al., 2005; Jetten et al., 2005; Kuypers et al., 2005; Pilcher, 2005; Op Den Camp et al., 2006).

C.1.3.2. N Budgets

The greatest uncertainty in the development of detailed N budgets for coastal ecosystems is quantifying how much of the N deposited on the watershed is transferred through the terrestrial watershed to the estuary. The difficulty stems from (1) multiple agricultural and mobile and stationary fuel combustion emission sources in an estuary watershed, (2) quantifying dry deposition to the estuary surface and to the watershed, (3) measuring gaseous losses of NH_3 and NO_X compounds to the atmosphere, and (4) complex N flow pathways through the watershed (NRC, 2000). Published estimates of the contribution of atmospheric deposition to estuary N load exhibit wide variability. Such estimates for a specific estuary may differ. Some examples are summarized in Table C-1. Despite the variability, it appears that atmospheric sources of N loading to estuaries in the U.S. can be quantitatively important. The major sources of N to estuaries and near-coastal marine waters in the U.S., in addition to atmospheric deposition, include wastewater effluent derived mainly from food imports and consumption, fertilizer application, livestock feed imports, and N-fixing crops (Boyer et al., 2002; Driscoll et al., 2003a).

Boyer et al. (2002) estimated that atmospheric deposition averaged 31% of total N inputs over the combined area of the 16 northeastern river basins. Contributions from atmospheric deposition ranged from 60% of N inputs for the basins in northern Maine to 15 to 20% for the Schuylkill and Potomac River Basins, the latter of which had large agricultural N inputs. Across all basins, estimated riverine export of N amounted to 25% of total N inputs, and ranged from 11% to 40%. This result is consistent with a similar analysis by Howarth et al. (1996), who found that basins draining to the North Atlantic exported approximately 25% of anthropogenic N inputs on average.

Table C-1. Estimated percent of total N load to Delaware Bay and Hudson River/Raritan Bay contributed by atmospheric deposition.

Reference	Percent of N Load Contributed by Atmospheric Deposition	
	Delaware Bay	Hudson River/Raritan Bay
Paerl (1985)	44	—
Hinga et al. (1991)	—	33
Scudlark and Church (1993)	15	—
Paerl (Paerl, 1995)	—	68
Jaworski et al. (Jaworski, 1997)	44	68
Alexander et al. (Alexander, 2001)	22	26
Castro et al. (2001)	—	10
Stacey et al. (Stacey, 2001)		
Land-based	16	10
Sparrow model	25	27
Castro and Driscoll (2002)	20	17
Castro et al. (2003)	23	18

Turner et al. (2001) found a strong correlation between population density (persons/ km^2) and the total N loading from watershed to estuary ($r^2 = 0.78$) for coastal watersheds in the United States. This finding is likely due to the prevalence of automobiles in heavily populated areas, along with their associated N emissions and deposition, plus the myriad non-atmospheric sources of N from human activities, particularly sewage releases. They also determined that direct atmospheric deposition becomes increasingly more important as a contributor to the total N loading to an estuary as the water surface area increases relative to total watershed area (terrestrial plus water surfaces). Turner et al. (2001) found that, on average, direct atmospheric deposition of N accounted for more than an estimated 25% of the estuarine N load when the estuary surface occupied 20% or more of the overall watershed area. Few of the estuaries in the eastern U.S. comprise such a large percentage of their watershed (Castro et al., 2001).

The estimates of the effect of direct atmospheric deposition to estuary surfaces are hampered by uncertainties in dry deposition rates. Many published studies have assumed that dry N deposition is equal to measured wet deposition (e.g., Fisher and Oppenheimer, 1991; Hinga et al., 1991; Scudlark and Church, 1993), and this is probably biased high (cf. Baker, 1991). However, other studies have assumed dry N deposition rates for estuarine and near coastal areas are equal to 40% of wet (Jaworski et al., 1997) or 67% of wet (Meyers et al., 2001). Of particular importance, the rate of dry deposition to open water surfaces is much lower than the rate of dry deposition to vegetated terrestrial surfaces. Paerl et al. (2001) estimated that dry deposition to open estuarine surfaces is three to five times lower than to vegetated surfaces. This difference is seldom considered in N-budgeting studies, and can have a substantial effect

on estimates of direct atmospheric loading to estuary surfaces, which is especially important for estuaries having low watershed area to estuary surface area ratio.

A number of empirical approaches have been developed to quantify N fluxes to the coastal zone which rely on estimates of N sources within the watershed and characteristics of the landscape. Alexander et al. (2002) compared several of these empirical methods, the most accurate and least biased of which was that of Howarth et al. (1996). A modified version of the Howarth et al. (1996) methodology was published by Boyer et al. (2006). More mechanistic approaches include those of Bouwman et al. (2005), Van Drecht et al. (2003), and Green et al. (2004).

C.1.4. Timing of Chemical Change

C.1.4.1. Interannual Change: Nitrate Leaching

Interannual changes in N cycling can be reflected in changes in streamwater chemistry. NO_3^- leaching from terrestrial ecosystems throughout the 1980s was observed in many of the original lakes in EPA's Adirondack Long Term Monitoring (ALTM) program (cf. Driscoll and Van Dreason, 1993), which was followed by a decline during the 1990s. As a consequence of this subsequent decline, Driscoll (2003b) reported an overall significant ($p < 0.1$) decrease in NO_3^- concentration for the period 1982 to 2000 for 8 of the 16 original ALTM monitoring sites. Only the one mounded seepage lake in the study (Little Echo Pond) had a small, but statistically significant, increase in NO_3^- concentration (0.01 µeq/L/yr, $p < 0.06$). It is not clear why many Adirondack watershed soils leached NO_3^- to a lesser extent during the 1990s than they did during the 1980s (Driscoll et al., 2003b). Decreasing stream NO_3^- concentrations during the 1990s was also observed in the Catskill Mountains (Stoddard et al., 2003) and in New Hampshire (Goodale et al., 2003). There was not a substantial change in N emissions or deposition in the Northeast region over that period. Climatic factors, insect defoliation, increases in atmospheric CO_2, and interactions with increasing availability of DOC have been proposed as possible contributing factors to regional decreases in NO_3^- leaching (cf. Mitchell et al., 1996; Aber et al., 2002; Driscoll et al., 2003b; Goodale et al., 2003, 2005), but the driver of this decadal scale pattern remains uncertain.

C.1.4.2. Episodic Change

Nutrient enrichment effects of N deposition are controlled to a large degree by biological and hydrological processes that operate on episodic (hours to days), seasonal, and interannual time scales. Nitrogen uptake and transformation reactions and processes vary greatly with season and with climatic factors. In particular, N export from terrestrial and transitional ecosystems to aquatic ecosystems is governed by seasonal fluctuations in temperature and biological uptake, and episodic fluctuations in water

movement associated with rainstorms and snowmelt. The role of N in driving biotic change in stream ecosystems due to episodic pulses of NO_3^- associated with spring snowmelt are discussed in detail in ISA section 3.2.

C.1.4.3. Reversibility of Impacts

Although there are relatively few studies of the reversibility of the biogeochemical effects of elevated N deposition, the few to date suggest the possibility of recovery. Experimental studies in Europe suggest that some ecosystem processes and characteristics are likely to recover rapidly following a reduction in N deposition. In a study in northern Sweden, high levels of fertilization (90 kg N/ha/yr) over 20 yrs induced substantial soil acidification, including loss of over half of the base cations in the mineral soil, a decrease in pH, and an increase in soluble Al (Högberg et al., 2006). However, 10 yrs after this treatment was stopped, the pH of the mineral soil had increased, and extractable NO_3^- was no higher than in the control plot. Stem volume growth did not substantially increase relative to the acidification period. "Clean roof" experiments that prevent N deposition inputs at sites receiving >40 kg N/ha/yr ambient atmospheric N deposition in The Netherlands increased wood and root production soon after the roof was installed (Boxman et al., 1998a), and NO_3^- exports below the rooting zone were reduced dramatically within 2 yrs (Bredemeier et al., 1998).

A study of alpine lake sediment cores in Rocky Mountain National Park, CO (Wolfe et al., 2003) suggested the possible reversibility of N enrichment effects on lake biota. Although increased dominance of mesotrophic diatom species was correlated with increased N inputs during the 20th century, it did not appear that any of the oligotrophic species had been totally lost from study lakes. Thus, reduced future N loading may allow renewed dominance by oligotrophic diatom species.

It is not necessarily true, however, that nutrient enrichment effects of N deposition will, in all cases, be easily reversible. For example, it has been suggested that vegetation conversion in the coastal sage scrub community in California has altered hydrologic function to an extent that may be difficult to reverse. The depth of rainwater percolation into soil has been reduced as a result of invasion of non-native annual grasses. This hydrologic change inhibits the growth of deep-rooting native shrubs (Wood et al., 2006).

C.1.5. Tables Supporting Cross Ecosystem Evaluation of N_2O, CH_4 and CO_2 Flux

Table C-2 summarizes key information from the experiments included in the meta- analysis presented in ISA section 3.3.4.

Table C-2. The study site, experimental condition, ecosystem type, N form, amount of N addition and citations is presented for all studies used in NEE, EC, CH_4 uptake, CH_4 emission and N_2O emission meta analyses.

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
Net Ecosystem Carbon Exchange (NEE)					
Swiss FACE (Lollium)	field	grassland	NH_4NO_3	320	Aeschlimann et al. 2005
Swiss FACE (Trifolium)	field	grassland	NH_4NO_3	320	Aeschlimann et al. 2005
Ottawa, Canada	field	wetland	NH_4NO_3	32	Basiliko et al. 2006
Ottawa, Canada	field	wetland	NH_4NO_3	64	Basiliko et al. 2006
Ottawa, Canada	field	wetland	NH_4NO_3	16	Bubrie et al. 2007
Ottawa, Canada	field	wetland	NH_4NO_3	32	Bubrie et al. 2007
Ottawa, Canada	field	wetland	NH_4NO_3	64	Bubrie et al. 2007
Laqueuille, France	field	grassland	.	175	Soussana et al. 2007
Oensingen, Switzerland	field	grassland	slurry	200	Soussana et al. 2007
Toolik Lake, AK	field	tundra	NH_4NO_3	100	Shaver et al. 1998
Toolik Lake, AK	field	tundra	NH_4NO_3	100	Shaver et al. 1998
Orange county,CA	field	grassland	.	100	Harpole et al 2007
Orange county,CA	field	grassland	.	100	Harpole et al 2007
Switzerland	field	grassland	.	40	Diemer 1997
Finland	field	wetland	NH_4NO_3	.	Saarnio et al. 2003
Abisko, Sweden	field	tundra	NH_4NO_3	100	Christensen et al. 1997
Ecosystem Carbon Content (EC)					
WA	field	coniferous	.	.	Canary et al. 2000
Placerville CA	field	coniferous	NH_4	100	Johnson et al. 2006
Placerville CA	field	coniferous	NH_4	200	Johnson et al. 2006
Clayey, AL	field	coniferous	DAP	45	Leggett et al. 2006
Sandy, MS	field	coniferous	DAP	45	Leggett et al. 2006
Harvard forest, MA	field	deciduous	NH_4NO_3	150	Magill et al. 2004
Harvard forest, MA	field	coniferous	NH_4NO_3	150	Magill et al. 2004
Harvard forest, MA	field	deciduous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field	deciduous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field	coniferous	NH_4NO_3	50	Magill et al. 2004
Harvard forest, MA	field	coniferous	NH_4NO_3	50	Magill et al. 2004
BBWM	field	deciduous	NH_4	25.2	Parker et al. 2001; Elvir et al. 2006
MI (site A)	field	deciduous	NO3	30	Pregitzer et al. 2008; BURTON et al. 2000
MI (site B)	field	deciduous	NO3	30	Pregitzer et al. 2008; BURTON et al. 2000
MI (site C)	field	deciduous	NO3	30	Pregitzer et al. 2008; BURTON et al. 2000
MI (site D)	field	deciduous	NO3	30	Pregitzer et al. 2008; BURTON et al. 2000
FL	field	coniferous	.	.	Shan et al. 2001

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
CH4 emission					
Netherland	incubation	wetland	NH_4	.	Aerts and Caluwe 1999
Netherland	incubation	wetland	NH_4	.	Aerts and Caluwe 1999
Polish	incubation	wetland	NH_4	.	Aerts and Caluwe 1999
Netherland	incubation	wetland	NH_4	.	Aerts and Toet 1997
Swiss FACE	field	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE	field	grassland	NH_4NO_3	84	Baggs and Blum 2004
Minnesota	incubation	wetland	NH_4	20	Keller et al 2005
Minnesota	incubation	wetland	NH_4	60	Keller et al 2005
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Finland	incubation	wetland	NH_4NO_3	30	Nykanen et al. 2002
Finland	incubation	wetland	NH_4NO_3	100	Nykanen et al. 2002
Salmisuo, Finland	field	wetland	NH_4NO_3	30	Sarrnio and Silvola 1999
Salmisuo, Finland	field	wetland	NH_4NO_3	30	Sarrnio and Silvola 1999
Sanjiang mire, China	field	wetland	NH_4NO_3	240	Zhang et al. 2007
CH4 uptake					
Quebec, Canada	incubation	coniferous	NH_4	.	Adamsen and King 1993
Quebec, Canada	incubation	coniferous	NO3	.	Adamsen and King 1993
Michigan	field	coniferous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	coniferous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	grassland	NH_4NO_3	10	Ambus and Robertson 2006
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Bousson, PA	field	deciduous	NH_4NO_3	100	Bowen et al. 2000
Perridge Forest, UK	incubation	deciduous	NO3	.	Bradford et al. 2001
Perridge Forest, UK	incubation	deciduous	NO3	.	Bradford et al. 2001
MT Ascutney, VT	field	coniferous	NH_4	31.4	Castro et al. 1992
Bousson, PA	field	deciduous	NH_4NO_3	100	Chan et al. 2005
Abisko, Sweden	field	tundra	NH_4NO_3	100	Christensen et al. 1997
Finland	field	wetland	NH_4	100	Crill et al. (Crill, 1994)
Finland	field	wetland	NO3	100	Crill et al. (Crill, 1994)
Finland	field	wetland	urea	100	Crill et al. (Crill, 1994)
Villingen, Germany	field	coniferous	NH_4	150	Gulledge and Schimel 2000
LTER Alaska	field	deciduous	NH_4NO_3	66.7	Gulledge and Schimel 2000
LTER Alaska	field	coniferous	NH_4NO_3	12.3	Gulledge and Schimel 2000
LTER Alaska	field	deciduous	NH_4NO_3	171.4	Gulledge and Schimel 2000
LTER Alaska	field	coniferous	NH_4NO_3	142.9	Gulledge and Schimel 2000
Swiss FACE	field	grassland	NH_4NO_3	560	Ineson et al. 1998
Swiss FACE	field	grassland	NH_4NO_3	560	Ineson et al. 1998

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
Scotland	incubation	heathland	NH_4	40	Macdonald et al. 1997
Scotland	incubation	heathland	NH_4NO_3	40	Macdonald et al. 1997
Scotland	incubation	heathland	NO3	40	Macdonald et al. 1997
Finland	field	coniferous	NH_4NO_3	200	Maljane et al. 2006
Swale, CO	field	grassland	urea	450	Mosier et al 1991
Midslope, CO	field	grassland	urea	450	Mosier et al 1991
Passture, CO	field	grassland	urea	450	Mosier et al 1991
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Villingen, Germany	field	coniferous	NH_4	150	Papen et. al 2001
Finland	field	wetland	NH_4NO_3	30	Saarnio et al. 2003
Gjovelandsnesset, Norway	incubation	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Norway	incubation	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Harvard forest, MA	field	coniferous	NH_4NO_3	37	Steudler et al. 1989
Harvard forest, MA	field	deciduous	NH_4NO_3	37	Steudler et al. 1989
Harvard forest, MA	field	coniferous	NH_4NO_3	120	Steudler et al. 1989
Harvard forest, MA	field	deciduous	NH_4NO_3	120	Steudler et al. 1989
Belgium	incubation	wetland	NH_4	.	VanderNat et al. 1997
Belgium	incubation	wetland	NH_4	.	VanderNat et al. 1997
Costa Rica	field	tropical forest	.	65	Weitz et al (Weitz, 1999)
Costa Rica	field	tropical forest	.	65	Weitz et al (Weitz, 1999)
N_2O emission					
Michigan biological Station	incubation	deciduous	NH_4NO_3	.	Ambus and Robertson 1999
Michigan biological Station	incubation	deciduous	NH_4NO_3	.	Ambus and Robertson 1999
Michigan biological Station	incubation	deciduous	NH_4NO_3	.	Ambus and Robertson 1999
Michigan biological Station	incubation	deciduous	NH_4NO_3	.	Ambus and Robertson 1999
Michigan	field	coniferous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	grassland	NH_4NO_3	10	Ambus and Robertson 2006
Michigan	field	coniferous	NH_4NO_3	30	Ambus and Robertson 2006
Michigan	field	deciduous	NH_4NO_3	30	Ambus and Robertson 2006
Hyytiälä	incubation	coniferous	NH_4	.	Ambus et al. 2006
Speulderbos	incubation	coniferous	NH_4	.	Ambus et al. 2006
San Rossore	incubation	coniferous	NH_4	.	Ambus et al. 2006
Glencorse	incubation	coniferous	NH_4	.	Ambus et al. 2006
Nyirjes	incubation	coniferous	NH_4	.	Ambus et al. 2006
Achenkirch	incubation	coniferous	NH_4	.	Ambus et al. 2006
Höglwald	incubation	coniferous	NH_4	.	Ambus et al. 2006
Sorø	incubation	deciduous	NH_4	.	Ambus et al. 2006
Bosco negri	incubation	deciduous	NH_4	.	Ambus et al. 2006
Schottenwald	incubation	deciduous	NH_4	.	Ambus et al. 2006
Hyytiälä	incubation	coniferous	NO3	.	Ambus et al. 2006
Speulderbos	incubation	coniferous	NO3	.	Ambus et al. 2006
San Rossore	incubation	coniferous	NO3	.	Ambus et al. 2006

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
Glencorse	incubation	coniferous	NO3	.	Ambus et al. 2006
Nyirjes	incubation	coniferous	NO3	.	Ambus et al. 2006
Achenkirch	incubation	coniferous	NO3	.	Ambus et al. 2006
Höglwald	incubation	coniferous	NO3	.	Ambus et al. 2006
Sorø	incubation	deciduous	NO3	.	Ambus et al. 2006
Bosco negri	incubation	deciduous	NO3	.	Ambus et al. 2006
Schottenwald	incubation	deciduous	NO3	.	Ambus et al. 2006
Swiss FACE	field	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE	field	grassland	NH_4NO_3	84	Baggs and Blum 2004
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Swiss FACE	field	grassland	NH_4NO_3	420	Baggs et al 2003
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	18.5	Borken et al. 2002
Solling, Germany	field	coniferous	NH_4NO_3	24.2	Borken et al. 2002
Harvard forest	field	deciduous	NH_4NO_3	37	bowden et al. 1991
Harvard forest	field	coniferous	NH_4NO_3	37	bowden et al. 1991
Harvard forest	field	deciduous	NH_4NO_3	120	bowden et al. 1991
Harvard forest	field	coniferous	NH_4NO_3	120	bowden et al. 1991
Solling, Germany	field	deciduous	NH_4	140	Brumme and Beese 1992
Gullane	incubation	deciduous	NH_4	.	Castaldi and Smith 1998
Gullane	incubation	deciduous	NO3	.	Castaldi and Smith 1998
Ascutney , VI	field	coniferous	NH_4	31.4	Castro et al. 1993
Allt, UK	field	heathland	NH_4NO_3	20	Curitis et al 2006
Allt, UK	field	heathland	NH_4NO_3	20	Curitis et al 2006
Afon Gwy, UK	field	grassland	NH_4NO_3	20	Curitis et al 2006
Afon Gwy, UK	field	grassland	NH_4NO_3	20	Curitis et al 2006
Afon Gwy, UK	field	grassland	NH_4NO_3	20	Curitis et al 2006
River Etherow, UK	field	heathland	NH_4NO_3	20	Curitis et al 2006
River Etherow, UK	field	heathland	NH_4NO_3	20	Curitis et al 2006
St. James Parish, LO	field	wetland	NO3	100	Delaune et al. 1998
St. James Parish, LO	field	wetland	NH_4	100	Delaune et al. 1998
Saratoga	field	grassland	NH_4NO_3	168	Delgado et al. 1996
Puerto Rico	field	tropical forest	urea	300	Erickson et al. 2001
Jasper Ridge , CA	incubation	grassland	urea	200	Hungate et al. 1997
Jasper Ridge , CA	incubation	grassland	urea	200	Hungate et al. 1997
Swiss FACE	field	grassland	NH_4NO_3	560	Ineson et al. 1998
Swiss FACE	field	grassland	NH_4NO_3	560	Ineson et al. 1998
Manaus, Brazil	field	tropical forest	NO_3	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NO_3	.	Keller et al. (Keller, 1988)

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
Manaus, Brazil	field	tropical forest	NO_3	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NO_3	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NH_4	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NH_4	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NH_4	.	Keller et al. (Keller, 1988)
Manaus, Brazil	field	tropical forest	NH_4	.	Keller et al. (Keller, 1988)
gardsjon watershed	field	coniferous	NH_4NO_3	35	Klemedtsson et. al 1997
gardsjon watershed	field	coniferous	NH_4NO_3	35	Klemedtsson et. al 1997
Avoyelles, LO	field	wetland	NH_4	100	Lindau et al. 1994
Avoyelles, LO	field	wetland	NH_4	300	Lindau et al. 1994
Avoyelles, LO	field	wetland	NO_3	100	Lindau et al. 1994
Avoyelles, LO	field	wetland	NO_3	300	Lindau et al. 1994
Harvard forest	field	coniferous	NH_4NO_3	113	Magill et al. 1997
Finland	field	coniferous	.	200	Maljane et al. 2006
Swale, CO	field	grassland	urea	450	Mosier et al 1991
Midslope, CO	field	grassland	urea	450	Mosier et al 1991
Passture, CO	field	grassland	urea	450	Mosier et al 1991
Puerto Rico	field	wetland	NH_4	15.4	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NH_4	130.2	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NH_4	266	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NO3	15.4	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NO3	130.2	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NO3	266	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NH_4	15.4	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NH_4	266	Munoz-Hincapie et al. 2002
Puerto Rico	field	wetland	NO3	15.4	Munoz-Hincapie et al. 2002
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Niwot Ridge, CO	field	grassland	urea	250	Neef et al. 1994
Villingen	field	coniferous	NH_4	150	Papen et. al (2001)
Duke FACE	incubation	coniferous	NO3	.	Phillips et al. 2001
Duke FACE	incubation	coniferous	NO3	.	Phillips et al. 2001
Finland	field	wetland	NO3	100	Regina et al. 1998
Finland	field	wetland	NH_4	100	Regina et al. 1998
Finland	field	wetland	urea	100	Regina et al. 1998
Mojave	incubation	desert	NO3	.	Schaeffer et al. 2003
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	30	Sitaula et al. 1995
Gjovelandsnesset, Sweden	field	coniferous	NH_4NO_3	90	Sitaula et al. 1995
Scotland	field	coniferous	NH_4NO_3	48	Skiba et al. 1998
Deepsyke forest	field	coniferous	NH_4NO_3	48	Skiba et al. 1999
Deepsyke forest	field	coniferous	NH_4NO_3	96	Skiba et al. 1999

Site	experimental condition	ecosystem	N form	N addition (kg ha/yr)	Reference
Costa Rica	field	tropical forest	.	65	Weitz et al (Weitz, 1999)
Costa Rica	field	tropical forest	.	65	Weitz et al (Weitz, 1999)
Sanhuabg Mire, China	field	wetland	NH_4NO_3	240	Zhang et al. 2007

C.2. Terrestrial Ecosystems

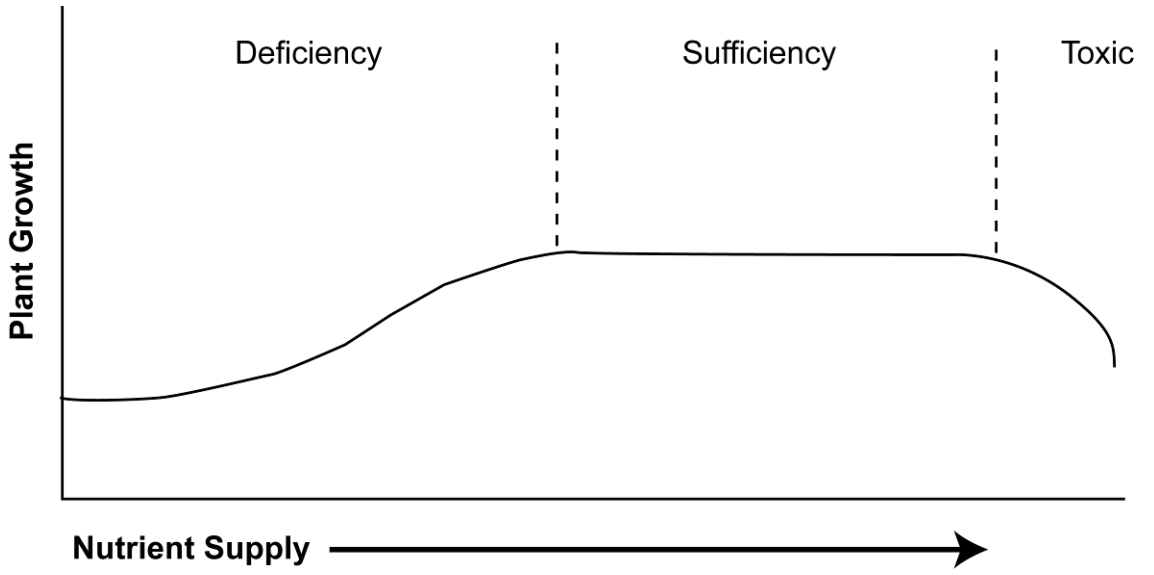
The following sections are organized by ecosystem type and combine information that is supplemental to section 3.3 of the ISA.

C.2.1. General C cyling

C cycling is a complex process that includes C capture from the atmosphere by autotrophic biota, the primary producers of the ecosystem, and respiration (autotrophic + heterotrophic). In general, atmospheric nutrient (e.g., N) deposition on an ecosystem that is deficient in that nutrient will often cause an increase in growth, at least initially, especially of the primary producers. If that same nutrient is deposited on an ecosystem that has an adequate supply of that nutrient, there may be no appreciable nutrient enrichment effect, at least up to a point. Nutrient input that is greatly in excess of biological demand will often cause toxicity, reduced growth, or problems other than those associated with nutrient enrichment (i.e., N-saturation, acidification, base cation depletion) (Figure C-1).

C.2.2. Forest Growth Interactions with Herbivores

Light availability, nutrient balance, and C:N:P stoichiometry are closely relate, and affect the composition of autotrophic species that will occupy a particular habitat. The resulting stoichiometric balance of C:N:P in the autotrophic community can have additional feedbacks on nutrient cycling by herbivores, detritivores, and decomposers (Sterner and Elser, 2002). Such effects also extend to herbivores, and likely other members of the food web. Forkner and Hunter (2000) altered plant growth of oak (*Quercus prinus* and *Q. rubra*) saplings through fertilizer (N, P, K) addition and then censused the densities of insect herbivore guilds and predaceous anthropods on experimental and control trees. In general, leaf chewers, phloem feeders, and leaf miners were more common on fertilized, as compared with non-fertilized, trees. Predaceous arthropods were also more abundant on fertilized trees and their densities were correlated with herbivore densities.



Source: EPA (1993).

Figure C-1. Schematic representation of the response of vegetation to nutrient addition.

C.2.3. Forest Growth Interactions with Herbivores

Light availability, nutrient balance, and C:N:P stoichiometry are closely relate, and affect the composition of autotrophic species that will occupy a particular habitat. The resulting stoichiometric balance of C:N:P in the autotrophic community can have additional feedbacks on nutrient cycling by herbivores, detritivores, and decomposers (Sterner and Elser, 2002). Such effects also extend to herbivores, and likely other members of the food web. Forkner and Hunter (2000) altered plant growth of oak (*Quercus prinus* and *Q. rubra*) saplings through fertilizer (N, P, K) addition and then censused the densities of insect herbivore guilds and predaceous anthropods on experimental and control trees. In general, leaf chewers, phloem feeders, and leaf miners were more common on fertilized, as compared with non-fertilized, trees. Predaceous arthropods were also more abundant on fertilized trees and their densities were correlated with herbivore densities.

C.2.4. Southern California Coniferous Forest

Wet N deposition is generally low throughout the region, in the range of 1 to 3 kg N/ha/yr. However, dry deposition is highly variable, but ranges up to about 30 kg N/ha/yr or more (Bytnerowicz and Fenn, 1996; Fenn and Bytnerowicz, 1997; Takemoto et al., 2001). Available data (e.g., Minnich

et al., 1995) suggest progression toward less needle retention, higher shoot:root biomass ratios, increasing depth of litter, and high NO_3^- in soil solution in response to high N deposition. These changes may eventually lead to replacement of pine species with nitrophilous and O_3-tolerant species such as fir and cedar (Takemoto et al., 2001).

Streamwater NO_3^- concentrations in montane watersheds that are downwind of the greater Los Angeles area are the highest in North America. Some streams in the San Gabriel and the San Bernardino Mountains have been documented to have levels of NO_3^- in stream water with peaks as high as 370 µeq/L (Fenn and Poth, 1999), reflecting very high N deposition and N-saturation of the terrestrial ecosystem. In contrast, N leaching is low in most watersheds in the Sierra Nevada, and NO_3^- concentrations in streams are usually below 1 µeq/L. Nevertheless, some of the higher elevation watersheds in the Sierra Nevada export appreciable NO_3^- from the terrestrial environment, particularly during the early phases of snowmelt. Fenn et al. (2002) reported springtime peaks of NO_3^-concentration in lakewater up to 38 µeq/L at high elevation and for watersheds dominated by talus. At lower elevation areas, however, most of the inorganic N deposition loading is retained within the watersheds and concentrations of NO_3^- in stream and lake waters are low (Fenn et al., 2003a). Surface water NO_3^- concentrations in these areas provide an index reflecting the general levels of N deposition. For example, where surface water NO_3^- concentrations are high, N deposition to the terrestrial watershed is also high.

C.2.5. Boreal forests

The boreal forest represents the largest terrestrial biome on Earth, and as such can have a large influence on global cycling of N and other nutrients. Plant growth in the boreal forest is limited mainly by N availability, in part because of slow mineralization of organic materials in the harsh climate (Vitousek and Howarth, 1991). Conceptual models of N cycling in the boreal forest have typically assumed that mineralization of organic N is required for plant uptake of N (Näsholm et al., 1998). However, it has been demonstrated in laboratory studies (Chapin et al., 1993) and field studies (Näsholm et al., 1998) that some boreal plants are capable of directly taking up amino acids from the soil, and therefore bypassing the need for prior mineralization. The interactions among soil abiotic processes, mycorrhizal associations, microbes, and plants are complex and poorly understood. Nevertheless, these interactions are important to global N cycling and to boreal plant species composition because organic N concentrations are typically high in the soil of boreal forests. It appears that atmospheric N deposition and climate warming have the potential to alter boreal forest plant communities by shifting nutritional processes from organic to inorganic N uptake (Näsholm et al., 1998).

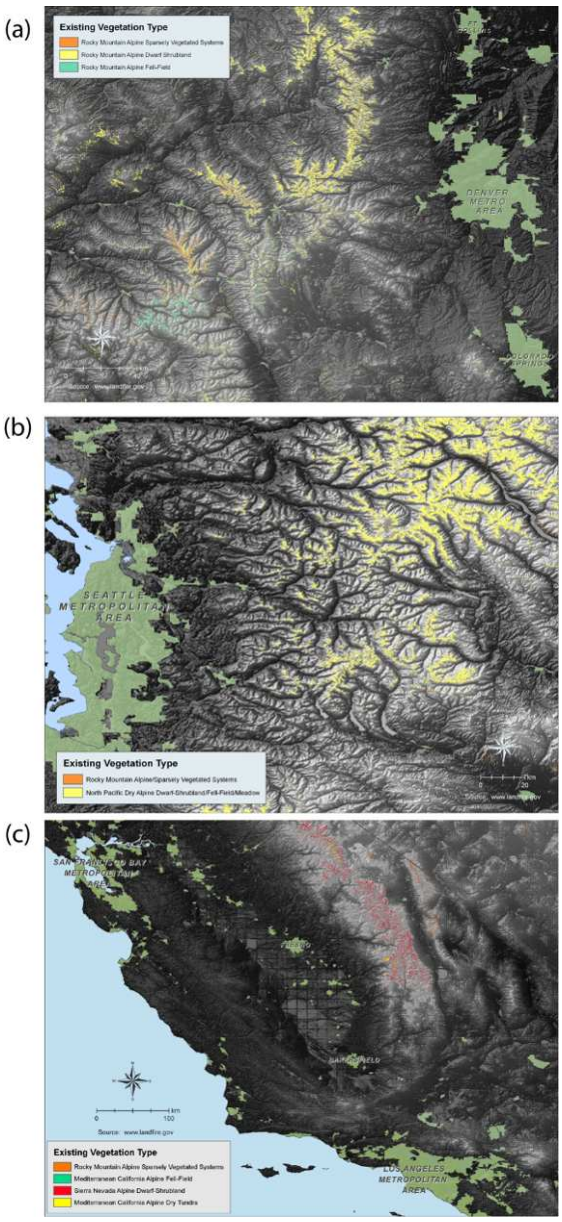
C.2.6. Alpine

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 (Fenn, 2003). Alpine plant communities occur in some of the areas that receive moderately elevated atmospheric N deposition such as those located in the Sierra Nevada in southern California, the Front Range in Colorado, and the Cascade Mountains in Washington (Figure C2).

Alpine plant species are typically adapted to low nutrient availability and their soil-forming processes are poorly developed, therefore they are often sensitive to effects from N enrichment (Bowman et al. 2006) including changes in species composition (Bowman et al., 1995; Seastedt and Vaccaro, 2001). Other reasons alpine tundra are sensitive to N enrichment include factors such as low rates of primary production, short growing season, low temperature, and a wide variation in moisture availability (Bowman and Fisk, 2001).

N cycling in alpine environments is strongly tied to variations in moisture regime (Bowman et al., 1993; Bowman, 1994; Fisk et al., 1998). Blowing snow is transported across alpine landscapes by wind and tends to accumulate in certain depression areas. These areas receive much higher levels of moisture and winter season N deposition than other more wind-swept portions of the alpine environment (Bowman, 1992). Fenn et al. (2003a) suggested that as much as 10 kg N/ha/yr may leach through the snow during the initial phases of snowmelt in some of the alpine areas in Colorado that accumulate substantial snowpack. It is these moist meadow areas that may be most affected by N deposition and are also the areas most likely to show changes in plant species composition and impacts on N cycling (Bowman and Steltzer, 1998).

N deposition to the alpine tundra of Niwot Ridge in the Colorado Front Range altered N cycling and provided the potential for replacement of some native plant species by more competitive, faster-growing native species (Bowman and Steltzer, 1998; Baron et al., 2000; Bowman, 2000). Many plants that grow in alpine tundra, as is true of plants growing in other low resource environments (e.g., infertile soil, desert), tend to have some similar characteristics, including slow growth rate, low photosynthetic rate, low capacity for nutrient uptake, and low soil microbial activity (Bowman and Steltzer, 1998; Bowman, 2000). Such plants generally continue to grow slowly when provided with an optimal supply and balance of resources (Pearcy et al., 1987; Chapin, 1991).



Source: Vegetative distribution data were taken from the national map LANDFIRE (September 2006) (http://gisdata.usgs.net/website/landfire/).

Figure C-2. Distribution of alpine vegetation in three western regions that are in close proximity to urban and agricultural sources of atmospheric N emissions: a) the Denver-Fort Collins region of Colorado, b) the Seattle-Tacoma region of Washington, and c) the Fresno-Los Angeles area of California (the blue line on the map is the California/Nevada border). Alpine vegetation in these areas is sensitive to nutrient enrichment effects from atomospheric N deposition.

In addition, plants adapted to cold, moist environments grow more leaves than roots as the relative availability of N increases. These patterns of vegetative development and their response to added N affect plant capacity to respond to variation in available resources and to environmental stresses such as

frost, high winds, and drought. Vegetation in the southern Rocky Mountains responds to increased N supply by increasing plant productivity for some species, but this increase in productivity is also accompanied by changes in species composition and abundance (Bowman et al., 1993). Many of the dominant plant species do not respond to additional N supply with increased production. Rather, many subdominant species, primarily grasses and some forbs, increase in abundance when the N supply is increased (Fenn et al., 2003a).

In alpine ecosystems, changes in plant species composition due to N deposition can result in 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 pre-existing species (Bowman et al., 1993, 2006; Steltzer and Bowman, 1998; Suding et al., 2006).

Total organic N pools in the soils of dry alpine meadows are large compared to pools of NH_4^+ and NO_3^- (Fisk and Schmidt, 1996). However, positive response to inorganic N fertilization has been demonstrated, and thus some plant species appear to be restricted in their ability to take up organic N from the soil and are growth-limited by the availability of inorganic N (Bowman et al., 1993, 1995; Theodose and Bowman, 1997). Miller and Bowman (2002) analyzed patterns of foliar ^{15}N, NO_3^- reductase activity, and mycorrhizal infection compared with N uptake quantified by stable isotope tracer additions in the greenhouse. ^{13}C enrichment subsequent to ^{13}C, ^{15}N-glycine addition indicated that all of the 11 genera studied were able to take-up labeled glycine to some extent. Glycine uptake ranged from about 35% to more than 100 % of NH_4^+ uptake. Only Festuca (*fescue grass*) showed glycine uptake exceeding both NH_4^+ and NO_3^- uptake (Miller and Bowman, 2002).

C.2.7. Arctic Tundra

Soluble N in tundra soil solution is dominated by organic N, including free amino acids, rather than NH_4^+ or NO_3^- (Kielland, 1995). Tundra plants appear to exhibit a range of interspecific differences that allow coexistence under conditions that reflect a single limiting element. Species differ in rooting depth, phenology, and uptake preferences for organic and inorganic forms of N (Shaver and Billings, 1975; Chapin et al., 1993; Kielland, 1994; McKane et al., 2002). McKane et al. (2002) demonstrated, based on ^{15}N field experiments, that arctic tundra plant species were differentiated in timing, depth, and chemical form of N utilization. Furthermore, the species that exhibited greatest productivity were those that efficiently used the most abundant N forms.

Ericoid mycorrhizae provide host plants with the capacity to take up N in the form of amino acids (Stribley and Read, 1980; Bajwa and Read, 1985). This is important in arctic plant communities that occur on acidic organic soils because amino acids are typically readily available in such soils, and N availability generally limits primary productivity.

Future climate warming could have important effects on N cycling in arctic tundra ecosystems. In the past, organic materials have accumulated in tundra soils, largely because decomposition has been slower than plant growth. Climate warming may increase the decomposition of soil organic matter, thereby increasing the availability of stored N (Weintraub and Schimel, 2005). The distributions of woody plant species are also increasing in response to warming, with likely feedbacks on C and N cycling. For example, the dominant shrub species in the arctic tundra in Alaska, Betula nana, is expanding its distribution in tussock vegetation communities (Weintraub and Schimel, 2005).

Poor soil aeration is caused by permafrost, resulting in poor water drainage and the development of anaerobic conditions. Vegetation composition and primary productivity vary in response to differences in soil moisture and aeration (Everett and Brown, 1982; Gebauer et al., 1995). Reduced soil O_2 can limit nutrient availability. For example, under anaerobic conditions, N mineralization and nitrification rates decrease while denitrification increases (Ponnamperuma, 1972; Gebauer et al., 1995).

C.2.8. Arid Land

From 1989 to 2004 in the Chihuahuan desert, Baez et al. (2007) observed a 43% increase in ambient N deposition, from 1.71 to 2.45 kg N/ha/yr, resulting in an additional 5.88 kg N/ha/yr deposition over that time period. They suggest that these deposition trends may result in significant plant community changes, as indicated by fertilization studies of blue gramma (*Bouteloua gracilis*) and black gramma (*B. eriopoda*). In a field addition with additions of 20 kg N/ha/yr in one season, blue gramma was favored over black gramma, the current dominant species (Baez et al., 2007).

C.2.9. Lichens

There are several potential uses of lichens for air pollution and deposition monitoring. These include measurement of tissue lichen concentrations of specific pollutants (i.e., lichens as passive monitors), determination of changes in species composition or the presence/absence of sensitive species, and identification of areas having relatively high levels of air pollution, where monitoring instrumentation could be installed to more quantitatively measure pollution levels. Assessment of long-term change in the epiphytic lichen community can be especially valuable to provide an early indication of either improving or deteriorating air quality and atmospheric deposition. Such monitoring was incorporated in 1994 into the USFS Forest Inventory and Analysis (FIA) Program (See Annex A).

Lichen communities in the Pacific Northwest show signs of air pollution damage under current air pollution levels. Symptons include decreases in the occurrences of sensitive taxa and replacement by

pollution-tolerant and nitrophilous taxa (Fenn et al., 2003a; Geiser and Neitlich, 2007). Indicators of clean sites and polluted sites (Table C-3) were used by Geiser and Neitlich (2007) to create six lichen zones of air quality within the region, from worst (all sensitive species absent) to best (all sensitive species present). Air pollution was associated with effects on community composition of lichens, rather than species richness. The most widely observed effects included paucity of sensitive, endemic species, and enhancement of nitrophilous and non-native species (Geiser and Neitlich, 2007). The strongest relationship was with wet NH_4^+ deposition, consistent with findings in California (Jovan and McCune, 2005) and Europe (van Dobben et al., 2001). The zone of worst air quality was associated with absence of sensitive lichens, enhancement of nitrophyllous lichens, mean wet NH_4^+ deposition > 0.06 mg N/L, lichen tissue N and S concentrations > 0.6% and 0.07 %, and SO_2 levels harmful to sensitive lichens.

Jovan and McCune (2005) constructed a model based on non-metric multidimensional scaling ordination to analyze lichen species distribution from 98 FIA plots in the greater Central Valley of California. The model used epiphytic macrolichen community data to reflect air quality and climate in forested areas. Some species respond negatively to NO_X and SOx deposition (McCune, 1988; Gauslaa, 1995; van Haluwyn and van Herk, 2002). Other species respond positively to NH_Y deposition (de Bakker, 1989; van Dobben and de Bakker, 1996; van Herk, 1999, 2001; Jovan and McCune, 2005).

Similarly, Jovan and McCune (2006) developed a model of NH_3 exposure to epiphytic macrolichens in the Sierra Nevada region. They found that lichens provide a relatively inexpensive tool for estimating fine-scale distributions of NH_3 exposure to terrestrial ecosystems. Because NH_3 has a high deposition velocity (Asman and van Jaarsveld, 1992), dry deposition of reduced N exhibits high spatial variability. Monitoring of species composition of epiphytic lichen communities can therefore help quantify spatially variable eutrophication risk to forest health in the Sierra Nevada region (Jovan and McCune, 2006).

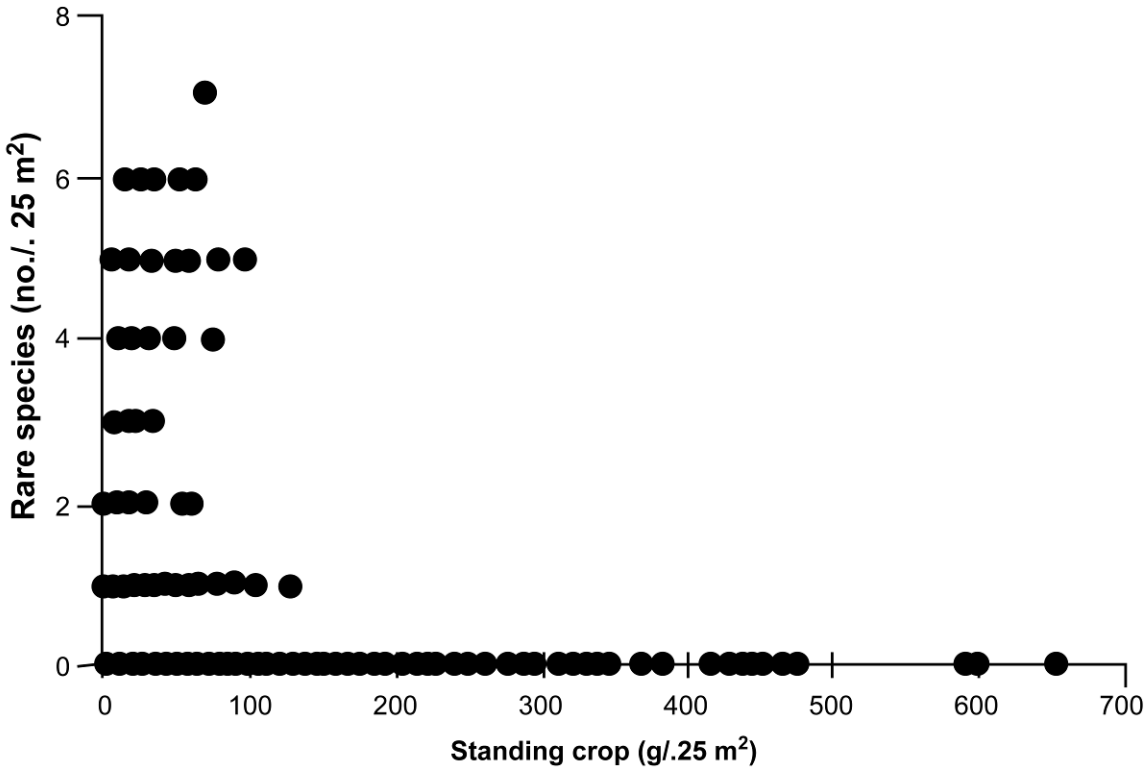
Table C-3. Principal Air Quality Indicator Lichen Species in Oregon and Washington

Group	Sub-Group	Indicator Species
Clean Air	Regional distribution	Bryoria capillaris, Lobaria oregana, Sphaerophorus globosus, Usnea filipendula, Usnea scabrata
	Sub-regional distribution	Ahtiana pallidula, Alectoria sarmentosa, Bryoria fuscescens, Hypogymnia enteromorpha, Nephroma bellum, Nodobryoria oregana
Polluted Air	Regional nitrophytes	Candelaria concolor, Physcia adscendens, Xanthoria polycarpa

* Includes only species with highest indicator value, used by Geiser and Neitlich (2007) to define air quality zones.
Source: Geiser and Neitlich (2007).

C.3. Transitional Ecosystems

The sensitivity of wetlands is particularly important given that they contain a disproportionately high number of rare plant species (Figure C-3) (Moore et al., 1989). EPA reported that, of the 130 plant species from the conterminous U.S. that were listed as threatened or endangered in 1987, 14% occurred principally in wetlands (U.S. Environmental Protection Agency, 1993). Bedford and Godwin (2003) indicated that a disproportionately high number of rare plant species occur in fens relative to their percent land cover (Table C-4) (Bedford and Godwin, 2003). For example, fens comprise only 0.01% of northeastern Iowa but contain 12% of the region's rare plant species and 17% of the listed endangered, threatened, and species of concern (Table C-4).



Source: Moore et al. (1989).

Figure C-3. Number of nationally rare species versus standing crop in each of 401 quadrants from wetlands in Ontario, Quebec, and Nova Scotia.

Table C-4. Contribution of fens to support of plant species diversity in selected states

	Number of Vascular Species Found in Fens (# Native)	Percent of State Vascular Flora Found in Fens (% Native)	Non-Vascular Species Found in Fens	Number of Uncommon & Rare Species Found in Fens	Percent of State Uncommon & Rare Species Found in Fens	Percent of State Area in Fens

	Number of Vascular Species Found in Fens (# Native)	Percent of State Vascular Flora Found in Fens (% Native)	Non-Vascular Species Found in Fens	Number of Uncommon & Rare Species Found in Fens	Percent of State Uncommon & Rare Species Found in Fens	Percent of State Area in Fens
Colorado	~500	~14		20	3.3	0.08–0.15
Idaho	327		20	35	12.0	
Iowa	320	18		134	12.0	0.01
	(307)	(17.2)				
Montana	174		60	40		0.0015
New Hampshire	340	17.2	91	52	13.7	0.078
Calcareous fens						0.0058
Open fens						0.0726
New Jersey				96	13.5	0.00733
Calcareous fens	245			60		0.0073
Acidic seeps	169		13	36		0.00003
New York	440	13.8	77	55	7.0	0.07
	(397)	(19.0)				
North Carolina				77	11.0	0.0023

Source: Bedford and Godwin (2003).□

C.4. Aquatic Ecosystems

Aquatic systems can be subdivided into major types based on hydrology. At the broadest level, freshwater aquatic ecosystems can be classified as riverine, lacustrine, and palustrine systems. Riverine systems can be identified at varying scales, including valley segment, river reach, and channel unit. Lacustrine systems include deepwater habitats associated with lakes and reservoirs. Palustrine systems include small, shallow, or intermittent water bodies, including ponds. Each type of aquatic ecosystem is potentially sensitive to nutrient enrichment effects from N deposition. Nevertheless, available data documenting such effects are limited.

The dose-response data for aquatic organisms such as those cited here are generally expressed in concentration units, as mg/L or µmol/L of N, for example. Such exposure concentration data cannot be directly related to ecosystem exposure, which is generally expressed in such units as kg/ha. This is because a given N deposition exposure 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^+.

C.4.1. History of Evaluating N Enrichment in Freshwater Aquatic Ecosystems

The role of N deposition in freshwater eutrophication and acidification processes has been considered secondary to P and S, and only within the past 20 years have there been studies questioning the established science and showing N-limitation in some fresh waters, N excess in some terrestrial systems, and N-caused acidification in poorly buffered fresh waters. A number of things have conspired to prevent extensive evaluation of the effects of atmospheric N deposition on aquatic organisms via nutrient-enrichment pathways. These include assumptions, or prevailing paradigms, that have channeled scientific thought in one direction and away from others.

First were the assumptions for many years that atmospheric deposition was caused primarily by sulfur (S) emissions and that effects on aquatic ecosystems were primarily caused by acidification processes. Only after S emissions began to decrease substantially in response to the Clean Air Act amendments did the role of NO_X, and still later, NH_3, emissions become recognized as potential agents of environmental change. And even then, that role was assumed to be restricted mainly to acidification from NO_3^-, a strong acid anion, not eutrophication (Reuss and Johnson, 1985). Second, because N is the nutrient most limiting to primary production in most ecosystems, it was assumed until fairly recently that N was tightly cycled in terrestrial systems, and that excess NO_3^- leaching rarely occurred in natural environments (Vitousek and Howarth, 1991). Finally, the attention of aquatic biologists has been strongly focused on the role of P in eutrophication of freshwaters for the past 40 years, largely due to the demonstrated role of P in causing large increases in algal productivity worldwide (Schindler et al., 1971; Schindler, 1974). P is an essential, and often limiting, nutrient to aquatic organisms. A large number of highly influential studies in the 1960s and 1970s exposed the role of wastewater, in particular phosphate detergents, in causing excessive algal production and anoxia in Lake Mendota (Wisconsin), Lake Washington (Washington), Lake Erie, and many other locations (Hasler, 1947; Vollenweider, 1968; Edmondson, 1969, 1991). Because of the emphasis on P as a major cause of fresh water eutrophication, Downing and McCauley (1992) wrote as recently as 1992: "opinions differ on the role of N as a limiting nutrient in lakes."

C.4.2. Interactions between N and P loading

Results from surveys, paleolimnological reconstructions of past conditions, experimental results, and meta-analyses of hundreds of studies all consistently show N-limitation to be common in fresh waters, especially in remote areas, and there is a nearly universal eutrophication response to N-enrichment in lakes and streams that are N-limited. Surveys of lake N concentrations and trophic status along

gradients of N deposition show increased inorganic N and increased productivity to be strongly related to atmospheric N deposition. Where N-enrichment has occurred, P limitation, N+P colimitation, and a few instances of Si depletion have been reported. Paleolimnological records show increases in productivity and changes in algal assemblages in the recent past (since 1950) that are correlated with increased societal use of synthetic N fertilizers and human. The paleolimnological evidence is strongest in regions with the highest N deposition, and is weaker where N deposition is lower (Wolfe et al., 2001, 2003, 2006; Saros et al., 2003). In additions to changes in productivity, algal community reorganization has been observed in the paleolimnological record, experiments, and observations of N-enriched lakes, especially those where enrichment has come from N deposition. A summary of additional studies addressing N-limitation is given in Table C-5.

It is generally 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. During spring, phytoplankton growth was not limited by P, N, or silica (Si), but perhaps by light or temperature (Levine et al., 1997).

Data from 28 Sierra Nevada lakes sampled in 1985 and again in 1999 suggested that NO_3^- concentrations decreased during that period and total P concentrations increased in more than 70% of the lakes sampled. Sickman et al. (2003a) concluded that lakes throughout the Sierra Nevada appear to be experiencing measurable eutrophication in response to atmospheric deposition of nutrients, but N deposition is only part of the process. Based on the evidence of increased P loading throughout the Sierra Nevada, Sickman et al. (2003a) concluded that site-specific P sources were unlikely to be the cause of observed trends. They proposed that atmospheric deposition and accelerated internal cycling of P in response to changes in climatic factors were the most likely sources of increased P loading to the Sierra Nevada Lakes, but it is not known why atmospheric deposition of P to these lakes has increased over time. Possibilities include use of organo-phosphate pesticides and aeolian transport of soils and dust that are high in P from the San Joaquin Valley to the Sierra Nevada Mountains (Bergametti et al., 1992; Lesack and Melack, 1996; Sickman et al., 2003a).

Data from a survey of 44 lakes east and west of the Continental Divide in Colorado 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 Continental Divide averaged 10.5 µeq/L of NO_3^- concentration. In the Colorado Front Range, NO_3^- concentrations in lakes above15 µeq/L have commonly been measured, suggesting some

degree of N-saturation (Baron, 1992). A meta-analysis of 42 regions in Europe and North America suggested that a majority of lakes in the northern hemisphere were limited by N in their natural state. While many of these lakes now receive sufficient N from deposition that they are no longer N-limited, some lakes in remote regions still maintain their original oligotrophic or ultra-oligotrophic status.

Table C-5. Summary of additional evidence for N limitation on productivity of freshwater ecosystems.

Region	Endpoint	Observation	Ecosystem Type	Reference
Sweden	N limitation	a consistent pattern of nutrient limitation showing N limitation for deposition below approximately 2.5 kg N/ha/yr, co-limitation of N and P for deposition between ~2.5 and 5.0 kg N/ha/yr, and P limitation in areas with N deposition greater than 5.0 kg N/ha/yr.	lakes	Bergström et al. (2005)
Rocky Mountains of Colorado and Wyoming	N limitation	Review: the author concluded that the effects of atmospheric N deposition were uncertain and that a widespread shift from N to P limitation had not been clearly demonstrated.		Burns (2004)
Texas	N limitation	some instances of seasonsal N-limitation, and other instances of year-round N-limitation	rivers	Stanley et al., 1990
Rocky Mountains of Colorado and Wyoming	N limitation	Review: Author stated that recent studies did suggest a change in diatom species dominance in the 1950s, but widespread species changes across lakes in the region and the role of N deposition in these changes needed confirmation. Thus, the available data were not clear at that time, but suggested that some changes had likely occurred in some aquatic ecosystems.		Burns (2004)

C.4.3. Aquatic Species Affected

The following section contains studies in which the amount of N added was less than 10 mg NO_3^- N/L, or 714 µM, and most studies tested the effects of 5 mg NO_3^--N/L or less. Many of these studies are summarized in Table C.6. Overall, several major effects were reported on biota treated with N enrichment: (1) the effects on algae included growth stimulation, increased cell densities, decline or stimulation of individual taxa, and decline in diversity; (2) the amount of N required to stimulate growth in phytoplankton is extremely low: 3 µM or less; and (3) animal responses included no response, decreased reproductive capability, declines in growth rate and biomass, mortality, and in one case, increased fitness because NO_3^- was detrimental to a fungal parasite.

C.4.3.1. Phytoplankton and Plants

Two species of diatom, *Asterionella formosa* and *Fragilaria crotonensis*, now dominate the flora of at least several alpine and montane Rocky Mountain lakes (Interlandi and Kilham, 1998; Baron et al.,

2000; Wolfe et al., 2001, 2003; Saros, 2003; Saros, 2005). These species are opportunistic algae that have been observed to respond rapidly to disturbance and slight nutrient enrichment in many parts of the world. They were among the first diatoms to increase in abundance following watershed settlement and agricultural development in European lake watersheds in the 12th and 13th centuries (Anderson et al., 1995; Lotter, 1998), and North American settlements in the 18th and 19th centuries (Christie and Smol, 1993; Hall et al., 1999). In these studies, as well as in a Swedish lake influenced by acidic deposition, these two diatom species expanded following initial disturbance, and were later replaced by other species more tolerant of either acidification or eutrophication (Renberg et al., 1993; Hall et al., 1999). Moreover, the growth of *A. formosa* has been stimulated with N amendments during in situ incubations, using bioassays and mesocosms (6.4 to 1616 µM N/L; McKnight et al., 1990) (76 µM N/L; Lafrancois, 2004) (18 µM N/L; Saros, 2005).

It may seem obvious that additions of N stimulate cell growth, but not all species of diatoms or other algae are equally responsive to N supply. *A. formosa* and *F. crotonensis* have extremely low resource requirements for P, enabling them to outcompete other algae for resources and such differences in resource requirements allow some species to gain a competitive edge over others upon nutrient addition, and as a consequence, shifts in assemblages have been observed (Wolfe et al., 2001, 2003; Lafrancois, 2004; Saros, 2005). This is in keeping with findings of Interlandi and Kilham (2001), who demonstrated that maximum species diversity was maintained when N levels were extremely low (<3 µM N) in lakes in the Yellowstone National Park (Wyoming, Montana) region. The implication is that species diversity declines with increasing availability of N, and this finding complements the results of terrestrial studies that also showed a negative relationship between species diversity and N availability (Stevens, 2004; Suding et al., 2005; Gilliam, 2006).

P limitation and co-limitation of both N and P are reported for fresh waters in the literature, particularly during summer (Morris and Lewis, 1988; Elser, 1990) Downing and McCauley, 1992; Sickman et al., 2003b). Because diatoms in northern temperate freshwaters respond rapidly and favorably to N enrichment and also have relatively high Si requirements, Si can be depleted, at least seasonally, from waters that are relatively high in N and P.

Silica depletion due to nutrient enrichment has been reported for the Great Lakes (Conley et al., 1993). Increased growth of silicate-utilizing diatoms as a result of NO_3^- and phosphate (PO_4^-)-induced eutrophication, and subsequent removal of fixed biogenic Si via sedimentation has brought about changes in the ratios of nutrient elements Si, N, and P. In turn, such changes can cause shifts from diatoms to non-siliceous phytoplankton in large rivers and coastal marine regions (Ittekot, 2003). Reduction in dissolved Si in lakewater corresponded to phytoplankton blooms under ice and large numbers of diatoms during spring in Loch Vale Watershed, Rocky Mountain National Park (Campbell et al., 1995). This is a

potential seasonal issue in water bodies underlain by aluminosilicate rocks because mineral weathering can replenish the Si supply.

C.4.4. Seasonal N Input and Cyanobacteria

Some ecosystems are seasonally enhanced with N from atmospheric deposition, either from snowmelt flushing of accumulated N in winter snow, or from flushing during dormancy of terrestrial vegetation (Stoddard, 1994). While many eutrophic and hypereutrophic freshwater ecosystems have seasonal or perennial cynaobacteria that fix atmospheric N, obviating the need for an external source of N (Wetzel, 2001), we found only one study of an oligotrophic lake with obligate N-fixing bacteria (Reuter et al., 1985). N-fixation is energy expensive and sometimes limited by trace metal availability, so obligate N-fixing cyanobacteria (formerly called blue-green algae) are rarely found in ultra-oligotrophic waters (McKnight et al., 1990; Vitousek and Howarth, 1991). Because of this, oligotrophic and ultraoligotrophic waters are extremely sensitive to even low inputs of N from atmospheric deposition. *Anabaena circinalis*, an obligate N-fixing cyanobacterium, was suppressed with additions of 500 µM/L N (Higley et al., 2001), and DIN levels >~200 µM/L N completely inhibited N fixation in Castle Lake, CA (Reuter et al., 1985).

C.4.5. Nitrate Toxicity: Invertebrates

Toxic responses to N exposure by aquatic invertebrates have been identified in a number of studies. Toxic response thresholds are typically much higher than the levels of N in surface waters that could be attributable to N deposition in the U.S. Safe Concentrations (SC), or threshold values of N, were determined by Camargo and Ward (1995) for several aquatic insects at different life stages. Early instars are generally more sensitive to N in solution than later or adult stages. The SC for late instars of *Hydropsyche occidentalis*, a caddis fly, was found to be 171 µM/L, and concentrations greater than this value induced mortality. The SC was 100 µM/L for early instars of the same species (Camargo and Ward, 1995). Another caddis fly, *Cheumatopsyche pettiti*, tolerated higher concentrations, with safe concentrations of 171 and 250 µM N/L, respectively for early and late instars (Camargo and Ward, 1995). Two species of amphipod did not survive after 120-hr exposure to NO_3^- concentrations of 200 µM N/L for one species, and 314 µM N/L for the other (Camargo et al., 2005). No observable effect concentrations above which *Ceriodaphinia dubia* exhibited reduced reproductive capability ranged broadly in laboratory experiments, but some effects were seen at concentrations greater than 507 µM N/L (Scott and Crunkilton, 2000). A decline in *Daphnia spp.* was observed in mesocosm nutrient enrichment experiments where 75 µM N/L was added, but this was attributed to lower food quality of the algal assemblage that replaced the original species as a result of fertilization (Lafrancois, 2004). Thus, toxic

responses seem to occur at N concentrations that are much higher than the concentrations required to elicit a response in competitive interactions.

A whole-ecosystem experiment at the Bear Brook watershed, ME simulated the effects of N and S deposition by means of experimental $(NH_4)_2SO_4$ addition over a period of 10 years. Researchers found that elevated N inputs had minimal effect on stream detritus processing (Chadwick and Huryn, 2003). They also found that N additions had no significant effect on stream macroinvertebrate secondary production or varying production by functional feeding groups. They concluded that climate-related variables such as flow duration and litter inputs controlled secondary production when N was not limiting (Chadwick and Huryn, 2005).

Changes to aquatic food webs have not been as thoroughly explored as changes to algal assemblages, but a few studies have shown declines in zooplankton biomass (Paul et al., 1995; Lafrancois, 2004) in response to N-related shifts in phytoplankton biomass toward less palatable taxa with higher C:P ratios (Elser et al., 2001). N enrichment of arctic streams not only increased periphyton biomass and productivity, but also stimulated the entire ecosystem, increasing decomposition rates, fungal biomass, and invertebrates (Benstead et al., 2005).

C.4.6. Nitrate Toxicity: Amphibians and Fish

A summary of studies the effects of nitrate on amphibians and fish is given by Table C-6. It appears that very high NO_3^- concentrations in surface water are required to elicit a toxic response in amphibian populations. Concentrations that caused no observed effects and no observed adverse effects ranged from 357 to 714 µM N/L for frogs, salamanders, and the American toad (*Bufo americanus*) (Hecnar, 1995; Laposata and Dunson, 1998; Johansson et al., 2001; Romansic et al., 2006). In one experiment, the red-legged frog (*Rana aurora*) exhibited a decreased susceptibility to *Saprolegnia* mold when exposed to elevated NO_3^- concentrations (Romansic et al., 2006).

According to one review, adverse direct effects of N deposition on fish due to nutrient enrichment are probably minimal (Burns, 2004). N concentrations alone are not high enough to influence fish metabolism, and the extent of eutrophication is insufficient (due to induced P limitation in oligotrophic waters) to cause O_2 depletion.

Other research suggests that the eggs and fry of rainbow trout (*Oncorhyncus mykiss*; including steelhead), cutthroat trout (*O. clarki*), and chinook salmon (*O. tshawytscha*) are susceptible to elevated concentrations of NO_3^-, with rainbow trout mortality occurring after 30 day incubations in concentrations >79 µM N/L (Kincheloe et al., 1979). There were no observed effects reported below this concentration. Chinook salmon and cutthroat trout eggs and fry responded to slightly higher concentrations; no observed effects occurred below 164 µM N/L, but mortality occurred at higher concentrations (Kincheloe et al.,

1979). Lake whitefish (*Coregonus clupeaformis*) and lake trout (*Salvelinus namaycush*) embryos displayed developmental delays at concentrations greater than 446 and 114 µM N/L, respectively (McGurk et al., 2006). All of these toxic threshold concentrations are much higher than the concentrations of NO_3^- in surface water that would routinely be expected to occur solely in response to atmospheric N deposition in the U.S. Nevertheless, such high concentrations of streamwater NO_3^- have been measured in the Great Smoky Mountains, NC (Cook, 1994) and in mixed conifer forests in southern California (Fenn and Poth, 1999).

Table C-6. Summary of effects of N enrichment on aquatic biota in freshwater ecosystems.

Species	Common Name	Life Stage	N Concentration (mg NO_3^- -N/L)	Observed Effects	Reference
Algae					
Phytoplankton					
Asterionella formosa	diatoms		0.252 mg/L	stimulated growth	Saros et al. (Saros, 2005)
Asterionella formosa	diatoms		6.4 umol/L	stimulated growth	McKnight et al. (1990)
Multiple species	diatoms		1.06 mg/L	(low ambient N-deposition):increase in chlorophyll-a content and growth rate; no cell density effect	Lafrancois et al. (Lafrancois, 2004)
Asterionella formosa	diatoms		5.7 × 10−4 (>0.041 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Fragilaria crotonensis	diatoms		0.252 mg/L	stimulated growth	Saros et al. (Saros, 2005)
Multiple species	diatoms		1.06 mg/L	(low ambient N deposition):increase in chlorophyll-a content and growth rate; no cell density effect	Lafrancois et al. (Lafrancois, 2004)
Fragilaria crotonensis	diatoms		3.5 × 10−4 (>0.028 uM) (high light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Fragilaria crotonensis	diatoms		8.4 × 10−6 (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Staurosirella pinnata	diatoms		8.4 × 10−6 (>0.006 uM) (med light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Tetracyclus glans	benthic diatoms		1.7 × 10−4 (>0.012 uM) (low light)	increased growth rate (measured at half the maximum growth rate)	Michel et al. (2006)
Multiple species	phytoplankton assemblages		3.0 uM	N saturation value for maximum diversity in WY low N lakes	Interlandi et al. (1999)
not identified	phytoplankton assemblages		0.5 mg/L	NO3 stimulated growth seasonally, while tributary periphyton communities were P limited	Stanley et al. (1990)
not identified	phytoplankton assemblages		0.3 uM	NH4 additions more effective at stimulating growth than NO3	Levine and Whalen (2001)
not identified	phytoplankton assemblages		100 ug/L	stimulated NO3 uptake	Axler and Reuter (1996)
Multiple species	crysophytes		1.21 mg/L	(elevated ambient N deposition): no response to NO3 additions; increased chlorophyll-a and cell density when NO3 combined with acid and P	Lafrancois et al. (Lafrancois, 2004)
Multiple species	epilimnetic algae		0.012 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)

Species	Common Name	Life Stage	N Concentration (mg NO_3^--N/L)	Observed Effects	Reference
Multiple species	hypolimnetic algae		0.050 mg/L	increased growth rate (measured at half the maximum growth rate)	Priscu et al. (1985)
Periphyton					
	attached benthic algae		0.5 M NaNO3 in 2%agar	biomass increased in response to N and N&P additions during period of seasonal N-limitation (July-August)	Smith and Lee (2006)
	attached benthic algae		2.5 M	NO3 stimulated stream algal growth during seasonal N-limitation	Bushong and Bachmann (1989)
not identified	attached benthic algae		0.5 M NaNO3 in 3%agar	NO3 alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Wold and Hershey (1999)
not identified	attached benthic algae		0.5 M NaNO3 in 3%agar	NO3 alone stimulated stream algal growth during seasonal N-limitation, while N & P co-limited growth in other times	Allen and Hershey (1996)
not identified	attached benthic algae		0.036 mg/L	stimulated NO3 uptake	Axler and Reuter (1996)
not identified	attached benthic algae		0.5 M NaNO3 in 2%agar	no growth response	Higley et al. (2001)
not identified	epilithic		~700 ug NO3-N	suppressed N2-fixation	Reuter et al. (1985)
not identified	attached benthic algae		0.16 mg/L	increased summer growth rate (measured at half the maximum growth rate)	Reuter et al. (1985)
not identified	attached benthic algae		0.32 mg/L	increased winter growth rate (measured at half the maximum growth rate)	Reuter et al. (1986)
not identified	sublittoral epilithic algae		0.259 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	eulittoral epilithic algae		0.126 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
not identified	epipelic algae		0.713 mg/L	increased growth rate (measured at half the maximum growth rate)	Reuter and Axler (1992)
Cyanobacteria					
Anabaena circinalis	N fixing cyanobacteria		0.5 M NaNO3 in 2%agar	decreased abundance	Higley et al. (2001)
Microcycstis sp.	non-N-fixing cyanobacteria		0.28 mg/L	increased growth rate; increased mycrocystin and anatoxin-a concentrations	Gobler et al. (2007)
Invertebrates					
Hydropsyche occidentalis	caddis fly	early instaar	1.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	2.2 (SC)	mortality	Camargo and Ward (1995)
Cheumatopsyche pettiti	caddis fly	early instaar	2.4 (SC)	mortality	Camargo and Ward (1995)
		late instaar	3.5 (SC)	mortality	Camargo and Ward (1995)
Echinogammarus echinosetosus	amphipod	adult	2.8 (120-h LC0.01)	mortality	Camargo et al. (2005)
Eulimnogammarus toletanus	amphipod	adult	4.4 (120-h LC0.01)	mortality	Camargo et al. (2005)
Ceriodaphnia dubia	water flea/cladoceran	adult	7.1-56.5 (7-d NOEC)	decreased reproductive ability; fewer neonates produced per female	Scott and Crunkilton (2000)
Daphnia pulex	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO3	Lafrancois et al. Lafrancois

Species	Common Name	Life Stage	N Concentration (mg NO_3^--N/L)	Observed Effects	Reference
Daphnia schoedleri	Water flea	adult	1.06	(low ambient N-deposition): decreased biomass in response to NO3	Lafrancois et al. (Lafrancois, 2004)
Vertebrates					
Amphibians					
Rana temporaria	common frog	larvae	5 (70-d NOEC)	delayed development, lower growth rate and body mass at metamorphosis	Johansson et al. (2001)
Rana sylvatica	wood frog	fertilized eggs	9 (NOAEL)	no effect of NO3 on survivorship	Laposata and Dunson (1998)
Ambystoma jeffersonianum	Jefferson's salamander	fertilized eggs	9 (NOAEL)	no effect of NO3 on survivorship	Laposata and Dunson (1998)
Ambystoma maculatum	spotted salamander	fertilized eggs	9 (NOAEL)	no effect of NO3 on survivorship	Laposata and Dunson (1998)
Ambystoma gracile	northwestern salamander	larvae	5-20	no effect of NO3 on survivorship	Romansic et al. (2006)
Rana aurora	red-legged frog	larvae	5-20	no effect of NO3 on survivorship; NO3 decreased susceptibility to Saprolegnia mold	Romansic et al. (2006)
Hyla regilla	Pacific tree frog	larvae	5-20	no effect of NO3 on survivorship	Romansic et al. (2006)
Pseudacris triseriata	striped chorus frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
Rana pipiens	northern leopard frog	tadpole	10 (100-d LOEC)	mortality	Hecnar (1995)
Bufo americanus	American toad	fertilized eggs	9.0 (NOAEL)	no effect of NO3 on survivorship	Laposata and Dunson (1998)
Fish					
Oncorynchus mykiss (anadromous)	steelhead	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus mykiss (nonanadromous)	rainbow trout	eggs	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus mykiss (nonanadromous)	rainbow trout	fry	1.1 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Oncorynchus tshawytscha	chinook salmon	fry	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Salmo clarki	cutthroat trout (Lahontan)	eggs	2.3 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Salmo clarki	cutthroat trout (Lahontan)	fry	4.5 (30-d NOEC)	mortality occurred above this value	Kincheloe et al. (1979)
Coregonus clupeaformis	lake whitefish	embryo	6.25 (~120-d NOEC)	hatching and developmental delays	McGurk et al. (2006)
Miscellaneous					
Saprolegnia spp.	pathogenic water mold		5-20 mg NO3/L	decreased ability to infect and kill the larvae of the red-legged frog, Rana aurora	Romansic et al. (2006)

NOEC = No-observed-effect concentration; NOAEL = No-observed-adverse-effect level; SC = Safe concentration

C.5. Estuary and Coastal Ecosystems

There are a variety of factors that govern the sensitivity of estuaries and near-coastal marine waters to eutrophication from atmospheric N deposition. Of critical importance is the total N input from all

sources, including both atmospheric and non-atmospheric sources. Other key elements include the dilution capacity of the watershed, which reflects the volume of water available to dilute added N, and flushing rate, which reflects the time required for inflowing water to replace estuary volume, (Bricker et al., 1999; NRC, 2000). Other potentially important factors can include the following (NRC, 2000):

- Physiography (geomorphology, dominant biological communities, biogeographic province);
- Type of primary production base (i.e., seagrasses, phytoplankton, coral, attached intertidal algae, etc.);
- Stratification and extent to which phytoplankton occupy the nutrient-rich photic zone; and
- Allochthonous inputs of organic matter.

A number of factors control the N loading rates to estuaries and the potential effects of N deposition on nutrient loading and algal blooms. Estuaries communicate with fresh water on the upstream side and with the ocean on the downstream side. The flushing of fresh river water through the system and the movement and mixing of salt water from the ocean are complicated and are always changing in response to weather and tidal cycles. The surface area, volume, and depth of the estuary are also critical factors governing the sensitivity of an estuary to N inputs. Decreases in grazer, filter-feeder, and higher trophic level populations of fish and shellfish exacerbate problems associated with nutrient over-enrichment (Jackson et al., 2001).

At the upstream end of an estuary, the water is primarily fresh much of the time. Discharge of N from the land surface, only a part of which is of atmospheric origin (mainly as deposition to the land that subsequently leached to the river water), dominates new N inputs. Further downstream within the estuary, where fresh water is more thoroughly mixed with saltwater, much of the terrestrial N load is assimilated by phytoplankton and benthic flora or removed by microbes in the process of denitrification (Paerl, 2002). The importance of atmospheric N as a contributor to the total N load beyond this zone probably increases, but there are no data to evaluate that.

The principal watershed features that control the amount of increased N flux to estuaries in the U.S. include human population, agricultural production, and the size of the estuary relative to its drainage basin (Peierls et al., 1991; Caddy, 1993; Fisher et al., 2006). Dense human populations generate large volumes of nutrient-rich wastewater. Tertiary sewage treatment can reduce effluent N concentrations to less than 35 µM, but these technologies have not been promoted as aggressively in the U.S. as elsewhere (Conley et al., 2002; EPA, 2003). Agricultural production is heavily dependent on fertilizer application to generate high yields from small areas. Fertilizer application has dramatically increased NO_3^- concentrations in ground water in many agricultural areas (Bohlke and Denver, 1995), which can leach to

surface waters. Large terrestrial drainage basins that drain into small estuaries tend to have high nutrient flux if the land is heavily populated or used for agriculture.

In addition to estuaries, coastal marine ecosystems are highly susceptible to nutrient enrichment, especially from N. Land clearing, agricultural land use, sewage treatment discharge, and atmospheric deposition can all result in high loadings of N to the coastal zone. Excessive N inputs contribute to a range of impacts, including enhanced algal blooms, decreased distribution of seagrasses, and decreased dissolved oxygen (DO) concentration (Valiela et al., 1992; Nixon, 1995; Borum, 1996; Bricker, 1999). Because of human population growth and the great popularity of coastal areas, there is substantial potential for increased N loading to coastal ecosystems from both atmospheric and non-atmospheric sources.

C.5.1. Interacting Factors with Productivity

Results of empirical observations and short-term (3 weeks) marine mesocosm experiments suggest that there can be wide variation in the response of autotroph biomass to nutrient addition (Cloern, 2001; Olsen et al., 2006). Such variation may be attributable to the time scale of the observations, rate of water exchange, grazing pressure, and other environmental factors (Olsen et al., 2006).

C.5.2. Hydrology Interactions with Phytoplankton Biomass

River discharge has a huge influence on the hydrology and nutrient cycling of estuaries. For example, discharge from the large watershed of the Susquehanna River is important to the seasonal and interannual variability in the hydrology of Chesapeake Bay (Fisher et al., 1988; Malone et al., 1988). When discharge from the Susquehanna River is low, summer phytoplankton biomass in Chesapeake Bay tends to be low compared to spring conditions, and the phytoplankton community is dominated by small and flagellated forms (Marshall and Lacouture, 1986). Under higher river flows, summer phytoplankton biomass in the bay is higher, and has an increased prevalence of diatoms (Paerl et al., 2006).

Hydrologic variation interacts with nutrient supply to control phytoplankton seasonal patterns in Chesapeake Bay. High biomass during the spring diatom bloom leads to consequent sedimentation of organic material out of the photic zone during the transition to summer (Malone et al., 1996; Harding et al., 2002). Microbial decomposition of this material then fuels the pattern of summer anoxia in bottom waters (Paerl et al., 2006). N loading to Chesapeake Bay and its tributaries during spring high runoff periods contributes to periods of P limitation and co-limitation (Boynton et al., 1995). The ecosystem then returns to N limitation during low flow summer months (Paerl, 2002).

C.6. Effects on Watersheds and Landscapes

C.6.1. Interactions among Terrestrial, Transitional, and Aquatic Ecosystems

Streams, and to a lesser extent lakes, can serve as indicators of regional environmental change (Seastedt et al., 2004), partly because they integrate conditions within their watersheds including atmospheric, edaphic, geologic, and hydrologic conditions. Streams reflect the terrestrial environment most closely during high flow when much of the stream water enters the channel from the upper soil where most of the biological activity occurs. The terrestrial signal can be less clear in lakes because they have the capacity to store water and modify water chemistry through internal processes to a greater degree than streams (Lawrence et al., in review).

Young and Sanzone (2002) provided a checklist of ecological attributes that should be considered when evaluating the effects of an environmental stressor on the integrity of ecological systems (Table C-7). The Essential Ecological Attributes (EEAs) listed in the table represent groups of related ecological characteristics (Harwell et al., 1999), including landscape condition, biotic condition, chemical and physical characteristics, ecological processes, hydrology and geomorphology, and natural disturbance regimes. The first three ecological attributes listed in Table C-7 can be classified primarily as "patterns," whereas the last three are "processes" (cf. Bormann and Likens, 1979). They can be affected by a variety of environmental stressors (Figure C-4).

Of concern in this annex are relationships between NO_X atmospheric deposition, derived from anthropogenic sources, and one or more of the EEAs. The ranges of likely changes in ecosystem patterns and processes associated with changes in deposition are discussed in the subsections that follow.

The following discussion assesses and characterizes the overall condition or integrity of ecosystems within the U.S. that are affected by the deposition of atmospheric N and its role as a nutrient. The six EEAs – landscape condition, biotic condition, chemical/physical characteristics, ecological processes, hydrology/geomorphology, and natural disturbance regimes (Table C-7) – provide a hierarchical framework for assessing ecosystem status. Characteristics related to structure, composition, or functioning of ecological systems may be determined by the use of endpoints or ecological indicators of condition that are measureable and significant either ecologically or to society (Harwell et al., 1999).

Table C-7. Essential ecological attributes and reporting categories

Landscape Condition	Ecological Processes
Extent of Ecological System/Habitat Types	Energy Flow
Landscape Composition	Primary Production
Landscape Pattern and Structure	Net Ecosystem Production
Biotic Condition	Growth Efficiency
Ecosystems and Communities	Material Flow
Community Extent	Organic Carbon Cycling
Community Composition	N and P Cycling
Trophic Structure	Other Nutrient Cycling
Community Dynamics	**Hydrology and Geomorphology**
Physical Structure	Surface and Groundwater flows
Species and Populations	Pattern of Surface flows
Population Size	Hydrodynamics
Genetic Diversity	Pattern of Groundwater flows
Population Structure	Salinity Patterns
Population Dynamics	Water Storage
Habitat Suitability	Dynamic Structural Characteristics
Organism Condition	Channel/Shoreline Morphology, Complexity
Physiological Status	Extent/Distribution of Connected Floodplain
Symptoms of Disease or Trauma	Aquatic Physical Habitat Complexity
Signs of Disease	Sediment and Material Transport
Chemical and Physical Characteristics	Sediment Supply/Movement
(Water, Air, Soil, and Sediment)	Particle Size Distribution Patterns
Nutrient Concentrations	Other Material Flux
N	**Natural Disturbance Regimes**
P	Frequency
Other Nutrients	Intensity
Trace Inorganic and Organic Chemicals	Extent
Metals	Duration
Other Trace Elements	
Organic Compounds	
Other Chemical Parameters	
pH	
Dissolved O_2	
Salinity	
Organic Matter	
Other	
Physical Parameters	

Source: Young and Sanzone (2002).

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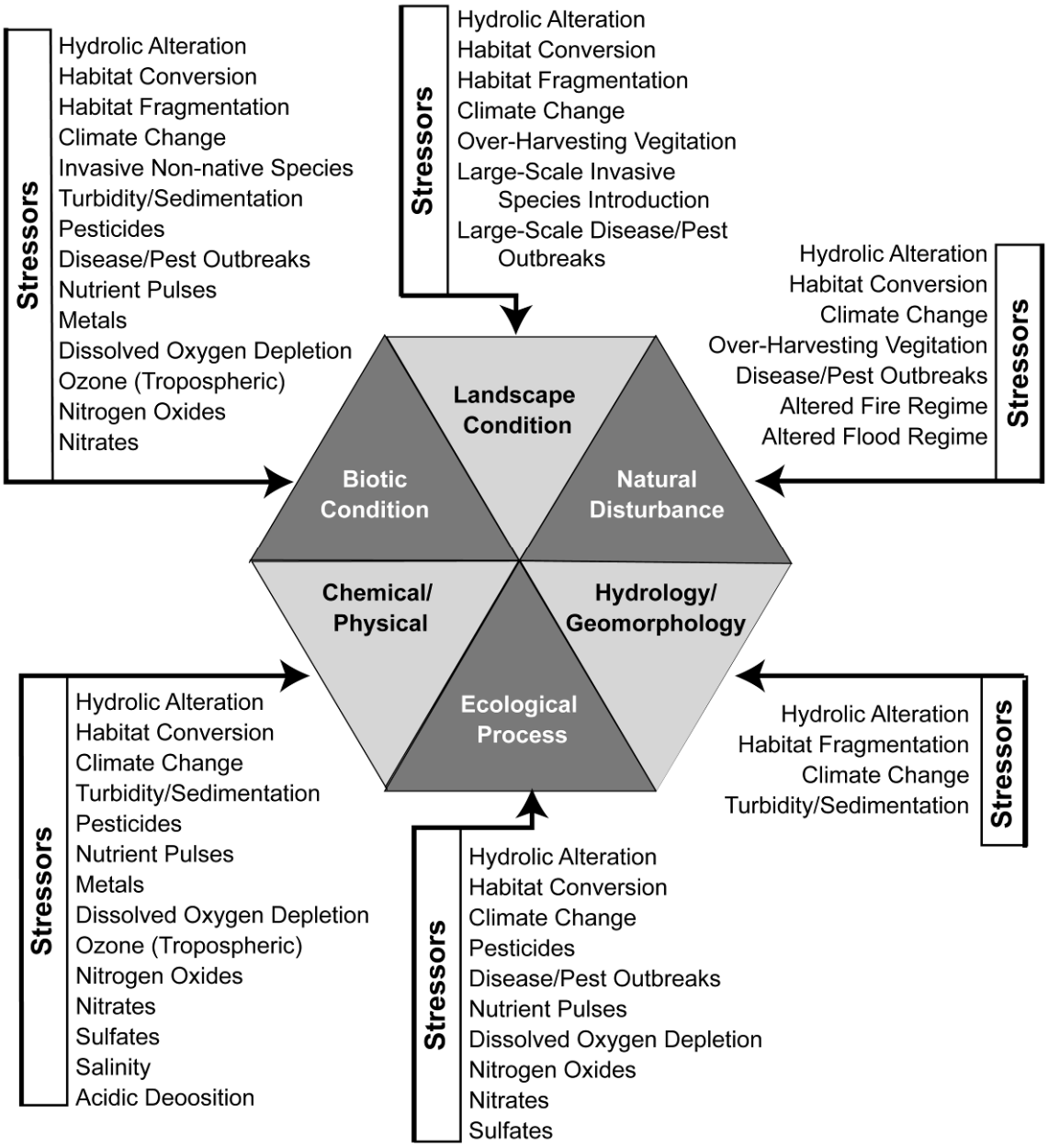

Figure C-4. Sample stressors and the essential ecological attributes they affect.

Source: Young and Sanzone (2002).

The relationships among the EEAs are complex because all are interrelated. Changes in one EEA may affect, directly or indirectly, every other EEA. Ecological processes create and maintain environmental patterns, and these patterns affect how the processes are expressed (Young and Sanzone, 2002). Changes in patterns or processes can result in changes in the status and functioning of an ecosystem.

Changes in the biodiversity, composition, and structure of ecosystems relate directly to functional integrity. Changes in biodiversity are of particular significance in altering ecosystem function. The energy obtained by plants (producers) from sunlight during photosynthesis and the chemical nutrients taken up by those plants from the soil and the atmosphere are transferred to other species (consumers) within the ecosystem through food webs. The movement of chemical nutrients through an ecosystem is cyclic, as the nutrients are used or stored and eventually returned to the soil by microorganisms and fungi (decomposers). Energy is transferred among organisms through the food webs and eventually is dissipated into the environment as heat. The flows of energy and cycling of nutrients provide the interconnectedness among the elements of the ecosystem and transform the community from a random collection of numerous species into an integrated whole.

Human existence and welfare on this planet depend on life-support services provided by the interaction of the EEAs. Both ecosystem structure and function play essential roles in providing goods and services (Table C-8) (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. 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). See discussion in Annex F.

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, 1997b; EPA, 2004). The deposition of nutrient N from the atmosphere has the potential to alter ecosystem structure and function by altering nutrient cycling and changing biodiversity. It is important to understand how ecosystems respond to stress to determine the extent to which anthropogenic stresses, including N deposition, affect ecosystem services and products (Table C-8).

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 (Figure C-5) (Pimm, 1984; Tilman and Downing, 1994; Tilman, 1996; Chapin et al., 1998; Levlin, 1998; Peterson et al., 1998; Daily and Ehrlich, 1999; Wall, 1999).

Table C-8. Primary goods and services provided by ecosystems.

Ecosystem	Goods	Services
Agroecosystems	Food crops Fiber crops Crop genetic resources	Maintain limited watershed functions (infiltration, flow control, and partial soil protection) Provide habitat for birds, pollinators, and soil organisms important to agriculture Sequester atmospheric carbon Provide employment
Coastal Ecosystems	Fish and shellfish Fishmeat (animal feed) Seaweeds (for food and industrial use) Salt Genetic resources	Moderate storm impacts (mangroves, barrier islands) Provide wildlife (marine and terrestrial (habitat and breeding areas/hatcheries/nurseries 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 Fuelwood Drinking and irrigation water Fodder Nontimber 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 recreation

Source: World Resources Institute (2000).

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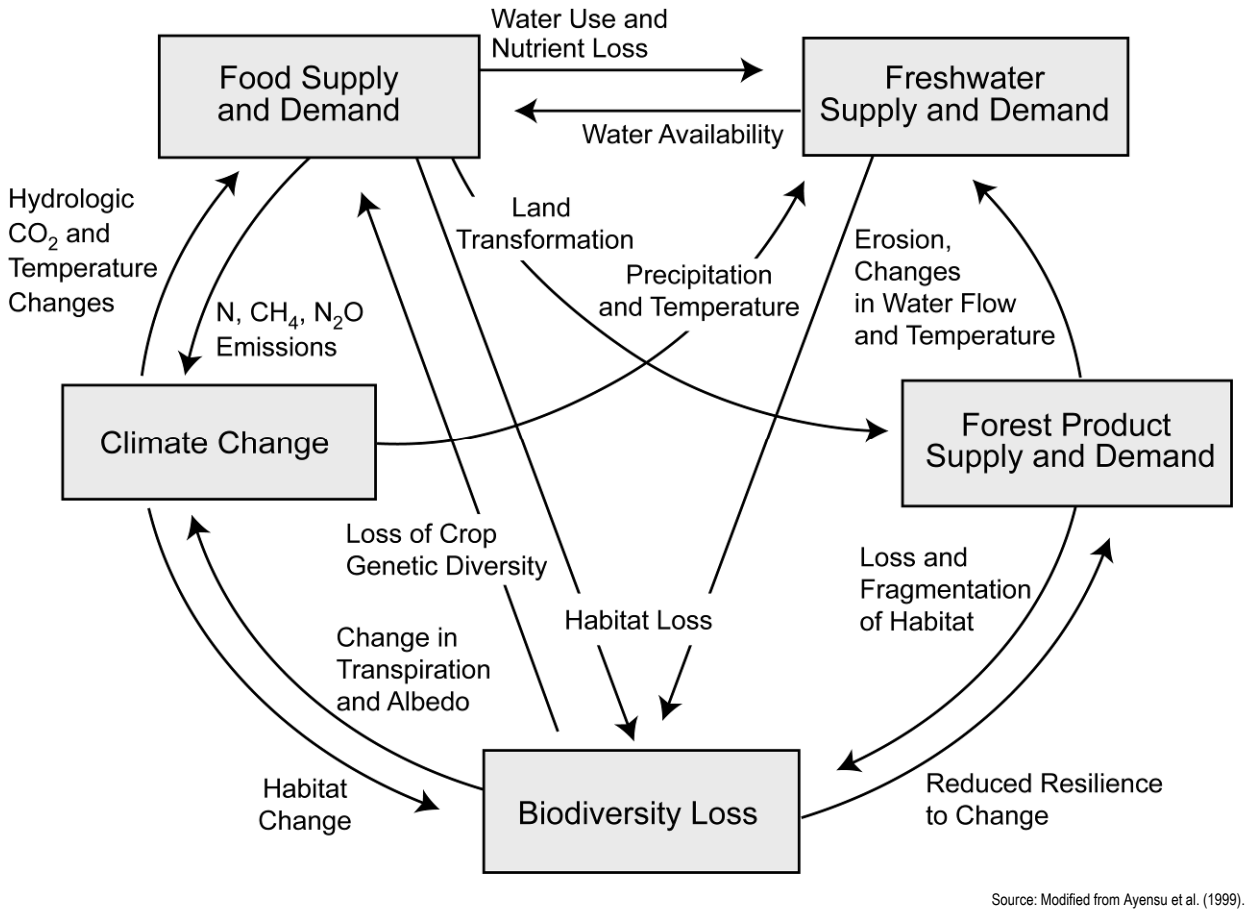

Source: Modified from Ayensu et al. (1999).

Figure C-5 Linkages among various ecosystem goods and services (food, water, biodiversity, forest products) and other driving forces (climate change).

C.6.2. Interactions with Land Use and Disturbance

Scientific understanding of N cycling in forested watersheds is complicated by ecosystem response to climatic variation, human land use, and various kinds of landscape disturbance, including insect infestation, wind storm, fire, and disease (Aber and Driscoll, 1997; Goodale, 2000) Mitchell et al., 2006). N dynamics in watersheds of mixed land use (i.e., agriculture, urban, forest) are even more complicated. It is clear that disturbances have major impacts on nutrient enrichment from N deposition, and that these effects can be long-lasting. Nevertheless, the scientific community is only in the early stages of learning how to quantify these interactions.

Changes in land use can affect nutrient heterogeneity in the mineral soil of forest stands. For example, Fraterrigo et al. (2005) found that patterns of variance in soil C, N, and Ca^{2+} concentration increased with the extent of intensive past land use in western North Carolina. Land use might alter the local patchiness of soil nutrients by decoupling interactions among microclimate, topography, vegetation, and soil biota. In particular, mechanical soil mixing and maintenance of agricultural monocultures can

homogenize soils in cultivated systems (Robertson et al., 1993; Paz-Gonzalez and Taboada, 2000). Such effects may be important if the land use is changed to forest. Similarly, changes in species composition can alter the spatial distribution of nutrients in litter inputs (Dijkstra and Smits, 2002; Fraterrigo et al., 2005).

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. In a comparison of small watersheds in eastern New York, concentrations of N were highest and most variable in a stream draining a watershed where the predominant land use was row crop production. Total dissolved N concentration in streams in sewered suburban and urban watersheds were somewhat lower and less variable than in streams draining the agricultural watershed. Streams in urban and suburban watersheds may also experience high episodic N loading caused by combined sewer overflows (Driscoll et al., 2003c).

C.6.3. Timber Harvest and Fire

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). The extent of nutrient loss is determined, at least in part, by the intensity of the logging and whether or not it is accompanied by fire (Latty, 2004). The species composition of the regrowth vegetation also has important effects on nutrient cycling. Fire is sometimes followed by establishment of N-fixing vegetation that provides substantial sources of N_r (Johnson, 1995; Johnson et al., 2004). Tree species also vary dramatically in their N cycling properties, especially in their influence on litter mass and quality (Finzi et al., 1998; Ferrari, 1999; Ollinger, 2002). Thus, over time, the extent of effect of logging and fire on nutrient cycling can increase, depending largely on shifts in tree species composition and the degree to which C and N pools are altered in the mineral soil and the forest floor.

Dissolved N exports have been clearly shown to increase substantially after major watershed disturbance, often reaching peak concentrations in streamwater within 1 to 3 years of disturbance, and then returning to background concentrations after about 5 to 10 years (Likens et al., 1978; Bormann and Likens, 1979; Eshleman et al., 2000). Such transient NO_3^- leakage has been shown to occur subsequent to both logging (Martin et al., 1984; Dahlgren and Driscoll, 1994; Yeakley et al., 2003) and insect infestation (Eshleman et al., 1998, 2004).

The extent to which timber harvesting influences leaching of NO_3^- and base cations from soils to drainage waters depends on changes in primary productivity, nutrient uptake by plants and microorganisms within the terrestrial ecosystem, and hydrological pathways for transferring nutrients to drainage water (Hazlett et al., 2007). Because of the variety of responses and interactions of

environmental and forest litter and soil conditions, it is difficult to generalize about the influence of harvesting on N cycling (Grenon et al., 2004; Hazlett et al., 2007).

We do know, however, that land use history constitutes a major influence on N leaching from forested watersheds that receive moderate to high levels of atmospheric N deposition (Pardo, 1995; Aber and Driscoll, 1997; Goodale, 2000; Lovett et al., 2000). The severity of effect and length of the recovery period probably vary according to the nature of the past disturbance. Extensive past logging appears to have considerable and long-lasting effects on nutrient cycling (Goodale and Aber, 2001; Fisk et al., 2002). Latty et al. (2004) compared soil nutrient pools and N cycling among three forest stands in the Adirondack Mountains: old growth, selectively logged, and selectively logged and then burned. The logging and fire had occurred about 100 years previously. Results suggested that even relatively light logging, plus burning, may influence the extent of subsequent N limitation over time scales of decades to centuries (Latty, 2004). Models of forest ecosystem response to disturbance incorporate such long-lasting effects of land use on C and N storage, cycling, and release (Aber et al., 1997).

Chen and Driscoll (2004) simulated the response of five forested watersheds in the Adirondack and Catskill regions of New York to changes in atmospheric deposition and land disturbance. Simulation results suggested that forest harvesting caused increased leaching of base cations and NO_3^- from the watersheds. These changes also affected model projections of future pH and acid neutralizing capacity (ANC) of lake water. Model results suggested that lakewater pH and ANC were lower in response to forest cutting as compared with undisturbed conditions.

Nitrification rates at old growth sites in the White Mountains of New Hampshire (63 ± 4.3 kg N/ha/yr) were approximately double those at previously burned (34 ± 4.4 kg N/ha/yr) and previously logged (29 ± 4.7 kg N/ha/yr) sites (Goodale, 2001). Fire and logging disturbances had occurred about 100 years previously on these study sites. Nitrification increased as forest floor C:N ratio decreased, resulting in higher NO_3^- concentrations in streamwater. These results suggest that forest disturbance can have long-lasting effects on N cycling and the potential for N saturation.

Thus, disturbance can affect N cycling and the response of forest ecosystems to N deposition. In addition, it also appears that vegetative changes stimulated by N deposition may affect the frequency and severity of disturbance. Excess N_r deposition is thought to be impacting essential ecological attributes associated with terrestrial ecosystems and how they respond to disturbance. Effects of N_r deposition influence habitat suitability, genetic diversity, community dynamics and composition, nutrient status, energy and nutrient cycling, and frequency and intensity of natural fire disturbance regimes. For example, 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 coastal sage shrub (CSS) to grassland in California (Minnich and Dezzani, 1998).

High grass biomass has also been associated with increased fire frequency in the Mojave 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).

C.6.4. Insect Infestation and Disease

Insect infestation and plant disease, via atmospheric N deposition, can alter the effects of nutrient enrichment on forest ecosystems. Such disturbances alter the pool of N_r in the forest floor with short-term impacts on NO_3^- and base cation leaching. Positive influences of N deposition on root and seed biomass of an annual plant, common ragweed, were suppressed by herbivory, which increased with higher available plant shoot N (Throop, 2005).

Eshleman et al. (2004) applied a regional lithology-based unit N export response function model to simulate NO_3^- export to streams in the Chesapeake Bay watershed. The model considered the geographic distribution of bedrock classes and the timing and extent of defoliation by gypsy moth (*Lymantria dispar*) larvae. Modeling results suggested that the regional annual NO_3^--N export increased during the year following peak insect defoliation by about 1500%, from an initial rate of 0.1 kg N/ha/yr to nearly 1.5 kg N/ha/yr.

Between the mid-1980s and the early 1990s, the southward expanding range of the gypsy moth traversed Shenandoah National Park, VA (Webb, 1999). Some areas of the park were heavily defoliated 2 to 3 years in a row. The White Oak Run watershed, for example, was more than 90% defoliated in both 1991 and 1992. The gypsy moth population in White Oak Run then collapsed due to pathogen outbreak. This insect infestation of the forest ecosystem resulted in substantial effects on streamwater chemistry. The most notable effects of the defoliation on park streams were dramatic increases in the concentration and export of N and base cations in streamwater. Figure C-6 shows the increase in NO_3^- export that occurred in White Oak Run. Following defoliation, NO_3^- export increased to previously unobserved levels and remained high for over 6 years before returning to predefoliation levels. The very low baseline levels of NO_3^- export in park streams were consistent with expectations for N-limited, regenerating forests (e.g., Aber, 1989; Stoddard, 1994). Release of NO_3^- to surface waters following defoliation was likewise consistent with previous observations of increased N export due to forest disturbance (e.g.,

Likens et al., 1970; Swank, 1988). The exact mechanisms have not been determined, but it is evident that the repeated consumption and processing of foliage by the gypsy moth larva disrupted the ordinarily tight cycling of N in the forests within this park.

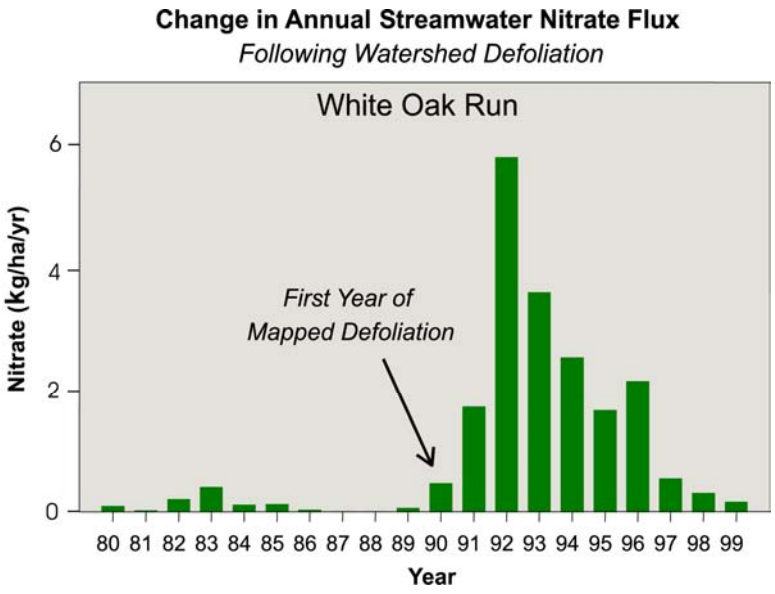

Figure C-6. Effect of watershed defoliation by the gypsy moth caterpillar on NO_3^- flux in streamwater.

White Oak Run was heavily defoliated for three consecutive years. The watershed area defoliated was 46.5% in 1990, 92.9% in 1991, and 90.4% in 1992. In 1993, the gypsy moth population collapsed and there was no further defoliation.

Source: Sullivan et al. (2003).

The elevated concentrations of NO_3^- following defoliation did not appear to contribute to baseflow acidification in White Oak Run. This was due to a concurrent increase in concentrations of base cations in streamwater (Webb et al., 1995). Both NO_3^- and base cation concentrations also increased during high-runoff conditions, although the increase in base cations did not fully compensate for the episodic increase in NO_3^-. As a consequence, episodic acidification became more frequent and more extreme (Webb et al., 1995).

Large trees in old growth forests may resorb less N from foliage than do younger trees on previously logged or burned sites (cf. Killingbeck, 1996). This process would be expected to contribute to an alleviation of N limitation on plant processes in old-growth forests (Latty, 2004). This effect might also extend to herbivores, which are often N-limited (Mattson, 1980). Latty et al. (Latty, 2004) attributed the high severity of beech bark disease in old growth forests to such a mechanism. Beech bark disease is

caused by an introduced scale insect (*Crytococcus fagisuga*), which has high N requirements (Wargo, 1988; Houston, 1994). The N-rich foliage in the old growth forest may improve insect fitness, contributing to a higher rate of infestation in the old growth stands (Latty, 2004).

Source: Sullivan et al. (2003).

C.6.5. Urbanization

Perhaps the most noteworthy impact of urban land use on processes of nutrient enrichment from N deposition concerns the transport of Nr to N-limited estuarine and near-coastal waters. In agricultural, and especially in forested areas, it is generally expected that most atmospherically deposited N is taken up by terrestrial vegetation. Relatively little of the deposited N is available for transport to downstream receiving waters. This is not the case for urban land use. Urbanization often involves substantial clearing of vegetation and compaction of soil (Poff et al., 1997; Burges et al., 1998; Jones et al., 2000; Trombulak and Frissell, 2000; Alberti et al., 2007). Due to the relatively large impervious surface area in the urban landscape (buildings, roads, parking lots, etc.), a higher percentage of precipitation is routed directly to surface waters, with less opportunity for vegetative uptake of deposited N (Arnold and Gibbons, 1996; Montgomery and Buffington, 1998). Therefore, atmospheric N deposition contributes proportionately more NO_3^- to surface waters in urban settings than it does with other land uses. The reduction in riparian and wetland coverage and functionality also diminishes the ability of the urban watershed to filter contaminants from runoff, including atmospherically deposited N (Peterjohn and Correll, 1984). Because many large urban areas are both located close to the coastline and expected to receive relatively high NO_X deposition, they can constitute sizeable sources of body contribution to estuarine and marine waters.

C.6.6. Agriculture

Agricultural ecosystems are not sensitive to levels of N deposition typically found in the U.S. Rather, such ecosystems often act as net sources of NH_3 emissions rather than as sinks (Grünhage et al., 1992; Krupa, 2003). Atmospheric N deposition can contribute a quantitatively important component of the N_r requirements of pastures and croplands. In such settings, atmospheric N deposition provides an additional chronic source of N fertilizer. This may be viewed as a beneficial outcome. Nevertheless, some of the N that is atmospherically deposited on agricultural land may eventually leach to drainage waters and contribute to eutrophication, especially in estuarine and near-coastal marine environments. Industrial livestock operations also contribute substantial amounts of NH_Y to the atmosphere, some of which is deposited on coastal waters.

Agriculture also experiences indirect effects of NO_X emissions through the formation of ground-level O_3. Such effects are not considered in this review.

C.6.7. Other Disturbances

In some ecosystems, chronic additions of atmospherically derived N may have had irreversible consequences that involve interactions with invasive, non-native plants. For example, California has many plant species that occur in shrub, forb, and grasslands that receive high N deposition. There are up to 200 sensitive plant species in southern California coastal sage scrub (CSS) communities alone (Skinner and Pavlik, 1994). About 25 plant species are thought to be extinct in California, most of them forbs that occurred in sites that have experienced conversion to annual grassland (EPA, 2005). As CSS vegetation continues to convert to grassland dominated by invasive species, loss of additional rare plant species may occur. Invasive plant species are often identified as a major threat to rare native plant species. However, the occurrence of invasive species may combine with other stress factors, including N deposition, to promote increased productivity of invasive species at the expense of native species.

As sensitive vegetation is lost, wildlife species that depend on these plants can also be adversely affected. There are several threatened or endangered wildlife species listed by the U.S. Fish and Wildlife Service, including the desert tortoise (*Gopherus agassizii*) and checkerspot butterfly that are native to plant communities in California thought to be sensitive to atmospheric N input. A native to the San Francisco Bay area, the bay checkerspot butterfly has declined in association with invasion of exotic grasses that replaced the native forbs on which the butterfly depends. In particular, the larval stage of the butterfly is dependent on *Plantago erecta*, which is increasingly being outcompeted by exotic grasses (EPA, 2005).

Decline in the population of the desert tortoise may be due to a number of co-occurring stresses, including grazing, habitat destruction, drought, disease, and a declining food base. In the desert shrub inter-spaces, sites where native forbs once flourished, invasive grasses now dominate, reducing the nutritional quality of foods available to the tortoise (Nagy et al., 1998; Fenn, 2003a). N deposition contributes to the productivity and density of grasses at the expense of native forbs (Brooks, 2003).

C.6.8. Multiple Stress Response

Ecosystems are often subjected to multiple stressors, of which nutrient enrichment from atmospheric deposition of N is only one. Additional stressors are also important, including O_3 exposure, climatic variation, natural and human disturbance, the occurrence of invasive non-native plants, native and non-native insect pests, and disease. Atmospheric N deposition interacts with these other stressors to affect ecosystem patterns and processes in ways that we are only beginning to understand.

For example, terrestrial ecosystems at many locations are subjected to high N deposition and high exposure to O_3. This is especially true in portions of southern California and the Appalachian Mountains. Mixed conifer forests in the San Bernardino and San Gabriel mountains in southern California are

exposed to high levels of atmospheric O_3 and receive atmospheric N deposition in the range of about 5 to over 30 kg/ha/yr (Takemoto et al., 2001). Spatial variability in N deposition is high due to the patchy characteristics of these forests and associated canopy effects on dry deposition processes. The forest ecosystems have reached N-saturation, as evidenced by high NO_3^- concentrations in stream water. However, evaluation of N effects on vegetation is complicated by the concurrent effects of O_3, which has damaged sensitive plant species, especially ponderosa and Jeffrey pine. Bytnerowicz (Bytnerowicz, 2002) summarized N/O_3 interactions and consequent effects.

Peak diurnal concentrations of atmospheric O_3 and NO_2 co-occur at Tanbork Flat in the San Bernardino Mountains (Bytnerowicz et al., 1987). They can have counteracting effects, with O_3 reducing growth and N deposition enhancing growth of pine trees (Grulke and Balduman, 1999).

Jeffrey and ponderosa pine are the most sensitive western coniferous tree species to injury from O_3 pollution (Miller et al., 1983; Duriscoe and Stolte, 1989). In some areas of the western Sierra Nevada Mountains, O_3 concentrations have been high enough to cause visible foliar injury to these species and reduced needle retention (Bytnerowicz, 2002). Reduced radial growth has also been observed (Peterson et al., 1987, 1991). In the San Bernardino Mountains, trees of these species that exhibit severe foliar injury from O_3 do not show growth reductions (Arbaugh et al., 1999), and this has been attributed to the fertilizing effects of high N deposition (Takemoto et al., 2001; Bytnerowicz, 2002). This may be an example of counteracting effects from O_3 and N air pollution. It is also possible that N deposition in the western Sierra Nevada Mountains may increase growth of pines, especially on nutritionally poor granitic soils (Takemoto et al., 2001).

Table C-9. Ecological effects of N deposition described for study sites 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. (1996), Fenn and Poth (1999), Fenn et al. (Fenn, 2003)
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. (2003a)

Ecological or Environmental Impact	Location	Level of Uncertainty	Possibility of Broader Occurrence (at other sites)	Reference
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 NO3– levels. There is also evidence of impacts on low-elevation lakes.	Sickman et al. (2002)
Effects in Terrestrial Systems				
Enhanced growth of invasive species	Costal sage scrub, southern California; San Francisco Bay area	N deposition, fertilization studies, and plant community data supportive, but moderate uncertainty remains	It is not known if this effect occurs elsewhere, but it is expected that nitrophilous species will be selected for if N accumulates in soil.	Weiss (1999), Allen et al. (in press)
Lichen community changes	Parts of the Pacific Northwest; many areas in California; north and central Colorado	Well-established response; a highly sensitive air pollution indicator	Because of the sensitivity of many lichen species, it is likely that this effect occurs elsewhere.	Nash and Sigal (Nash, 1999)
Deleterious effects on threatened and endangered species	San Francisco Bay area; southern California	Supportive evidence, but high degree of uncertainty about the precise role of N deposition	There is a high likelihood of effects in some habitats where N accumulates in soils	Weiss (1999), Brooks (2003)
Altered fire cycle	Coastal sage scrub in southern California	Hypothesis based on observations, fertilization studies, and N deposition and N cycling data; high level of uncertainty	Because it has not been studied elsewhere, it is uncertain whether this effect occurs in other areas.	Allen et al. (in press)
Altered forest C cycling and fuel accumulation	San Bernardino Mountains	Documented response	It is uncertain whether this effect occurs in other areas.	Grulke and Balduman (1999)
Physiological perturbation of overstory species	San Bernardino Mountains	Documented response	This effect has not been widely studied but is expected for sensitive plant species exposed to O_3 and adapted to N limitation but growing in N-enriched soils.	Grulke et al. (1998), Grulke and Balduman (1999), Takemoto et al. (2001)
Forest expansion into grasslands	Great Plains of western Canada	Supportive evidence found, but high degree of uncertainty as to the role of N deposition	It is not know whether this effect occurs in other areas.	Köchy and Wilson (2001)
N emissions as a major contributor to regional haze problem	National forests and parks throughout California, the Pacific Northwest, and some sites in the Interior West	Well-established effect; contribution from Nous pollutants has been quantified	This is known to occur in areas far removed from emissions sources because of long-range transport.	Fenn et al. (2003c), IMPROVE data (4 March 2003; http://vista.circa.colostate.edu/improve)
NO_X emissions as precursors for phytotoxic levels of O_3, leading to O_3 injury to sensitive plant species	Southern California; Sierra Nevada	Well-established effect	Significant O_3 injury to vegetation has not been reported from other sites downwind of urban centers but cannot be ruled out as urban regions expand.	Miller and McBride (1999), Carroll et al. (2003)

Note: Summary includes the degree of uncertainty regarding the role of N deposition in each effect and the likelihood that these effects may occur elsewhere in the West.

ANNEX C - References

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Annex D. Critical Loads

D.1. Background

Critical loads and critical levels are used to express how much deposition of an atmospheric pollutant (a "load") or how large a concentration of an airborne pollutant (a "level") can be tolerated by natural or artificial systems without significant harm or change occurring in those systems (see Section D.2.1). The critical load and critical level approaches to quantifying the effects of pollutants attempt to estimate the atmospheric deposition load or concentration that would be likely to cause environmental harm. The expectation is that environmental harm can be avoided by keeping pollution levels or loads below these critical values. This approach is commonly used to estimate loads or levels of pollution required to protect lakes, streams, or forest soils from environmental harm. The basic principles are, however, transferable to any sensitive receptor. Since the present evaluation deals primarily with the effects of atmospheric deposition of S and N compounds, this chapter focuses on critical loads more than critical levels.

Most critical load studies in North America have been undertaken in Canada. The critical load approach has been used in Canada to design emission reduction programs (RMCC, 1990; Jeffries, 1993). Modeling of critical loads for the 1997 Canadian Acid Rain Assessment (Jeffries, 1997) was conducted for six regional clusters of lakes, four in eastern Canada, one in Alberta, but also the Adirondack Mountains in New York. More recently, critical loads have been determined and mapped for waters (Hindar, 2001; Henriksen, 2002; Aherne, 2004; Dupont, 2005; Watmough, 2005) and forest soils (Arp, 1996; Moayeri, 2001; Watmough, 2003; Ouimet, 2006), for a number of regions in eastern Canada. There have also been a number of regional critical loads studies (cf. Henriksen, 2001; Ouimet, 2006) focused on acid-sensitive lakes on the Canadian pre-Cambrian shield. Much of this work is summarized and presented, along with steady state critical load maps for eastern Canada, in the 2004 Canadian Acid Deposition Science Assessment (Jeffries, 2005).

At the regional, cross-border level, critical loads in northeastern North America have been developed by a joint U.S.-Canadian cooperative. The Conference of New England Governors and Eastern Canadian Premiers (NEG/ECP) has undertaken a program with the objective to "estimate sustainable acidic deposition rates and exceedances for upland forests representative of the New England States and the Eastern Canadian Provinces…" (NEG/ECP Forest Mapping Group, 2001). The Forest Mapping Working Group within the NEG/ECP conducts regional assessments of the sensitivity of northeastern North American forests to current and projected S and N emissions levels. The group is charged with identifying specific forested areas most sensitive to continued S and N deposition and estimating

deposition rates required to maintain forest health and productivity at large spatial scales (cf. Miller, 2006). The NEG/ECP has also provided estimates of critical loads for surface waters in northeastern North America (Dupont, 2005).

Aside from the NEG/ECP studies, the use of critical loads to assess S and N deposition effects in the U.S. has not been as geographically extensive as elsewhere in North America or Europe. Most critical loads studies in the U.S. have focused on smaller sub-regional areas or individual sites. Critical loads studies for forests in the U.S. have been centered in the northeast and have usually used a catchment-based approach (Pardo, 1993; Pardo, 1996; cf. Aber, 2003; Driscoll, 2003). Critical load studies for surface waters have been more extensive along the eastern seaboard. Critical loads have been estimated for lakes in the Northeast (cf. Driscoll, 2001; Pembrook, 2004) and for streams in the Mid-Atlantic States and central Appalachians (cf. Sverdrup et al., 1992; Sullivan et al., 2004). In the western U.S. there have been a few studies of critical loads for acidification of surface waters (cf. Sullivan et al., 2004). The primary concern in the West, however, has been the critical load of N deposition affecting both terrestrial and aquatic resources through eutrophication and/or through N enrichment and its impact on community structure (cf. Baron, 1994; Baron, 2000); Williams and Tonnessen, 2000; Fenn et al., 2003; Nydick et al., 2003, 2004a; Wolfe et al., 2003; Burns, 2004; Stevens, 2004; Baron, 2006); Bowman et al., 2006).

The critical load approach has been used extensively in Europe for organizing information about effects, and for specifying emissions reductions that would be required to protect ecosystems and other sensitive receptors from the harmful effects of atmospheric S N deposition. During the 1970s, it was recognized that transboundary air pollution in Europe had adverse ecological and economic consequences. In response, the countries of the UN Economic Commission for Europe (UNECE) developed the Convention on Long-range Transboundary Air Pollution (LRTAP), the first international legally binding instrument to deal with problems of air pollution on a broad regional basis (see http://www.unece.org/env/lrtap). Signed in 1979, it entered into force in 1983. The LRTAP Convention requires that its Parties cooperate in research into the effects of S compounds and other major air pollutants on the environment, including agriculture, forestry, natural vegetation, aquatic ecosystems, and materials. To this end, the Executive Body for the Convention established a Working Group on Effects (WGE) that is supported by a number of International Cooperative Programmes (ICPs). The ICP for Mapping and Modeling generated maps of critical loads for all of Europe in 1995 (Posch et al. 1995). Those maps are modified on a continuing basis (e.g. Posch et al. 2001). By comparing current or expected future deposition to the critical loads maps, mapped estimates of exceedances have been generated. An exceedance is the amount of S and N deposition that occurs at some specific time (past, current, or future), above the critical load of deposition that would be required to protect against adverse effects on the environment. The maps of estimated exceedances are used in negotiations to regulate pollutant

emissions in Europe (for example, the 1999 Gothenberg Protocol via the UNECE Convention on LRTAP).

Outside of North America and Europe, there is an increasing use of critical loads for assessment purposes, and to inform policy development. Examples include studies in Siberia (Bashkin et al., 1995), Thailand (Milindalekha et al., 2001), and South Africa (Van Tienhoven et al., 1995). In China, several studies have been carried out to study the sensitivity of surface waters to acidification and the critical loads of acid deposition (Duan et al., 2000a; Li et al., 2000; Ye et al., 2002; Hao et al., 2001), and to calculate the critical loads of S and N acidity for soils at both the local and regional scales (Zhao and Seip, 1991; Xie et al., 1995; Duan et al., 2000b, 2001).

D.1.1. The Critical Load Process

The process of estimating critical loads is not a purely scientific enterprise. Management or policy input to the process is needed to insure that the appropriate science is included and the appropriate questions are addressed. The critical load process integrates knowledge of a multitude of physical, chemical and biological mechanisms affected by ambient air quality, and presents the current scientific understanding in a format that is most useful for assessing current or future management practices and policy decisions regarding air quality, or the resources affected. The critical loads process provides decision-making insight based on both scientific evidence and policy priorities.

Science and policy are closely coupled in the critical loads process. In the development of critical load estimates, it is important to identify those elements that are essentially scientific in nature as opposed to those elements that are driven by management or policy priorities. The scientific elements include tasks such as: relating ambient air quality to pollutant deposition, quantifying the relationships between pollutant deposition and resource responses, identifying the resources at risk to adverse effects, understanding the temporal and spatial responses of resources to pollutant deposition, and more. The policy-dependent elements include tasks such as: identifying the environmental resources to be protected, establishing appropriate criteria for different land use areas (e.g., Class I areas, national parks, wildlife refuges), defining significant harm to protected resources, and more. When all elements are integrated, it is apparent that the critical load process provides a framework for alternate ways of examining and understanding the cascade of effects from ambient air quality to resource effects, described in the preceding four annexes. Changing scientific assumptions or understanding may result in different critical load estimates for the same resources. Changing policy or management assumptions or priorities may also result in different critical load estimates.

There is, therefore, no single “definitive” critical load for a natural resource. Critical load estimates are explicitly linked to policy, but their reliability is conditioned on the soundness of the underlying

science. As elements of the critical load process change, the critical load estimates will change to reflect both the current state-of-knowledge and policy priorities. Changes in scientific understanding may include: new dose-response relationships, better resource maps and inventories, larger survey datasets, continuing time series monitoring, improved numerical models, etc. Changes in the policy elements may include: new definitions of harm, new mandates for resource protection, focus on new pollutants, or inclusion of perceived new threats that may exacerbate the pollutant effects (e.g., climate change).

The critical load process is thus an iterative process — as science changes, the content is updated; as policy needs change, the content is re-directed. Being iterative, the process allows incremental improvement in understanding resource responses to ambient air quality. Individual elements of the process can be replaced as needed to reflect new science or policy. Continuing to update the process may reduce uncertainty and risk, as new data or techniques allow refinement of existing pieces. The piecewise nature of the process provides adaptability as new policy concerns arise, such as new pollutants or mandates. As the critical load process advances, a "library" of critical load estimates will result. Examining and comparing these accumulated results, and their underlying scientific and policy bases, may produce a "weight of evidence" consensus, even if any single estimate entails substantial uncertainty.

D.1.2. Organization of this Annex

This Annex chapter is intended as a review of the current state of critical loads science. It is not the intention to address questions of management or policy other than to point out where these activities influence the critical loads process. The material in Section D.2 presents necessary definitions and describes the conceptual framework for a critical load analysis. This framework identifies those elements that are primarily scientific in nature and those elements that require policy input. The framework also describes the steps that are taken in deriving a critical load estimate for a given resource. It is not an objective of this Annex to provide details of all critical loads studies that have been implemented in the U.S. or elsewhere. The conceptual framework, however, provides a generalized summary of the steps most critical loads studies have followed. Section D.3 discusses the time frame of responses for implementation of a critical load. Time frames of resource response are often ignored, or assumed implicitly, in defining a critical load analysis. The time required to implement the policy and technology to achieve a critical load can also affect the responses of the resources at risk. The time frames of response are important for selecting the data and models used to estimate critical loads. Section D-4 summarizes the tools (models and modeling approaches) commonly used in calculating critical loads. The Annex concludes in Section 5 with a summary of the current agreement on critical loads uses in the U.S. that was a product of the Multi-Agency Workshop on Critical Loads held in 2006. The workshop

produced a series of recommendations for current and future activities related to critical loads analyses in the U.S.

D.2. Definitions and Conceptual Approach

D.2.1. Critical Load Definitions

Critical loads and critical levels are used to express how much deposition of an atmospheric pollutant (a "load") or how large a concentration of an airborne pollutant (a "level") can be tolerated by natural or artificial systems without significant harm or change occurring in those systems. The generally accepted definition of a critical load or a critical level of atmospheric pollutants emerged from a pair of international workshops held in the late 1980s (Nilsson, 1986; Nilsson, 1988). The workshop participants defined a critical load or a critical level 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."

This evaluation deals primarily with the effects of atmospheric deposition of S and N compounds. This Annex, therefore, will deal exclusively with the concept of critical loads of S and N compounds from atmospheric deposition. Critical levels of pollutant concentration will not be addressed. As discussed in previous annexes, the deposition of both S and N has acidifying effects on receptors (Annex C), and the deposition of oxidized and/or reduced N compounds can produce eutrophication or nutrient-enrichment effects in receptors (Annex D). The following material, therefore, will focus on critical loads of S and N for acidification effects, and on critical loads of N for nutrient effects.

In addition to the generic definition of a critical load/level presented above, the participants in the second international workshop (the Skokloster Workshop) (Nilsson, 1988) developed a number of specific definitions related to known atmospheric pollutants. Two of those definitions are relevant to this Annex.

Recognizing that both S and N compounds contribute to the acidity of deposition, the workshop participants developed a definition for critical loads of S and N for acidification of an ecosystem: "the highest deposition of acidifying compounds that will not cause chemical changes leading to long-term harmful effects on ecosystem structure and function according to present knowledge." Recognizing that N in both oxidized (e.g. NO, NO_2, NO_3^-) and reduced (e.g. NH_3, NH_4^+) forms in deposition may influence the eutrophication and nutrient balances of ecosystems, the workshop participants defined the critical load of N for nutrient effects in an ecosystem as "the highest deposition of N as NH_X and/or NO_Y below which harmful effects in ecosystem structure and function do not occur according to present knowledge."

All three definitions can be applied to different receptors in a number of different environments (e.g., terrestrial ecosystems, transitional ecosystems, aquatic ecosystems, groundwater, agricultural crops, etc.). A sensitive element can constitute a part of, or the whole of, an ecosystem. Harmful effects can occur to individual organisms, to populations, or to entire communities within an ecosystem. Harmful effects can also be defined at the level of the ecosystem itself as changes in ecosystem processes, structure, and/or function.

While the concepts expressed in these definitions of critical loads and levels are easily understood and intuitively satisfying, the application of the critical load concept requires careful consideration and definition of a number of terms and procedures. It is apparent that there can be many different critical load values for a given atmospheric pollutant depending on the receptor or sensitive element(s) being considered. There can also be multiple different atmospheric pollutants that can produce the same harmful effects in a given receptor. Therefore, the critical load of a given pollutant can potentially be dependent on the deposition and/or atmospheric concentration of other pollutant species. Finally, the same atmospheric pollutant can produce a variety of different disturbances in a sensitive ecosystem that might occur at different pollutant loads. For example, N deposition produces both nutrient and acidification effects and the critical load of N for each type of disturbance may be different.

Therefore, in order to derive a quantitative estimate of the critical load of an atmospheric pollutant, a number of factors must be identified and defined Figure D-1. These include disturbance type, receptor, sensitive elements, and definition of what constitutes significant harm. In addition, a numerical relationship between pollutant deposition and the identified receptor response must be formulated, generally based on either an empirical dose-response relationship or a steady state or dynamic numerical model simulation. The next section outlines the steps (decisions) that must be taken to implement this process.

D.2.2. Critical Load Analysis Procedures

The development of a quantitative critical load estimate requires a number of steps. In this discussion, Figure D-1 is used to illustrate the procedure. The Figure is simplified to facilitate general discussion and does not represent the full complexity of the choices that must be made, or the scientific understanding underlying those choices.

Table D-1. An example of the matrix of information that must be considered in the definition and calculation of critical loads. Note that multiple alternative biological indicators, critical biological responses, chemical indicators, and critical chemical limits

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	???	???	???	???	???	???

There are eight general steps that must be taken to define the basic critical load question in any analysis.

1. Identify the ecosystem disturbance of concern (acidification, eutrophication, etc.). Not all disturbances will occur in all regions or at all sites, and the degree of disturbance may vary across landscape areas within a given region or site.

2. Identify the landscape receptors subjected to the disturbance (forests, surface waters, crops, etc.) Receptor sensitivity may vary locally and/or regionally, and the hierarchy of receptors most sensitive to a particular type of disturbance may vary as well.

3. Identify the biological indicators within each receptor that are affected by atmospheric deposition (individual organism, species, population, or community characteristics). Indicators will vary geographically and perhaps locally within a given receptor type

4. Establish the critical biological responses that define "significant harm" to the biological indicators (presence/absence, loss of condition, reduced productivity, species shifts, etc.). Significant harm may be defined differently for biological indicators that are already at risk from other stressors, or for indicators that are perceived as "more valued."

5. Identify the chemical indicators or variables that produce or are otherwise associated with the harmful responses of the biological indicators (stream water pH, Al concentration, soil base saturation, etc.). In some cases, the use of relatively easily measured chemical indicators (e.g., surface water pH or ANC) may be used as a surrogate for chemical indicators that are more difficult to measure (e.g., Al concentration).

6. Determine the critical chemical limits for the chemical indicators at which the harmful responses to the biological indicators occur (e.g., pH < 5, base saturation < 5%, Al concentrations >100 µg/L, etc.). Critical limits may be thresholds for indicator responses such as presence/absence, or may take on a continuous range of values for continuous indicator responses such as productivity or species richness. Critical limits may vary regionally or locally depending on factors such as temperature, existence of refugia, or compensatory factors (e.g., high calcium concentration mitigates the toxicity of Al to fish and plant roots).

7. Identify the atmospheric pollutants that control (affect) the pertinent chemical indicators (deposition of SO_4^{2-}, NO_3, NH_4, HNO_3, etc.). Multiple pollutants can affect the same chemical variable. The relative importance of each pollutant in producing a given chemical response can vary spatially and temporally.

8. Determine the critical pollutant loads (kg/ha/yr total deposition of S or NO_3^-N, etc.) at which the chemical indicators reach their critical limits. Critical pollutant loads usually include both wet and dry forms of pollutant deposition. The critical pollutant load may vary regionally within a receptor or locally within a site (as factors such as elevation or soil depth vary) and may vary temporally at the same location (as accumulated deposition alters chemical responses).

The definition of the critical load problem for a region or individual site generally requires that we work down the Table from top to bottom (Table D-1) What is the disturbance? What receptors are affected? What indicator organisms are, or were previously present and observable? What chemical indicators are changing and can be measured? What atmospheric pollutant is driving the changes in the chemical indicators?

The derivation of a quantitative estimate of a critical load generally requires that we work from the bottom of the Table back towards the top, as indicated by the arrows in Table D-1. What is the maximum load of a pollutant that will cause a shift in the chemical indicator to its critical limit such that a critical

indicator response occurs, or does not occur? From this point of view, it can be seen that steps 8 and 6 require the development of dose-response functions for the components of the ecosystem being considered (arrows in Table D-1). Step 8 describes the response of the chemical indicator as a function of the pollutant load, and Step 6 describes the responses of the biological indicator as a function of the chemical variable. As discussed in later sections, these response functions can be derived using empirical (e.g., statistical) or process-based (e.g., mechanistic) models that are either time-invariant (static or steady state) or time-variable (dynamic).

Each step in the development of the critical load, as summarized in Table D-1 can be classified as either a predominantly scientific task or as a task benefiting from, or perhaps requiring, collaboration and input from scientists, decision-makers, and other interested parties. For instance, tasks 1, 2, and 3 can be viewed as predominantly scientific tasks that can be completed by asking questions of fact. At task 4, however, questions of what defines "significant harm" entail subjective elements that cannot be determined by scientific techniques alone. In anticipation of the ultimate use of the critical load definition to set policy or establish management strategies, it is appropriate that political, socioeconomic, or perhaps ethical considerations be brought to bear in defining "significant harm." To define "harm" is to imply a corrective action, the cost of which will have to be borne by someone. Having reached agreement on task 4, however, tasks 5, 6, 7, and 8 are again predominantly scientific in nature, requiring determination of the causal links, represented as response functions or models, leading from the loading of the pollutant to the defined "significant harm."

This procedure will almost certainly result in calculation of multiple critical load values for a given pollutant and analysis 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" at step 4. 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, but in any critical load analysis there is nevertheless an a priori expectation of multiple values, or of a range of values.

The existence of multiple estimates of critical loads for a given pollutant and receptor should present no real problem. Examination of the range of critical loads derived may be deemed useful in subsequent discussions of the analysis, and in the decision-making steps that may follow critical load calculation. For instance, the lowest critical load of all those derived may be adopted as "the" critical load, as is often done in Europe. This however, is a policy choice. The scientific task is the derivation of the multiple values using best available information.

D.2.3. Target Load Definition

As seen in the previous section, it is expected that a potentially large number of critical load values may be objectively determined for a given atmospheric pollutant and a given receptor. Like the definition of "significant harm," the choice of which critical load value to use for management or decision-making is subjective, and should be driven by socioeconomic, political, and ethical considerations. The target load concept was developed to address these issues. Target loads are deposition loads of a given pollutant, based on critical load estimates for the pollutant, which incorporate policy and/or management decisions about the amount of pollutant deposition, and therefore the amount of resource damage that is deemed acceptable. Target loads can be set at, above, or below the various critical loads. If the target load is set above some of the estimated critical loads, one accepts the inevitability that some of the ecosystem components, generally the most sensitive, will be adversely affected. If the target load is set below all of the estimated critical loads, a safety margin has been established to account for uncertainty inherent in the process.

Given the spatial heterogeneity of natural systems, target loads might also be used to provide some measure of "cumulative resource protection." As discussed above, there typically exists a range of critical loads for a particular "significant harm" in a particular receptor. Selecting a target load within the range will provide protection for the fraction of the receptor with critical loads above the chosen target load, whereas that fraction with critical loads below the chosen target load will be expected to suffer some harm at that deposition level. In this way, it is possible to use the target load to define protection for some cumulative proportion of the receptor (i.e., a target load for protection of 95% of the resource from "significant harm").

While most of the steps involved in estimating critical loads depend on sound, objective scientific analysis, the selection of target loads is almost entirely a subjective judgment. The selection of target loads must begin with reliable estimates of critical loads to set the constraints, and define the expected consequences of the target load choices. Nevertheless, the final decisions of which indicators are the key indicators, how much cumulative resource should be protected, how much sooner or later resource protection will be implemented, cannot be answered scientifically. Political, socioeconomic, and ethical considerations will form the basis of the final target load selections. Frequently, the legal mandates for various public lands would have a determinant influence on the selection of target loads. For instance, Federal Class I areas may be held to one standard of harm because of mandates to protect "natural condition," whereas Federal mixed-use lands may be held to a different standard of harm, and cropland to yet another standard of harm.

It is also important to note that scientific understanding, modeling approaches, and the data used to estimate critical loads are continually improving. Furthermore, the political, economic, and social

environments surrounding selection of target loads are also constantly shifting. Therefore, the analysis and estimation of critical and target loads must be an iterative process.

D.3. Time Frame of Response

The critical load definitions and procedures discussed in the previous section do not explicitly consider the time frame of ecosystem response. When is "significant harm" expected? How long will it be before existing harm is reversed? When should critical loads be implemented? How long should a critical load be maintained? The use of critical and target loads in resource management always has some time frame of expected response, and some context of management priorities. For instance, it may be that a target load well below the critical load would hasten the recovery of a receptor with existing harm. Or, it may be that a receptor that has not yet been damaged can sustain a target load above the critical load for some finite period before incurring "significant harm." Such time frames can be very long (many decades or centuries).

The time frame of response between implementation of a critical load and the corresponding changes in biological or chemical indicators is a potentially important factor in establishing critical load analysis procedures and in selecting the final target load. Analyses can be designed to provide estimates of either "steady state critical loads" or "dynamic critical loads" depending on the perceived, or mandated, importance of the time frame of response and the types of models (transfer functions) used.

Steady state critical loads analyses provide estimates of the long-term sustainable deposition of a pollutant that will not cause "significant harm" to a receptor. This is the relevant information needed for any receptor to provide protection from damage by the pollutant in perpetuity as the receptor comes into equilibrium with the pollutant critical load (the implicit purpose of steady state analyses). However, no information is given concerning the time to achieve the equilibrium or what may happen to the receptor along the path to equilibrium. Estimated steady state critical loads for receptors that are currently damaged provide no information concerning when the desired long-term sustainable protection will occur and the existing "significant harm" will be mitigated. There exists the possibility that receptors with no current damage could suffer "significant harm" while waiting for implementation of the critical load. The possible occurrence, timing, and duration of such "interim periods of harm" are not the subject of steady state analyses.

Dynamic critical loads analyses provide estimates of a specifically scheduled deposition load of a pollutant that will not result in "significant harm" to a receptor at a specified time. This is the relevant information needed for any receptor to provide protection from damage by the pollutant within a specified time frame (the explicit purpose of dynamic analyses). However, care should be taken in interpreting the results of dynamic analyses to ensure that "significant harm" to the receptor does not occur after the

specific timetable has been completed. Many receptors can tolerate higher loads of a pollutant for a few decades (a common length of specified schedules for dynamic analyses) than can be sustained over longer periods. The use of dynamic critical load estimates in such cases may provide protection from harm during a time frame of immediate interest, but ultimately fail to provide long-term protection, unless these issues are considered.

D.3.1. Steady State Critical Loads

If the time frame of response is not important, for instance, if the target load is to provide long-term sustainable protection and the immediacy of the responses is not relevant, the use of static or steady state models (response functions) is justified in the critical load analysis procedure. Using steady state models to estimate critical loads and compare the estimated critical load to current or future deposition, only two cases can be distinguished: (1) current or future deposition is below the critical load, or (2) current or future deposition exceeds the critical load. In the first case, no problem is apparent, and no target load is deemed necessary, unless increases in deposition are anticipated. In the second case, there is by definition an increased risk of "significant harm" to the receptor and selection of a target load for resource protection is indicated.

The lack of explicit consideration of time in a steady state critical load analysis can lead to assumptions that are frequently not warranted. The critical load derived in a steady state analysis is an estimate of the long-term, constant deposition that a receptor can tolerate with no significant harm after it has equilibrated with the critical load deposition. However, biological and geochemical processes that affect a receptor may delay the attainment of equilibrium (steady state condition) for years, decades, or even centuries. By definition, steady state critical loads do not provide any information on these time scales. As a result, it is often assumed that reducing deposition to, or below the steady state critical load value will immediately eliminate or mitigate "significant harm." That is, it is assumed that the chemical indicator affected by the atmospheric pollutant immediately attains a non-critical value upon implementation of the critical load, and that there is immediate biological recovery as well. As discussed in the next section, these assumptions may not be valid.

D.3.2. Dynamic Critical Loads

The time frame of receptor response is important if the establishment of target loads is tied to defined schedules of deposition change or receptor responses. The use of time-dependent or dynamic model response functions will be necessary if the critical load analysis considers the response time frame. In the cascade of events that occur from changed deposition of an atmospheric pollutant to development

of responses of key biological indicators, there are many processes in natural systems that are time and/or resource dependent and therefore can introduce delays in the response pattern. In the decision-making process leading to the adoption of target loads, there are likewise considerations of when deposition changes can be initiated and completed and when biological indicator responses are desired. With dynamic models, either empirical or process-based, a wide range of estimated critical loads can be derived for comparison with current or future deposition depending on the temporal constraints imposed on the critical load analysis. Temporal constraints that can be imposed on a given critical load analysis are determined by: (1) the receptor responses—the characteristic time scales and inherent lags of the receptor being analyzed (a function of hydrobiogeochemical processes in the receptor), and (2) the deposition schedules—the years designated for beginning and completing the changes in deposition and for evaluating the indicator responses (a function of political, socioeconomic, and management constraints).

D.3.3. Receptor Responses

The general conceptual model of the linkages among pollutant deposition and the responses of chemical and biological indicators can be characterized as a series of delays. In the causal chain from deposition of pollutant to damage to key biological indicators there are two major links that can give rise to delays. First, hydrological and biogeochemical processes in catchments can delay the responses of chemical indicators. Second, biological processes and population dynamics can further delay the response of biological indicators. The pattern of chemical and biological indicator responses can be represented conceptually (Figure D-1) (adapted from Jenkins et al., 2003; Posch et al., 2003). Five stages in the conceptual pattern can be distinguished (Figure D-1):

- Stage 1: Pollutant deposition is below the critical load for either the critical chemical limit or the critical biological response, and there is no “significant harm” to the receptor. As long as deposition stays below the critical load, this is the ‘ideal’ situation.

- Stage 2: Pollutant deposition rises above the critical load, but chemical and biological indicators still do not violate their respective criteria because there is a delay. No damage is likely to occur at this stage, despite the exceedance of the critical load. The time between the first exceedance of the CL and first violation of the biological criterion (first occurrence of “significant harm”) is called the Damage Delay Time (DDT = t3–t1).

- Stage 3: Pollutant deposition is above the critical load and both the chemical and biological criteria are violated. Measures to reduce emissions are taken to avoid further harm to the receptor and pollutant deposition begins to decrease.

- Stage 4: Pollutant deposition has been reduced to a level below the critical load, but the chemical and biological criteria are still violated, and thus "recovery" has not yet occurred. The time between the first non-exceedance of the critical load and the subsequent non-violation of both criteria can be called the Recovery Delay Time (RDT = t6–t4).

- Stage 5: This stage is similar to Stage 1. Pollutant deposition has been reduced to a level below the critical load and neither the chemical nor biological criteria are violated. Only at this stage can the receptor be considered to have recovered to an undamaged level.

Stages 2 and 4 can be further subdivided into two sub-stages each: chemical damage and recovery delay times (DDTc = t2–t1 and RDTc = t5–t4; dark grey in Figure D-1 and (additional) biological damage and recovery delay times (DDTb = t3–t2 and RDTb = t6–t5; light grey). Given opportunities for "confounding effects" (i.e., mechanisms not related to acidic deposition but affecting biological indicators, such as forest pest infestation or climate change) occurring during the "delay periods," it is clear that unambiguous short-term patterns of recovery of biological indicators are unlikely to be observed, even in the presence of rather large declines in pollutant deposition. This has important implications for recovery expectations.

D.3.4. Deposition Schedules

Dynamic critical loads, by definition, must explicitly account for the receptor time scales and lags described above. Therefore, the process of estimating dynamic critical load values for a given pollutant must be based on a planned or assumed deposition schedule for changing the pollutant deposition and for assessing the receptor responses. Three different time periods are specified, as illustrated in Figure D-3. [The nomenclature used here for the three years specified in the deposition schedule conforms to that used in European "dynamic target loads analyses" (Posch et al., 2003)].

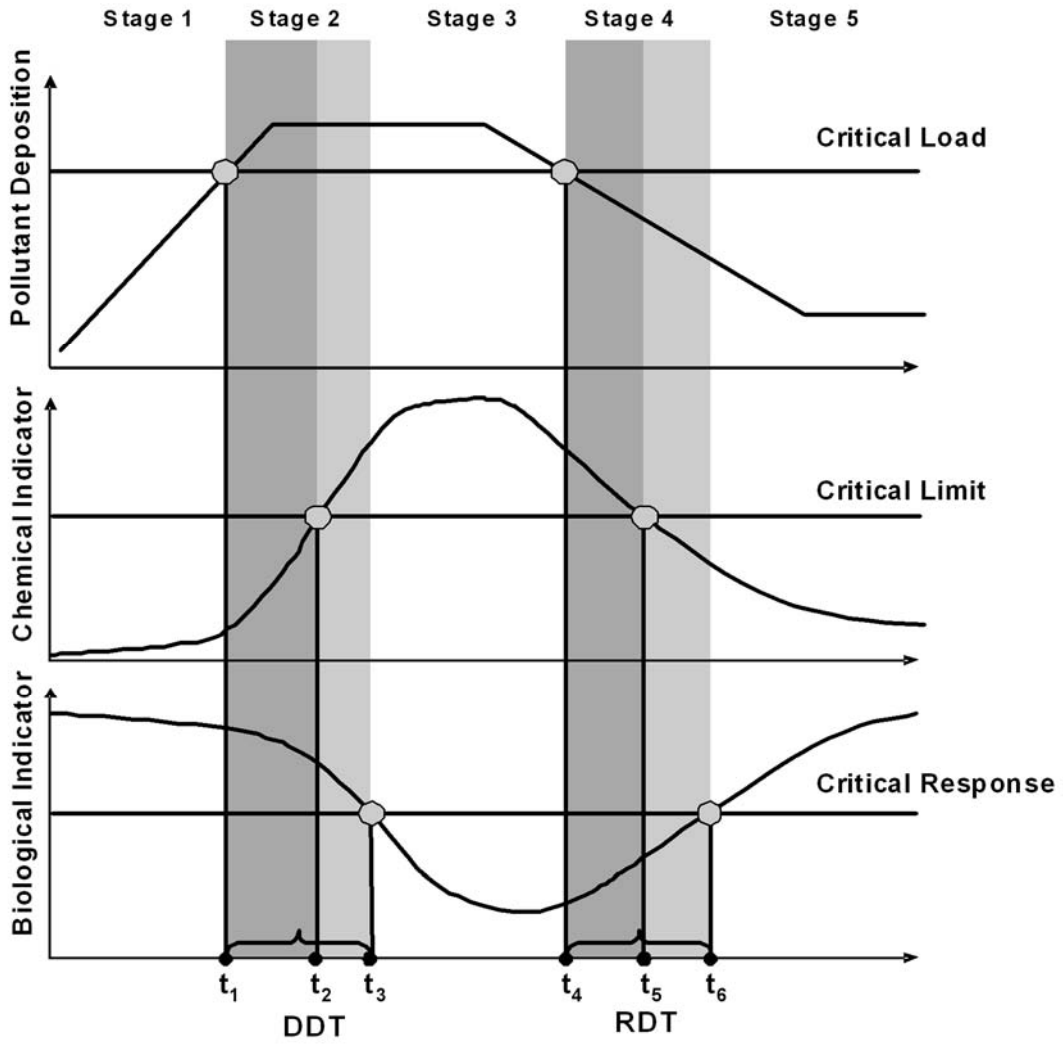

Figure D-1. Conceptual patterns of pollutant deposition effects on a chemical indicator and a corresponding biological indicator during increasing and decreasing deposition. Critical limits and responses for the chemical and biological indicators are indicated as horizontal lines, along with the critical load of deposition that produces these levels. The delays between the exceedance of the critical load (t1), the violation of the critical chemical limit (t2), and the crossing of the critical biological response (t3) are indicated in grey shades, highlighting the DDT. Similar delays in chemical and biological recovery during deposition reductions (t4, t5, and t6) define the RDT of the system.

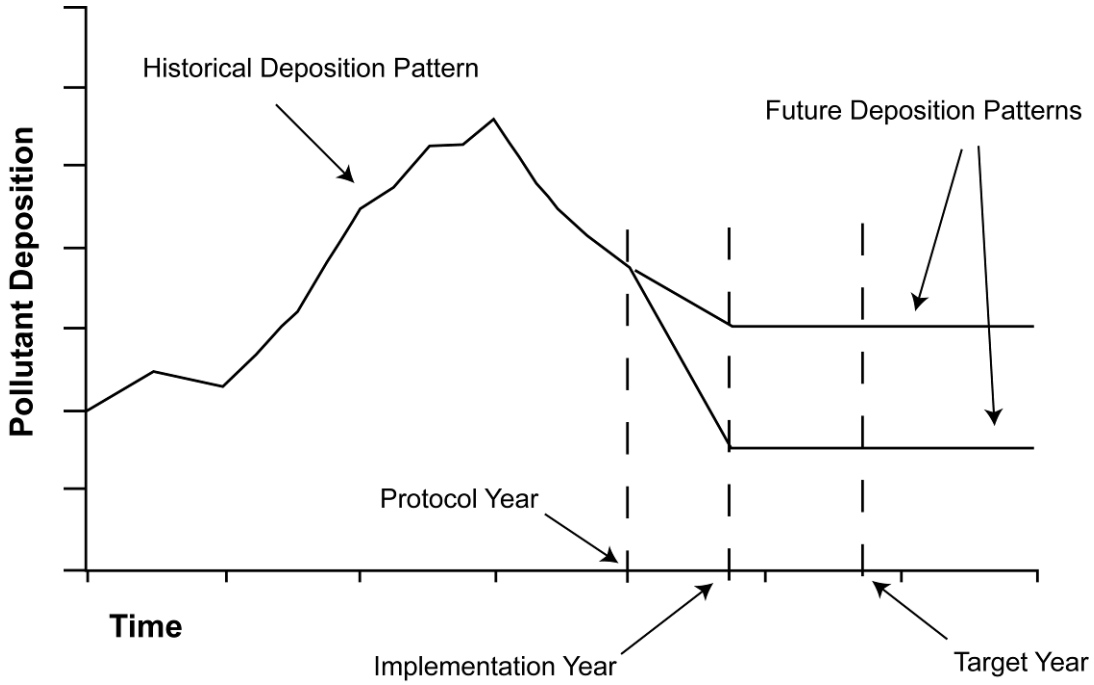

Figure D-2. Pollutant deposition patterns for defining the temporal parameters of dynamic critical loads analyses. The deposition schedule requires that three years be specified: (1) the year in which changes in pollutant deposition are begun, called the protocol year; 2) the year in which changes in pollutant deposition are completed, called the implementation year; and (3) the year in which the chemical or biological response indicator is evaluated, called the target year.

The first time period is the protocol year when deposition changes moving toward the critical load are begun. It will be the case that voluntary or mandated changes in deposition will require a number of years to get underway once a critical load has been calculated or target load has been selected. These delays in moving toward the critical load will affect the dynamic responses of the chemical and biological indicators and, therefore, must be included in the dynamic modeling of receptor response. Before the protocol year, it must be assumed that pollutant deposition will be continuing along the pattern of recent or historical deposition change or along the pattern dictated by future deposition scenarios already planned and assumed to take effect.

The second time period is the implementation year when deposition changes are complete and pollutant deposition has reached the desired critical or target load. It is likely that a number of years will elapse between the time changes in deposition toward the critical load are initiated, and the time when they are completed. During this transition period, pollutant deposition continues at a rate higher, or lower, than the critical load. The effects of these years of deposition inputs above or below the critical load value will affect the dynamic responses of the chemical and biological indicators, and must also be included in the dynamic modeling of receptor response. It is assumed in dynamic critical loads analyses that the

pollutant deposition to the receptor remains constant at the critical load for all years after the implementation year.

The final time period is the target year when the biological indicators are evaluated. Recognizing that there are inherent lags in receptor responses following changes in pollutant deposition, it a number of years will frequently be allowed to elapse after the implementation year before the receptor responses are assessed. It must also be recognized that receptor responses will continue to change over time. Thus, selection of the target year will affect attainment of the critical limit.

The deposition schedule for a dynamic critical load analysis can be driven by a number of considerations, and can be organized from protocol year to target year or vice versa. The selection of the protocol and implementation years is often a matter of political will and economic possibility. Large-scale pollution abatement programs take time to negotiate. Costs or engineering difficulties may delay the start of the abatement program and affect the length of time it takes to complete the program once it is begun. Once these constraints have been established, it is then possible to select a reasonable target year for evaluation of the receptor responses. Alternately, resource management mandates might require that "significant harm" to receptor indicators be mitigated or eliminated by a certain time. This establishes the target year for the dynamic analysis and the protocol and implementation years must be selected to allow time for any lags in the receptor responses to occur.

Clearly, there is tension between the two approaches when developing a deposition schedule. It is possible, for instance, to defer the protocol and implementation years so far into the future that extensive "significant harm" occurs to the receptor indicators in the intervening years. If that damage is especially severe, the critical load, when the target year is finally reached, may not be achievable. Similarly, if a receptor is currently suffering harm, it is possible to choose a target year for receptor response too close to the present day to allow time for the receptor to recover, even if the pollutant deposition was reduced to zero immediately.

Both of these hypothetical scenarios raise important points about dynamic critical load estimates. Because time is explicitly incorporated, there are certain dynamic critical loads questions that have no answer. Commonly called "you can't get there from here" problems, these deposition schedules choose protocol, implementation, or target years that are inconsistent with the time scales of receptor response. For example, setting a target year 5 years in the future for achievement of no "significant harm" in a receptor that is currently badly damaged, and has a history of high pollutant loading, may be asking the impossible. Critical load estimates derived in this case would require having set the pollutant deposition to zero some years in the past. In other words, the state of no significant harm cannot be reached within the specified five years regardless of how deposition is changed within that five-year period ("you can't get there from here"). This problem is moot for steady state critical loads. Steady state critical loads analyses will always provide some sensible estimate (zero or finite) of long-term sustainable pollutant

deposition for every receptor because time is not a factor. Dynamic critical loads analyses, on the other hand, may frequently provide non-quantitative results, but these results nonetheless convey useful information concerning the current status of the receptor and point out the necessity to continue the analysis with modified assumptions or expectations in order to develop realistic and achievable target load values.

D.3.5. Long-Term Implications

The explicit inclusion of time in critical loads estimation provides useful information for managers or policymakers when deciding when and how much to alter pollutant emissions and deposition, but the dynamic approach leads to implicit assumptions that must be recognized. Focus on the near-term aspects of receptor responses (the years included in the deposition schedule) can be misleading. The implicit assumption is that having attained the desired biological or chemical response in the target year, nothing more will happen, or at least that further changes in the receptor, if they do occur, will not produce "significant harm." Available dynamic model critical load estimates suggest that this is not always true, and the long-term implications of dynamic critical load estimates should be examined carefully.

The dynamic critical loads procedure assumes that pollutant deposition remains constant at the critical load from the implementation year until the target year, and the assessment of receptor response. Model simulations can be continued, assuming deposition at the constant critical load value, for a number of years after the specified target year to ensure that lags in the receptor response will not result in "significant harm" appearing at some later date, even though it was not present in the target year. Some receptors have chemical or biological lags that are many decades long, or longer. Critical loads analyses based on deposition schedules that cover only 20 to 30 years can produce the unwanted result of estimating a dynamic critical load that avoids "significant harm" to the receptor in the target year, only to have the receptor suffer damage some years later.

It is important to determine which receptor responses and which deposition schedules might lead to such an unwanted result. There are some general guidelines concerning this potential problem. For any receptor for which there is currently no "significant harm," the estimated critical load provided by the dynamic approach will be one that brings the biological or chemical indicators to the threshold of harm without crossing it (the definition of the critical load). However, this dynamic critical load has then put the biological or chemical indicator on a trajectory away from its currently good status and toward the threshold of harm. In most cases, the trajectory toward harm will continue past the target year and "significant harm" will occur in these receptors some time after the target year.

On the other hand, in any receptor for which there currently is "significant harm," the estimated critical load provided by the dynamic approach will be one that brings the biological and chemical

indicators to the threshold of harm and crosses it, just to return to a state of no harm. This dynamic critical load puts the biological or chemical indicator on a trajectory away from harm and towards good status. In most cases, it is likely that the upward trajectory will continue past the target year and significant further recovery will occur in these receptors after the target year.

These are, however, merely generalizations. Depending on the geochemical and biological process affecting a receptor, there exist possibilities that upward trajectories could become downward trajectories sometime after the target year and vice versa. The most straightforward procedure is to run the model(s) used in the dynamic critical loads analyses for a sufficiently long time after the target year so that any reasonable chance of delayed damage to the receptor or delayed recovery is either discovered or discounted.

D.3.6. Steady State and Dynamic Critical Loads – Complementary Information

There is no "correct" choice to be made between steady state and dynamic critical loads analyses. Both provide estimates of pollutant loads that are intended to avoid "significant harm" to a receptor. Both are valid scientific expressions of the receptor's sensitivity to the pollutant. They differ primarily in the time scales implicit in their use. Steady state analyses provide critical load estimates for long-term sustainable protection, but ignore questions of near-term recovery and avoidance of interim harm. Dynamic analyses provide critical load estimates that can be used to examine short-term or long-term options for recovery of damaged systems and avoidance of interim harm, but may ignore the ultimate long-term sustainability of the estimated deposition, which may evolve over centuries. Clearly, the two approaches provide complementary information.

The complementary nature of the two critical loads approaches can be exploited in the selection of a target load estimate for a receptor. Selecting the lower of the two critical load estimates for the receptor (steady state or dynamic) should result in facilitation of recovery, or avoidance of harm, in the short-term, as well as long-term sustainability once the receptor has reached equilibrium with the selected target load. Multiple lines of evidence reflecting multiple critical load values can provide important information that collectively provides the foundation for management decision-making.

The procedures, data requirements, and computational resources needed for each of the two critical loads approaches may differ significantly depending on the models (response functions) adopted for the analyses. Differences in the approaches may also depend on the disturbance, receptor, or indicator being evaluated. The next two sections discuss the disturbances, receptors, and indicators relevant to deposition of S and N, and the models used for calculation of critical load estimates by each approach.

D.4. Calculation of Critical Loads

The derivation of quantitative estimates of critical loads requires the development of dose-response functions (models) for the components of the ecosystem being considered. Models are needed to describe two different classes of dose-response function. Geochemical models describe the changes in the chemical indicators that occur as functions of changes in the pollutant loads. Biological response models describe the changes in the biological indicators as functions of changes in the chemical variables.

Models for either class of dose-response function can be developed using two general approaches. Empirical models are based on direct observations of indicator response to pollutant deposition. They are usually developed using statistical techniques and generally do not contain a mechanistic pathway linking pollutant deposition to indicator response. Process-based models are based on conceptual representations of chemical and biological mechanisms, and use mathematical equations to express the inter-relationships among system components. Whereas process-based models frequently also use observations of receptor responses to pollutant deposition for calibration and validation, they are fundamentally different from empirical models in that mechanistic pathways from pollutant deposition to indicator response are explicitly included in the model structures. In general, the geochemical models used to link S and N deposition to chemical indicator response are mostly process-based, whereas biological responses to acidification by S and N are mostly modeled using empirical approaches. Finally, both geochemical models and biological response models, whether developed using either empirical or process-based approaches, can be further classified as static or dynamic depending on whether or not time is included among variables.

D.4.1. Empirical Models

Empirical models can be constructed relating either chemical or biological indicators to pollutant deposition. The empirical models currently in use for calculating critical loads employ steady state approaches. This is not a necessary constraint, however, because even with no knowledge of the underlying mechanisms, there exist many statistical techniques for relating the time-series of outputs and inputs of ecosystems. The reason empirical critical loads models are usually based on a steady state approach is primarily because time-series data of long enough duration to parameterize dynamic empirical models are not generally available. In general, empirical models require less complex datasets, are more straightforward to implement, and are easier to understand than process-based models. For some receptors, the lack of conceptual understanding of the mechanisms of indicator response to pollutant deposition renders the use of process-based models problematic, and the use of empirical models is then the only viable critical load analysis approach.

D.4.2. Acidification Effects of Sulfur and N

Empirical models of critical loads for acidity assign critical loads to soils on the basis of soil mineralogy and chemistry (UNECE, 2004). For example, at the Critical Loads Workshop at Skokloster (Nilsson, 1988) soil forming materials were divided into five classes on the basis of the dominant weatherable minerals. A critical load range, rather than a single value, was assigned to each of these classes according to the amount of acidity that could be neutralized by the base cations produced by mineral weathering. The classification of soil materials developed at Skokloster used a relatively small range of primary silicate minerals and carbonates. A larger range of minerals was classified by Sverdrup and Warfvinge (1988) and Sverdrup et al. (1990) for use in the PROFILE model (Warfvinge and Sverdrup, 1992).

D.4.3. Nutrient Effects of N

Empirical models of critical loads for nutrient N have been developed in Europe within LRTAP to set critical loads for atmospheric N deposition (e.g., UNECE, 2004). Empirical critical loads of N for natural and semi-natural terrestrial ecosystems and wetland ecosystems were first presented in a background document for the 1992 workshop on critical loads held under the UNECE LRTAP Convention at Lökeberg, Sweden (Bobbink et al., 1992). A number of European expert workshops have taken place in order to reach agreement among specialists regarding the impacts of N for various ecosystems and related critical loads (Nilsson, 1988; Bobbink, 1992)1996; Hornung, 1995; Achermann, 2003). Empirical relationships have also recently been developed in the U.S., particularly for western ecosystems (e.g., (Baron, 1994; Baron, 2000) (Williams, 2000); Fenn, 2003) (Burns, 2004) (Nydick, 2004).

D.4.4. Process-Based Models

A number of process-based models are currently in use for calculating critical loads using both steady state and dynamic approaches. Developing a process-based modeling approach that includes all appropriate chemical and biological indicators is a complex task. Some process models incorporate both geochemical and biological response mechanisms in one program. An alternate approach is to chain individual process-based models, for example taking the output of a geochemical model and passing it as input to a biological-response model. In either approach, the level of process complexity varies a great deal among the various available models. The choice of a particular process-based modeling approach to be used in a critical load analysis (dynamic or steady state, all-in-one or chained, etc.) will depend on the

scope of the analysis, the quality and quantity of available data, and the availability of resources (time and money) for the analysis. The following is a brief overview of some of the process-based biogeochemical models that are commonly used to calculate critical loads.

D.4.5. Steady State Models

The Simple Mass Balance (SMB) model is the standard model for calculating critical loads for terrestrial ecosystems under the LRTAP Convention (Sverdrup et al., 1990; Sverdrup and De Vries, 1994). The SMB model is a single-layer model. There also exist multi-layer steady state models for calculating critical loads in terrestrial ecosystems. Examples are the MACAL model (De Vries 1988) and the widely used PROFILE model (Warfvinge and Sverdrup, 1992), which has at its core a model for calculating weathering rates from total mineral analyses.

The Steady State Water Chemistry (SSWC) model (Sverdrup et al., 1990; Henriksen et al., 1992; Henriksen and Posch, 2001) calculates critical loads of acidity for surface waters, based on the principle that acid loads should not exceed the balance of non-marine, non-anthropogenic base cation sources and sinks in a catchment, minus a buffer to protect selected biota from being damaged.

The First-order Acidity Balance (FAB) model for calculating critical loads for surface waters takes into account sources and sinks within the lake and its terrestrial catchment. The original version of the FAB model was developed and applied to Finland, Norway, and Sweden by Henriksen et al. (1992) and Posch et al. (1997). A modified version was first reported in Hindar et al. (2000, 2001) and is described in more detail by Henriksen and Posch (2001).

D.4.6. Dynamic Models

MAGIC is a lumped-parameter model of intermediate complexity, developed to predict the long-term effects of acidic deposition on surface water chemistry (Cosby, 2001)Cosby et al., 1985a,b, 2001). The model simulates soil solution chemistry and surface water chemistry to predict the monthly and annual average concentrations of the major ions in these waters. MAGIC consists of: (1) a sub-model in which the concentrations of major ions are assumed to be governed by simultaneous reactions involving $SO_4 2-$ adsorption, cation exchange, dissolution-precipitation- speciation of Al, and dissolution-speciation of inorganic carbon (C) and (2) a mass balance sub-model in which the flux of major ions to and from the soil is assumed to be controlled by atmospheric inputs, chemical weathering, net uptake and loss in biomass, and losses to runoff. At the heart of MAGIC is the size of the pool of exchangeable base cations in the soil. As the fluxes to and from this pool change over time owing to changes in atmospheric deposition, the chemical equilibria between soil and soil solution shift to give changes in surface water

chemistry. The degree and rate of change of surface water acidity thus depend both on flux factors and the inherent characteristics of the affected soils. MAGIC is described in more detail in Annex C.

PnET-BGC is an integrated dynamic biogeochemical model that simulates chemical transformations of vegetation, soil, and drainage water. It was formulated by adding the sub-model BGC (biogeochemistry) to PnET-CN, a model of C, water, and N balances (Aber and Federer, 1992; Aber and Driscoll, 1997; Aber et al., 1997), in order to expand the model to include vegetation and organic matter interactions of major elements (i.e., Ca_2^+, Mg2$^+$, K^+, Na^+, Si, S, P, Al_3^+, Cl^-, F^-), abiotic soil processes, solution speciation, and surface water processes (Gbondo-Tugbawa et al., 2001). The model was initially developed for, and applied to, the northern hardwood forest ecosystem. It was tested extensively at the Hubbard Brook Experimental Forest, New Hampshire, including a detailed sensitivity analysis of parameter values. The model has subsequently been applied to intensively-studied watersheds in the Adirondack and Catskill regions of New York and applied regionally to the Adirondacks (Chen and Driscoll, 2005b) and northern New England (Chen and Driscoll, 2005a,c). See additional description in Annex C.

Simulation Model for Acidification's Regional Trends (SMART2) is a soil acidification and nutrient cycling model and is an extension of the dynamic soil acidification model SMART (Kros et al., 1995). The original model was a relatively simple simulation of the response of soil and soil water quality to atmospheric inputs. Improvements in SMART2 include processes of canopy interactions, litter fall, root decay, mineralization, and root uptake of nutrients. SMART2 has been used primarily in European critical loads studies.

The Soil Acidification in Forest Ecosystems model (SAFE) was developed at the University of Lund in Sweden (Warfvinge et al., 1993; Alveteg and Sverdrup, 2002). The main differences between the SAFE and MAGIC models are: (a) weathering of base cations is not calibrated for SAFE, but it is modeled with the PROFILE sub-model, using soil mineralogy as input (Warfvinge and Sverdrup, 1992); b) SAFE is oriented to soil profiles in which water is assumed to move vertically through several soil layers, (c) cation exchange between Al, H, and (divalent) base cations is modeled in SAFE with Gapon exchange reactions rather than Gaines-Thomas reactions, and the exchange between the soil matrix and soil solution is diffusion-limited. The standard version of SAFE does not include S adsorption although a version, in which S adsorption is dependent on SO_4^{2-} concentration and pH of soil solution, has recently been developed (Martinson et al., 2003.

ForSAFE is a mechanistic model that simulates N and C cycling and soil chemistry. Climatic drivers within the model include temperature, precipitation, radiation, and deposition. ForSAFE combines three established models (SAFE, PnET-CN, and DECOMP). SAFE simulates soil chemistry (e.g., chemical weathering, cation exchange, leaching, and solution equilibrium reactions). PnET-CN (Aber et al., 1997) is used to predict forest growth within ForSAFE, through the simulation of C fixation,

litterfall, and C and nutrient allocation. DECOMP (Walse et al., 1998) is a dynamic, multi-layered process-oriented decomposition model that incorporates the influences of temperature, moisture, pH, and Al. Very Simple Dynamic soil acidification model (VSD) only includes a few key processes, such as cation exchange and N immobilisation, and a mass balance for cations and N (Posch et al., 2003). VSD does not consider seasonal variations, as the time step in the model is one year. The VSD model is based on mass balance equations that describe soil input-output fluxes and equations describing the rate-limited (e.g., uptake and silicate weathering) and equilibrium (e.g., cation exchange) soil processes. Soil solution chemistry is based solely on the net element input from the atmosphere (i.e., deposition minus net uptake minus net immobilization) and geochemical interactions in the soil (i.e., CO_2 equilibria, weathering of carbonates and silicates, and cation exchange). VSD simulates a single soil layer with a constant density and a fixed depth. The concentration of the soil water leaving the compartment is assumed to be equal to the annual precipitation excess.

D.5. Use of Critical Loads in the U.S. – Current Status

At the Multi-Agency Critical Loads Workshop for Sulfur and Nitrogen Deposition Effects on Freshwater and Terrestrial Ecosystems, convened by the EPA, the U.S. Forest Service (USFS), the National Park Service (NPS), and the USGS in May 2006, approximately 75 scientists, conservation representatives, and state and federal agency officials gathered to share information, discuss scientific advances, and develop a broad federal strategy for advancing critical loads in the U.S. (EPA, 2006). The conclusions and recommendations of that workshop are presented below. These conclusions and recommendations represent the current understanding of critical loads as scientific tool and policy instrument in the U.S.

The conclusions and recommendations below were reached by the Federal Agencies sponsoring the workshop. It is worth noting that some state agencies have pursued the use of critical loads independently in order to link science and policy in addressing the management of natural resources. For instance, in the State of Colorado, critical loads for N deposition that were developed for Rocky Mountain National Park (Baron, 2006) are being used to develop goals for N emissions reductions by the State of Colorado, EPA, and NPS. (See “Nitrogen Deposition Reduction Plan” at http://www.cdphe.state.co.us/ap/rmnp.html)

D.5.1. Current Recommendations on Critical Loads Uses in the U.S.

The participants in the Multi-Agency Critical Loads Workshop developed a set of findings and recommendations to help advance critical loads usage in the U.S. The "areas of agreement" published in the workshop report (EPA, 2006) included the following:

- A critical load is defined as: a quantitative estimate of the exposure to one or more pollutants below which significant harmful effects on specific sensitive elements of the environment do not occur according to present knowledge (Nilsson, 1988).

- Despite reductions in S and N emissions in the U.S., deposition rates still exceed preindustrial levels and acidification and eutrophication effects remain widespread.

- Critical loads can be used to better understand impacts of atmospheric deposition, assess the effectiveness of emissions programs, and guide natural resource management.

- The development of critical loads is a process that is subject to continued development and improvement as knowledge advances.

- Adequate information exists to move forward with the development and limited application of critical loads in some regions and ecosystems in the U.S.

- An intensive research and monitoring agenda should be pursued to support the development and refinement of critical loads in the U.S.

- Critical loads should be based on a matrix of biological and chemical indicators for aquatic and terrestrial ecosystems that account for acidification, N saturation, and eutrophication effects and are relevant to the geographic area or ecosystem of concern.

- Adequate information exists to establish harmful effect thresholds for some indicators based on specific protection and recovery objectives defined by policymakers and managers.

- Dynamic models provide the most accurate site-specific information and account for time-dependent processes, but are generally too data intensive to be applied across large geographic areas at present. Simple mass balance models can be applied to current conditions in large geographic areas, but in some instances do not adequately highlight some sensitive areas because they tend to average conditions across the landscape. Hybrid approaches that link observational datasets with dynamic and steady state models represent a useful approach for regionalizing site-specific information.

D.5.2. Questions and Limitations Regarding Critical Loads Uses in the U.S.

The participants in the Multi-Agency Critical Loads Workshop also developed a set of "Questions Needing Further Discussion" (EPA, 2006):

- What are the appropriate applications of critical load estimates to policy and management issues given current knowledge? For applications where buy-in to an incremental process does not exist, greater investment in critical loads methods may be needed before this application can be pursued.

- How strong is the relationship between specific indicators, thresholds, and biological responses?

- What are the suitable interpretations and uses of existing databases for the development of national simple mass balance critical load models?

D.5.3. Critical Loads Research and Monitoring Needs

Finally, the participants in the Multi-Agency Critical Loads Workshop presented a list of "Critical Loads Research and Monitoring Needs" (EPA, 2006), which are summarized below.

D.5.4. Emissions and Deposition

- Update N and S emissions inventories on a state-by-state basis back to the 1900s to correspond with methods used in current emissions inventories.

- Develop NH_3 emissions inventory.

- Improve dry deposition estimates for S and N.
- Improve total S and N deposition estimates.
- Measure gaseous NH_3 concentrations.
- Add NH_3 deposition measurements to current networks.
- Improve estimates of total deposition in complex terrain.
- Develop N and S deposition maps for North America.

D.5.5. Soils

- Improve spatial coverage and representativeness of soil chemistry databases, particularly in sensitive terrain.
- Increase soil monitoring.
- Improve estimates of mineral weathering rates.
- Develop soil archiving and well characterized reference samples to promote cross-laboratory comparisons.
- Expand research on the nature and size of soil nutrient pools.
- Conduct research on threshold values of soil quality for biologic responses.
- Determine N supply rates in different soil types.
- Investigate N soil accumulation rates in arid lands and implications for critical loads.

D.5.6. Surface Waters

- Incorporate TIME and LTM surface water monitoring programs into a larger network with better geographic coverage (e.g., the West and Southeast).
- Improve spatial coverage and representativeness of surface water chemistry databases, particularly in sensitive and complex terrain.

- Integrate fixed-site monitoring with regional probability monitoring design.
- Continue to monitor major drivers of acidity.
- Build critical loads considerations (e.g., validation, improvement, regionalization) into monitoring from the start by combining chemistry, hydrology, deposition and biology, and integrating site-specific models and measurements into regional contexts.
- Expand research to understand what is driving dissolved organic carbon (DOC) changes in the East.
- Analyze the impact of groundwater transport on recovery times.

D.5.7. Biological Effects

- Develop better understanding of the link between chemical indicators and biological response (e.g., quantify the minimum N level at which plankton communities shift).
- Conduct additional research on the sequential impacts of N and relationship between N deposition and ecosystem impacts.
- Integrate critical load estimates with biodiversity and climate change interactions.
- Undertake more research on biological change and "harmful effects" to help establish appropriate critical loads thresholds (e.g., in arid lands, what level of productivity of exotic invasive species will cause the reduction versus the extinction of native species?).
- Collect sediment cores from lakes that vary in rates of N deposition to track changes in diatom assemblages.

D.5.8. Critical Loads Models

- Improve representation of N dynamics in models.
- Expand models to include NH_3.
- Improve explicit consideration of changing base cations and DOC.
- Conduct ground-truthing of forest sensitivity and other models.

- Integrate water flowpaths into nutrient cycling models since lateral and vertically upward flowpaths are common.

- Understand and quantify uncertainties in models.
- Conduct site level model comparisons of dynamic and simple mass balance models.
- Integrate observational databases with steady state and dynamic models.
- Incorporate capacity to understand and evaluate climate change interactions.

Table D-2. 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 (Achermann, 2003).

ANNEX D - References

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Annex E. Effects of NO_Y, NH_X, and SO_X on Structures and Materials

E.1. Introduction

The purpose of this chapter is to summarize the research published since the most recent AQCDs on materials and structures damage caused by NO_Y, and NH_X, SO_X. Materials and structures exposed to the environment are subject to damage from exposure to sunlight, moisture, salt, windblown dust, and cycles of temperature and humidity, whether or not air pollutants are present. However, NO_Y, NH_X, and SO_X may cause such damage to be greater or occur more rapidly than with natural environmental factors alone. Damage to materials and structures may be physical, potentially affecting the durability or maintenance needs of a material or structure, or may be purely aesthetic, affecting only the outward appearance of the material or structure. In the case of historical buildings, monuments, or artifacts, aesthetic damage may be a relevant concern.

Note that very extensive work related to materials damage from acidic deposition related to S and N was conducted in the 1980s as part of the National Acid Precipitation Assessment Program (NAPAP, 1991) and so are not discussed here. In compiling information for this chapter on $NO_Y/NH_X/SO_X$ effects, the information presented in the 1993 AQCD for Oxides of Nitrogen (EPA, 1993) and the 2004 PM AQCD (EPA, 2004) was updated by literature searches reaching back to approximately 1992. This update was based on peer-reviewed literature, with a focus on studies that were conducted in the U.S., that evaluated effects at realistic ambient air pollutant levels, and that treated $NO_Y/NH_X/SO_X$ as components of a complex mixture of air pollutants. These latter two factors result in an emphasis on studies done with exposures to ambient atmospheric pollution, rather than exposures at high levels, e.g., in test chambers. The studies cited in this chapter were selected from those found in a broad literature search based on criteria that they (1) address damage caused by exposure to atmospheric contaminants, (2) focus on S and N containing species, (3) provide a clear link between pollutant concentrations and damage, and (4) give complete information on methods and data analysis used.

Broadly speaking, the pace of research on NO_Y, NH_X, and SO_X materials effects has slowed considerably since the publication of the previous AQCDs. In particular, although the literature searches conducted for this update emphasized studies conducted in the U.S., the great majority of the relevant publications found originated in Europe or Asia. The relative scarcity of recent U.S. studies on structural and materials damage from $NO_Y/NH_X/SO_X$ may be a natural fall-off in research in this area, following the extensive efforts that were summarized in the previous AQCDs and in the NAPAP report. Certainly the

greater number and age of aesthetically valuable buildings and archeological sites in Europe and Asia, relative to the U.S., may be a driving force for current research in those geographic areas. In this chapter, each discussion of the effects of $NO_Y/NH_X/SO_X$ on a material type begins with a brief summary of the state of knowledge as represented in the previous AQCDs, and then continues with a description of recent research on that type of material.

E.2. Environmental Exposures of Materials

E.2.1. Mechanisms of Materials Damage

As noted in the introduction to this chapter, materials damage may occur by natural physical processes without the involvement of $NO_Y/NH_X/SO_X$ air pollutants. When those pollutants are involved, the destructive processes may be chemical, physical, or even biological. Chemical processes include direct reactions with gaseous pollutants such as NO_2, SO_2, or nitric acid (HNO_3), reaction with electrolytes (proton (H^+), ammonium (NH_4^+), nitrate (NO_3^-), SO_4^{2-}, etc.) in water on material surfaces, and reactions with chemicals in deposited particulate matter. An example of a physical process is the deterioration of stone that occurs when gypsum ($CaSO_4 \cdot 2H_2O$) forms from reaction of SO_2 with the calcium carbonate ($CaCO_3$) in the stone. The gypsum thus formed occupies a larger volume than the original stone, causing the surface to deteriorate. Biological degradation can occur when deposited pollutants are oxidized to acids by fungi or bacteria.

A key factor affecting damage to certain materials, primarily metals and stone, is the frequency and duration of wetting of the surface. Liquid water on materials surfaces can dissolve deposited pollutants, producing reactive electrolyte solutions, and can serve as a reaction medium in which S and N oxides are converted to more damaging acids. Pollutants deposited on surfaces may contain or form hygroscopic salts, which enhance the formation of liquid water and thereby increase materials damage. As Dubowski et al. (2004) (2004) have shown, the deposition of HNO_3 onto surfaces can increase the extent of wetting of surfaces, and promote the damaging effects of both HNO_3 and other pollutants.

E.2.2. Deposition Processes

Air pollutants come into contact with surfaces through both dry and wet depositional processes. Dry deposition occurs in the absence of precipitation and is governed by factors such as atmospheric turbulence, the chemical and physical properties of the pollutant (e.g., water solubility and reactivity for gases; size, density, and shape for particles), and surface properties (e.g., reactivity, roughness, moisture

level, and pH). The deposition rate of a pollutant is proportional to the atmospheric concentration of that pollutant. Dry deposition of gases depends primarily on the water solubility of the gas, the moisture level on the surface, and the pH of the electrolyte formed on the surface of a material. Nitric acid and NH_3 are deposited very efficiently to most surfaces regardless of the surface properties of the material. Particle size plays an important role in determining the rate of deposition of particles to a surface. For very small particles, Brownian diffusion is the dominant deposition mechanism. For larger particles, inertial impaction and gravitational settling are important deposition processes. Particles between 0.05 and 2 μm, which include most atmospheric particles containing NO_3^-, SO_4^{2-}, and NH_4^+, may have long atmospheric lifetimes in the absence of moisture.

Wet deposition occurs when gas or particle species come into contact with moisture (as rain, fog, snow, or ice). Atmospheric species can be dissolved into moisture and then deposited as the moisture falls to the ground. Solubility and the chemical reactions of the dissolved species determine the degree of wet deposition. For acid gases, high dissolution is observed due to the dissociation of the dissolved species in water. Wet deposition of pollutants occurs at a faster rate than dry deposition, but is only an important mechanism when moisture is present.

E.2.3. Chemical Interactions of N and S Oxide Species

N and S oxide species are subject to many atmospheric reactions in both the gaseous and particulate phase. Emissions of S and N oxides are primarily in the form of gas phase SO_2 and NO_X. In the atmosphere, these species can be oxidized by reaction with other atmospheric species to gas and particle phase product species. On the surface of materials, the oxides are generally oxidized to their acid forms (nitrous acid (HNO_2), HNO_3, sulfurous acid (H_2SO_3), and sulfuric acid (H_2SO_4)), which then dissociate to form nitrite, nitrate, sulfite, and sulfate ions. These acids are the primary species responsible for damage to materials by S and N pollutants. NH_3, the primary gaseous basic compound in the atmosphere, can partly or completely neutralize these acids in particulate matter or in the aqueous phase, forming NH_4^+ ions.

On the surfaces of materials, N and S species can react to form a variety of degradation products. On metals and stone, the possible degradation products include nitrite, nitrate, sulfite, and sulfate species as well as minerals that incorporate nitrate or sulfate into a more complex composition. These degradation products may be more or less reactive to further degradation than the original material. Degradation products that are more reactive, or those that are soluble in water, do not have long lifetimes on a material surface. They undergo further chemical reactions and are transformed to other species, or they are washed off the surface by precipitation. Products which are less reactive and less soluble in water than the original material may form a protective layer on the surface of the material which inhibits or prevents further

damage from atmospheric pollutants. Products that are more reactive or water-soluble than the original material are readily removed, exposing the surface to more damage. The protectiveness of the products formed depends on the complex mixture of species present and the physical/chemical properties of the material.

Synergistic effects, which influence the rate of degradation of materials, are possible in atmospheres containing a complex mixture of pollutants. NO_X may enhance the oxidation of sulfite to sulfate and lead to faster rates of corrosion. The deposition velocity of SO_2 and NO_X may be influenced by the presence of HNO_3 deposited to the surface due to the increased degree of surface wetting.

E.2.4. Materials Damage Experimental Techniques

The $NO_Y/NH_X/SO_X$ air pollutants are comprised of numerous distinct chemical species, which may exist in the gaseous and/or particulate phases in the atmosphere, as well as in dissolved form in atmospheric precipitation and in condensed water on surfaces. In order to test the damaging effects of $NO_Y/NH_X/SO_X$ species on man-made materials, it is often necessary to simplify the system by testing under controlled laboratory conditions, typically with a very limited set of pollutants in a test chamber. Such tests generally use pollutant concentrations that are greatly elevated relative to ambient atmospheric levels, and may also use exaggerated temperature, humidity, or wetting, to accelerate the development of materials damage so that it can be detected. Chamber tests may not accurately mimic the mass transfer of pollutants in the atmosphere, and efforts in such tests to isolate the effects of one pollutant from the complex mixture present in the atmosphere are unrealistic. As a result, chamber tests may provide valuable information on potential effects and mechanisms involving ambient air pollutants, but cannot accurately predict the corrosion rates or effects of such pollutants in real situations.

Exposing materials of interest to the ambient atmosphere for extended time periods can provide a realistic look at the effects of air pollutants on materials. However, such ambient exposure tests are limited by the occurrence of natural (i.e., non-air pollutant) materials damage, and by the complexity of the $NO_Y/NH_X/SO_X$ system. While it is relatively easy to determine which materials suffer more or less damage during equivalent exposures to ambient air pollution, it is extremely difficult to determine which air pollutants are responsible for the observed damage. This is due to the co-occurrence of all air pollutants simultaneously, complexities in accurately measuring the suite of $NO_Y/NH_X/SO_X$ species, and interconversions among species (e.g. SO_X and SO_4^{2-}, NO_X and HNO_3) related to contact with materials or with moisture. The amount of time that surfaces are wet is a key factor in the extent of materials damage, and this factor may be difficult to determine in ambient exposures, because the presence of air pollutants themselves may enhance surface wetness on the microscale beyond that expected based on meteorological conditions (Dubowsky, 2004). Ambient exposure tests lead to retrospective analyses, in

which meteorological and air pollutant data, surface analyses, and measurements of chemical and physical properties are evaluated statistically to estimate the impacts of air pollutants on the exposed materials.

E.3. Effects on Dyes and Textiles

E.3.1. Fading of Dyes

The fading of dyes by N oxides has long been recognized, and dye manufacturers have worked to produce products less susceptible to this effect, through both improved dye chemicals and the use of inhibitors in dye formulations to minimize fading. Fading has been observed with both red and blue dyes, both on natural fibers (e.g., cotton, silk, wool) and on synthetics (e.g., nylon, rayon, polyester). The fading effect of NO_2 is generally reported to be greater than that of NO on various dyes with various fabrics. In exposures of dyed fabrics to ambient air, test samples must be shielded from sunlight, to avoid the substantial fading of dyes that results from sunlight exposure. Under such conditions, NO_2 and ozone (O_3) are often found to be about equally important in the fading of dyed fabrics.

and DeVries, 1993).

E.3.2. Degradation of Textile Fibers

N oxides can degrade a variety of synthetic fibers, with the greatest effects seen with nylon. With NO_2, the damage to nylon occurs due to breaking of the polymer chain (i.e., chain-scissioning). Similar weakening of nylon has been observed in tests with elevated concentrations of HNO_3. A synergistic effect was observed between mechanical stress and NO_X in the degradation of oriented nylon-6 fibers (Smith and DeVries, 1993).

E.4. Effects on Plastics and Elastomers

The group of materials called plastics includes a wide variety of polymeric materials such as polyethylene, polypropylene, polystyrene, polyurethanes, acrylic polymers, phenolics, and fluorocarbon polymers, among others. Plastic materials may include other components such as hardeners or plasticizers, and fillers that may impart properties such as physical strength. Elastomers are polymers that can stretch to at least their twice their normal dimensions and then return to their original dimensions when the stress is removed. Examples of elastomers include various rubber formulations and neoprene.

Plastics and elastomers can be damaged by NO_2, SO_2, and O_3, as well as by UV radiation in sunlight, and some studies have been designed to separate the effects of these factors.

Chamber studies at relatively high pollutant concentrations with sunlight or UV light have generally shown greater damage than from the pollutants alone. NO_2 is damaging to a variety of polymers and elastomers, causing either chain-scissioning or cross-linking (formation of additional bonds between polymer chains) depending on the polymer. Polypropylene is reported to be damaged more severely by SO_2 than by NO_2. Elastomers are damaged more severely than plastics. In tests where light and NO_2 have been present simultaneously, much of the damage observed in chamber tests has been attributed to O_3, produced by the interactions of the pollutants and UV light, rather than to NO_2 alone. In studies in which the same pollutant concentrations are present both with and without light, the greater damage observed in samples exposed to the light is often attributed to the light itself, when in fact chemical processes initiated by light (such as the formation of O_3) undoubtedly also play a part.

Cellulose nitrate can break down through hydrolytic, thermal, and photochemical reactions. Addition of plasticizer to cellulose nitrate slows the degradation substantially. NO_2 is of particular interest with regard to cellulose nitrate because it is not only capable of causing damage, but is also produced as a result of damage to the material (Shashoua, 2006). NO_2 is formed when N-O bonds connecting cellulose rings are broken. The NO_2 formed will then further degrade cellulose nitrate, thus the degradation is an autocatalytic process.

E.5. Effects on Metals

Metals are considered to be the materials most subject to damage from the $NO_Y/NH_X/SO_X$ air pollutants, and have been the subject of a great deal of research. The nature and concentration of the pollutant, its rate of deposition, and especially the duration of wetting of the surface are key factors in the corrosion of metals. Numerous studies have indicated corrosion rates of metal surfaces on the order of 1 to several micrometers per year (µm/yr) under real or simulated atmospheric conditions.

Table E-1 summarizes the materials tested, exposure conditions, and findings of recent studies related to the effects of $NO_Y/NH_X/SO_X$ air pollutants on metals. The studies listed in Table E-1 are discussed where applicable in the following sections.

E.5.1. Role of NO_Y, NH_X, and SOX in the Corrosion Process

In the atmosphere the $NO_Y/NH_X/SO_X$ pollutants occur together, along with other pollutants such as O_3 or chloride salts. While wetting of metals surfaces is the single greatest factor promoting corrosion, an important observation is the enhanced damage that occurs due to interactions among this mixture of

pollutants. It must be noted that in many studies the various $NO_Y/NH_X/SO_X$ species have not been adequately separated or quantified, and this may be the cause of conflicting observations from some studies. However, some generalizations can be made. Sulfur and chloride pollutants are generally more important at causing metals corrosion than N pollutants, however NO_X (or NO_Y) and SO_2 together have been shown to be more damaging than SO_2 alone. The combination of NO_2 and SO_2 has been shown to result in a synergistic effect where the total damage from the mixture is greater than the additive damage from the two pollutants separately (Svensson and Johansson, 1993a). This effect may be due to enhanced wetting of the surfaces caused by NO_Y pollutants, resulting in corrosion at lower relative humidities than would otherwise be the case. This enhancement has been attributed to the formation of hygroscopic nitrate salts, but may also be caused directly by the deposition of gaseous HNO_3 onto the surface (Dubowsky, 2004). The corrosion effect of HNO_3 on zinc, copper, and steel is larger than that of SO_2 alone or a mixture of SO_2 and NO_2 (Samie et al., 2007).

Although deposition of $NO_Y/NH_X/SO_X$ species in particulate matter can soil metal surfaces, such deposition does not directly result in substantial metals damage. However, under wet conditions these soluble species form an electrolytic solution that can cause corrosion. Corrosion of steel and zinc has been found to depend on the surface electrolyte irrespective of the presence of particles (Askey et al., 1993).

Temperature has been found to have a complex effect on metals corrosion. Lower temperatures tend to increase surface wetness, but decrease the diffusivity of gaseous pollutants, and may reduce the rates of some reactions that convert SO_2 and NO_X to sulfuric and nitric acids. Thus, the effect of temperature changes on long-term corrosion rates can be hard to predict.

E.5.2. Effect on Economically Important Metals

Steel is the most common and economically important structural metal, and is often used in galvanized form (i.e., with a protective coating of zinc). SO_2 is generally reported to be more corrosive than NO_X, however for well-protected steel the effects of ambient air pollutants are usually a small increment on top of the natural weathering process. The N pollutants can have an enhancing effect on the corrosion caused by the S pollutants. This is attributed to the increased wetting that can result from the presence of hygroscopic NO_3 salts. Relative humidity has been shown to be very important in the corrosion of steels by SO_2 with much slower corrosion rates observed when the relative humidity is below 70% (Dehri et al., 1994). The presence of SO_2 has been shown to reduce the corrosion pitting of iron induced by sodium chloride (NaCl) but there may be an overall synergistic effect among SO_2, NO_2, and NaCl (Weissenrieder et al., 2004). Steel corrosion rates have been shown to decrease over time (Almeida, 2000) (Damian and Fako, 2000) approaching steady state rates after approximately 4000 days (Damian and Fako, 2000).

Zinc corrosion has been shown to be inversely dependent on temperature (Svensson and Johansson, 1996). Corrosion products formed on zinc in polluted environments are less water soluble, and therefore more protective against further corrosion, than corrosion products formed in clean environments (Vilche et al., 1995). The combination of SO_2 and NO_2 showed synergistic (i.e., greater than simply additive) corrosive effects on zinc (Svensson and Johansson, 1993a). SO_2 slowed the $NaCl^-$induced corrosion of zinc while NO_2 accelerated that corrosion (Svensson and Johansson, 1993b).

Aluminum is naturally protected from corrosion by a formation of a durable surface film, but some effects of the $NO_Y/NH_X/SO_X$ pollutants have been observed. Minimal damage is caused to Al by NO_X. The mixture of SO_2 and NO_X is variously said to be either more or less corrosive to Al than SO_2 alone. The deposition rate of SO_2 to Al was shown to increase in the presence of O_3, but no effect on SO_2 deposition rate was found for NO_2 (Blucher et al., 2005). Interaction between SO_2 and NaCl results in an increased corrosion rate but decreased pitting of Al compared to NaCl alone (Blucher et al., 2005). Oesch and Faller (1997) found that SO_2 is more corrosive to Al than NO_2 and that there is no difference in Al corrosion rate when exposed to NO or clean air.

Mixtures of NO_X and SO_2 are more corrosive to copper than either pollutant alone. When hydrogen sulfide (H_2S) and O_3 were also evaluated for damage to copper, they also were found to be more damaging to copper than NO_X. The corrosion rate of copper exposed to SO_2 or NO_2 has been shown to slow over time (Oesch, 1997) (Oesch and Faller, 1997; Leuenberger-Minger et al., 2002). The corrosion rate of copper in the presence of NO_2 is greater than in clean air. In the first 24 h of exposure to NO_2, an acidic electrolyte is formed on the surface that dissolves copper oxides and results in an increased corrosion rate (Dante and Kelly, 1993). Synergistic effects have been seen between SO_2 and O_3 (strong) and NO_2 (weak) (Aastrup et al., 2000). High corrosion rates were observed for field exposures of copper at sites with a combination of SO_2 and O_3. After four years of exposure, 90% of the corrosion products formed on copper remained on the surface (Leuenberger-Minger et al., 2002). The copper hydroxy sulfates brochantite and antlerite are stable copper corrosion products formed in the presence of SO_2, O_3, and NO_2 (Strandberg, 1998).

Nickel is also damaged more severely by SO_2 or chloride salts than by NO_X. Nickel samples deployed at urban, industrial, and rural sites showed that corrosion rates increase with SO_2 concentrations. Soluble hydrated nickel sulfates were the main corrosion products and are easily removed from the surface by rainfall events, thereby exposing the underlying surface (Jouen et al., 2004).

Kim et al. (2004) conducted a study of the effects of ambient SO_2 and NO_2 on steel, bronze, copper, and marble at sites in China, Korea, and Japan. Both sheltered and unsheltered samples were exposed with the corrosion rates of the unsheltered samples higher in all cases. The corrosion rate of steel was the highest, followed by marble, bronze, and copper. Higher corrosion rates (especially for unsheltered samples) were found to be correlated with high SO_2 concentrations.

E.5.3. Effects on Electronics

The increasingly wide penetration of electronic devices into daily life offers greater opportunities for environmental damage to sensitive components. The hardware of communication systems may be exposed to pollutants in outdoor air, and the ubiquitous cell phones may be exposed in both indoor and outdoor environments. Sulfur and N oxides have been shown to corrode the metallic contacts in electronic equipment, which are often made of copper or brass coated with a precious metal such as gold, palladium, or nickel. Such materials are corroded more by NO_2 than by SO_2, but a mixture of these two pollutants is more corrosive than either alone. The combination of SO_2 and H_2S is also less damaging than either NO_2 alone or a combination of NO_2 and these pollutants. NO_2 is also moderately corrosive to solder in electronic components.

E.6. Effects on Paints

Painted surfaces are extremely common as a means of preventing damage to other materials, and may be categorized as architectural coatings (e.g., house paint), product coatings (e.g., automobile finishes), and special-purpose coatings (e.g., bridge paint). Environmental damage to painted surfaces is expected, and periodic repainting is normal, but any factor that causes more rapid degradation or discoloration of paints will require more frequent repainting and thus result in higher costs. Paint formulations may differ widely for different applications, so the extent of air pollution damage in a given application cannot necessarily be predicted from published information. Previous work at elevated pollutant concentrations has shown that oil-based house paint is readily damaged by SO_2 and moisture, and is more subject to damage by SO_2 than by NO_2. Sample weights increased with increasing NO_2, but it is not clear if this indicates direct reaction of NO_2 or an enhancement of the effects of SO_2 and moisture by NO_2. The effect of SO_2 may be due to reaction with $CaCO_3$ and zinc oxide (ZnO) present in the paint. Tests with various paints showed that NO_X becomes incorporated into the paint surface upon long exposure, apparently by reaction with polymers that make up the cured paint. In other tests HNO_3 was found to produce substantially more damage to paints containing both low and high levels of carbonate (CO_3^-) than did an equal mixing ratio of NO_2.

Grosjean et al. (1983) studied the fading of colorants on cellulose paper. Twelve colorants were exposed to various atmospheres including purified air, NO_2, SO_2, and a mixture of oxidants (O_3, NO_2, and peroxyacetyl nitrate (PAN)). Not all colorants were tested in each atmosphere. The mixture of oxidants resulted in the largest color change for each tested colorant. Only one colorant was exposed to SO_2, NO_2, and the mixture. For that colorant, the color change induced by the mixture of oxidants was approximately three times the color change with NO_2 alone; the color change with SO_2 was

approximately 70% of the color change with NO_2. An increase in relative humidity results in increased fading of colorants (Grosjean et al., 1993, 1994). Of 35 colorants exposed to a mixture of O_3, NO_2, and PAN, nine exhibited substantial color changes and three exhibited moderate color changes (Grosjean et al., 1993).

Paint samples were exposed to UV light, NO_X, SO_2, and a combination of the treatments by Colombini et al. (2002). The exposure conditions were chosen to produce accelerated aging of paint samples. Non-pigmented paints were chosen to isolate degradation of the paint binder from synergistic effects with pigments. Exposure to the combination of treatments resulted in increased cross-linking in the paint binder as well as formation of organic acids. An examination of paint samples taken from naturally aged paintings confirmed the presence of organic acids as degradation products.

E.7. Effects on Stone and Concrete

The effects of $NO_Y/NH_X/SO_X$ air pollutants on stone and concrete are undoubtedly the most widely studied because of their impact on historic buildings, monuments, and archeological treasures. Table E-2 summarizes studies of the effects of $NO_Y/NH_X/SO_X$ on stone, concrete, and mortars. Calcareous stone (i.e., that consisting of $CaCO_3$, such as marble, limestone, and cement) is most susceptible to damage. Mortar used in stone construction is often more porous than calcareous stone, and therefore more subject to damage. The damage to such materials is attributed primarily to the effect of SO_2 in forming gypsum ($CaSO_4 \cdot 2H_2O$):

$$CaCO_3 + SO_2 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2$$

The gypsum thus formed occupies a larger volume than the original carbonate, so the stone surface becomes pitted and damaged. Gypsum is also more soluble than the carbonate, so it can be removed by precipitation, exposing the surface to further reaction and damage. As a result, dry deposition of SO_2 to the stone surface between rain events is important, as it causes continued damage. The reaction of SO_2 with calcareous stone is more energetically favorable than the reaction of N oxides, and thus SO_2 is the primary cause of damage to stone, however the combination of SO_2 and NO_X is more damaging than SO_2 alone. This effect may be due to enhanced wetting of the stone, to oxidation of SO_2 by the N oxides, or to formation of calcium nitrate ($Ca(NO_3)_2$), which is much more soluble than $CaCO_3$ and is easily washed off the stone surface by precipitation. Removal of the nitrate salts in this way may result in underestimation of the role of N oxides in stone damage when surface layers are analyzed for chemical composition.

Concrete is more susceptible to damage from N oxides than are the calcareous stones, because concrete contains calcium hydroxide ($Ca(OH)_2$), which can react to form calcium nitrate ($Ca(NO_3)_2$). This product is soluble and can be washed out of the concrete, weakening the material.

Deposition of particulate matter onto stone primarily results in soiling of the stone, due to the elemental carbon and organic compound content of the deposited particles. The orientation of the surfaces and size of the particles affect deposition: vertical surfaces are more affected by deposition of fine particles, whereas horizontal surfaces are more affected by large particles. The fine particles carry the bulk of the carbon and organic material. Metal oxides present in deposited particles may enhance the reaction of SO_2 to form gypsum.

Gypsum crusts form more readily in rain-sheltered environments than on rain-washed stone surfaces (Zappia et al., 1998). The presence of fog water has been shown to increase the rate of gypsum formation on surfaces sheltered from rain washing (Del Monte and Rossi, 1997). Gypsum crust formation has been shown to proceed at a faster rate when the stone surface is sprinkled with fly-ash particles. In addition, fly-ash (or other carbonaceous particles) can become entrained in the gypsum matrix and affixed to the stone surface. Normally, gypsum crusts are gray in color, but when carbon containing particles are entrained, they become black (Ausset et al., 1999). While gypsum crusts are composed primarily of sulfates, they have been found to contain nitrate compounds as well (Marinoni et al., 2003; Martinez-Arkarazo et al., 2007). The inclusion of nitrates in gypsum crusts suggests that N oxides, as well as SO_2, play a role in the degradation of stone exposed to the atmosphere. The presence of particulate matter, in addition to SO_2, has been shown to increase gypsum formation by 20% (Boke et al., 1999). Ambient SO_2 concentrations alone are not adequate to predict the degree of damage to stone samples (Torfs and van Grieken, 1996).

Dolomite has been shown to be less sensitive to sulfation than calcite (Lan, 2005). Corrosion of marble due to S species has been found to be of the same order of magnitude as that caused by N species. Damage is caused not by the gas phase oxides (SO_2, NO_2, NO) but by acid (H_2SO_4, HNO_3) and salt (SO_4^{2-}, NO_3^-) species present in the electrolyte which forms on the marble surface (Sikiotis and Kirkitsos, 1995). The rate of marble surface recession by rain washing is faster than the rate of gypsum crust formation due to dry deposition of S and N containing pollutants. Marble is damaged by rain washing through two mechanisms, dissolution of the gypsum crust and dissolution of the underlying marble. The gypsum crust is more soluble in water than marble and is rapidly dissolved in rain. The naturally occurring acidity in rainwater from the dissolution of carbon dioxide (CO_2) is an important mechanism by which stone samples are degraded, but additional acidity from the dissolution of SO_2 and NO_2 in rainwater does not greatly increase the solubility of marble in rainwater (Yerrapragada, 1996).

While gypsum is the primary degradation product found on stone, mortar, and concrete samples, other damage products do occur. Sulfite species have been found on mortars as intermediate damage

products. On mortars, a secondary damage mechanism exists in which gypsum reacts with calcium Al hydrates present in the mortar to produce ettringite ($Ca_6Al_2(SO)_4(OH)_{12}\cdot 26H_2O$). Ettringite is an insoluble sulfate that may cause damage by expansion and lead to cracking of mortars (Sabbioni, 2002)(Sabbioni et al., 2001, 2002).

E.8. Effects of NO_X on Paper and Archival Materials

The cellulose fibers that make up paper are reactive with NO_2 and other NO_Y species, and storage condition standards have been set regarding acceptable levels of NO_X for archives, libraries, and museums. Exposure of archival materials to NO_Y species in such facilities can arise from normal outdoor or indoor sources, but also from generation of such NO_Y species from the materials themselves. Specifically, stored materials that include cellulose nitrate, e.g., in the form of photographic film, adhesives, or recording media, can slowly decompose to release NO_X and product species such as HNO_3. These emissions can degrade archival materials, and even be a safety hazard if allowed to accumulate. In terms of outdoor air pollutants, it is likely that HNO_3 is a key reactant in the degradation of paper archives. The rapid deposition velocity of HNO_3 and the numerous surfaces in archival facilities provide opportunity for attack by HNO_3, and probably result in the effects of HNO_3 being underestimated, relative to those of NO_X, based on indoor air measurements. Artists' pigments can also be damaged by extended exposure to ambient atmospheric NO_2.

The effects of SO_2 and O_3 on paper were studied by Johansson and Lennholm (2000). The deposition rate of SO_2 to fresh paper was found to decrease rapidly with time and approached steady state after ten hours. The deposition rate of SO_2 to fresh paper in the presence of O_3 was found to be elevated compared to SO_2 alone. The deposition rates to aged paper were much lower and there was no effect on the SO_2 deposition rate observed in the presence of O_3. The decrease in deposition rate with time is thought to be due to protonation of all available carboxylate ions to carboxylic acid.

Pigments in works of art can be degraded or discolored by atmospheric pollutants. H_2S has been shown to react with both copper and lead pigments, but only lead white has been seen to darken over time (Smith and Clark, 2002). A synergistic effect has been detected between NO_2 and both benzene and toluene resulting in an increased rate of attack on pigment oxides (Agelakopoulou et al., 2007). Deposition of S to the surface of paintings, either as SO_2 or ammonium sulfate ($(NH_4)_2SO_4$) particles, can damage, varnish, or cause discoloring of paint (Gysels et al., 2004). Paint models subjected to accelerated aging in SO_2 (10 ppm) and NO_X (10 ppm) as well as UV radiation for 15 days exhibited a variety of damage markers. Both nitrate and sulfate damage mechanisms were observed with sulfation sometimes masking other processes (Arbizzani et al., 2004).

E.9. Costs of Materials Damage from NO_y, NH_X, and SOX

Materials exposed to the ambient atmosphere are degraded and damaged through a number of mechanisms. Damage associated with air pollutants result in effects such as decreased usable lifetime, increased maintenance frequency, and loss of aesthetic appeal. It is difficult to separate the costs associated with air pollutants from costs associated with other damage mechanisms. Some estimates of cost have been based on empirically derived dose-response functions for specific materials. Other estimates have been developed using inspection of actual materials damage and maintenance guidelines for the materials (Cowell and Apsimon, 1996). Estimation of costs over large geographic areas is subject to considerable uncertainty due to unknown distribution of materials at risk and spatial variations in pollutant concentrations. A cost estimate for material cost savings from SO_2 emission reductions in Europe was performed by Cowell and Apsimon (1996). In this study, the cost savings of theoretical future emission reductions across Europe was modeled using cost data extrapolated from a study conducted in three Norwegian cities. Total theoretical SO_2 reductions of 15,904 kilotons per year resulted in modeled annual cost savings of $9,504 million total for Europe (Cowell and Apsimon, 1996; Apsimon and Cowell, 1996).

E.10. Summary

Many types of materials, including metals, electronics, plastics, paints, stone, and paper may be damaged by atmospheric $NO_Y/NH_X/SO_X$ species. Damage occurs due to dry and/or wet deposition of the pollutants onto the surface of a material and subsequent formation of an electrolytic solution in water present on the surface. At low relative humidity, when little water is present on surfaces, damage rates have been observed to be much lower, and in some cases, no damage has been observed. Both SO_2 and NO_2 have been implicated in damage processes for different materials. In general, damage to materials by SO_2 is greater than by NO_2. Little work has been conducted to investigate the effects of NO on material damage. What work has been conducted shows no damage, or very minor damage for NO containing environments compared to clean air. Synergistic effects between SO_2 and NO_2 lead to increased damage rates for the gases in combination. Other species such as O_3, NaCl, organics, or particulate matter have also been shown to have synergistic effects with SO_2 and NO_2. The corrosive effects of nitric acid have been found to be stronger than effects of other $NO_Y/NH_X/SO_X$ species. Costs associated with damage to materials by atmospheric pollutants are difficult to estimate because of the many sources of uncertainty in the estimation process. For heavily polluted environments, the cost savings due to decreased rates of material degradation could offset a significant portion of the costs to reduce emissions. In general, for polluted environments, reductions in SO_2 or HNO_3 concentrations will reduce damage rates more than

reductions in NO_2, NO, or NH_3. In areas with low SO_2 concentrations, reductions in NO_2, O_3, or particulate matter concentrations may reduce damage rates.

Table E-1. Studies on corrosive effects of $NO_Y/NH_3/SO_X$ effects on metals.

Materials	Exposure Conditions	Findings	Reference
Zinc Mild Steel	Samples were exposed to fly-ash in clean air and in air with SO_2 and/or HCl (presentation rates of 27 × $10^{-}6$ and 4.7 × $10^{-}6$ mg/cm^2s, respectively). A synthetic acid rain solution was used to model wet deposition.	Corrosion was found to depend on the surface electrolyte irrespective of the presence of particles. Inert particles were found to increase corrosion rates in relatively unpolluted atmospheres. With higher pollution levels, species leached from particulate matter contribute to the conductance of the surface electrolyte and thus increase the corrosion rate.	Askey et al. (1993)
Copper	Copper samples were exposed to 264 ppb NO_2 in a laboratory setting. Exposures were limited to 72 h to study the initial corrosion behavior.	The corrosion rate of copper in the presence of NO_2 was much greater than in clean air. The surface electrolyte was found to contain predominantly nitrate with only trace levels of nitrite. After 24 h, the electrolyte had become sufficiently acidic to dissolve the copper oxide layer. Once the copper oxide was dissolved, corrosion proceeded at a significantly faster rate.	Dante and Kelly (1993)
Zinc	Zinc samples were exposed to SO_2 (0.78 ppm) and/or NO_2 (1.06 ppm) for 420 h. Some samples were treated with NaCl prior to exposure.	SO_2 slowed the corrosion of zinc with moderate to high surface concentrations of NaCl due to the formation of sodium zinc hydroxychloride sulfate. NO_2 (which, alone, is unreactive toward zinc) accelerated the corrosion of zinc in the presence of small amounts of NaCl.	Svensson and Johansson (1993b)
Galvanized Iron Zinc	Samples were exposed to SO_2 or NH_3 in the laboratory. Air was supplied at 5 cm/s and the pollutant gases at 3 cm/s. The concentrations of the gases were very high to accelerate the tests.	Corrosion rates in SO_2 were found to be largely dependent on relative humidity. No such humidity dependence was observed for corrosion induced by NH_3. Corrosion rates in both gases decreased sharply with time (approaching steady state values after 30 h).	Dehri et al. (1994)
Aluminum Zinc	Samples were exposed to ambient air for 4 yrs at 6 sites. SO_2 deposition rates ranged from 10 mg/m^2day to non-detectable levels across the sites. Time of wetness was also measured at each site.	Corrosion products that developed in rural environments were found to be easily removed from the surface and thus result in poor protectiveness. Corrosion products formed in more aggressive environments were found to be more protective against continuing corrosion.	Vilche et al. (1995)
Zinc	Samples were exposed at temperatures of 4, 14, 22, and 30 C with 95% relative humidity. SO_2 was supplied at 500 (± 5) ppb and 107 (± 2) ppb.	SO_2 induced corrosion was found to be inversely dependent on temperature. The maximum corrosion rate (at 107 ppb SO_2) of 11 mg/cm2d was observed at 4 C. The corrosion rate at 30 C was 6.8 mg/cm2d.	Svensson and Johansson (1996)
Copper Zinc Aluminum	Samples were exposed in the laboratory to SO_2 (1.5 ppb, 0.5 ppm, 10 ppm), NO_2 (10 ppm), NO (10 ppm), or O_3 (10 ppm).	NO was found to have no effect on the corrosion of copper, zinc, or aluminum. Copper in the presence of SO_2 (10 ppm) and NO_2 led to significant material loss initially with a slowing of the rate with increasing time. O_3 was found to have the strongest influence on the corrosion of copper. Only very slight mass gains were observed for copper exposed to 0.5 ppm SO_2. A small effect on zinc was observed for NO_2 with SO_2 (10 ppm) resulting in the largest weight gain. SO_2 at 0.5 ppm had a much larger effect on zinc than on copper. For aluminum, O_3 had the largest effect followed by SO_2 and NO_2.	Oesch and Faller (1997)
Copper	Powdered samples of copper patina compounds (tenorite, cuprite, brochantite, antlerite, and atacamite) were exposed to SO_2 (476 ppb) alone or in combination with NO_2 (450 ppb) or O_3 (500 ppb). Some samples were pretreated with carbon.	Tenorite reacted rapidly with SO_2 to form brochantite and other sulfate containing products. Cuprite reacted slowly with SO_2 alone but addition of O_3 formed antlerite and brochantite. NO_2 did not produce the same effect. For samples with carbon on the surface, the oxidation reaction was greatly enhanced. Brochantite and antlerite were found to be stable in atmospheres with SO_2 in combination with O_3 or NO_2.	Strandberg (1998)
Copper	Samples were exposed to atmospheres containing approximately 200 ppb of SO_2, SO_2 and O_3, or SO_2 and NO_2. O_3 and NO_2 were introduced at different times in the exposure scenarios.	Copper sulfite and cuprous oxide formed on copper surfaces exposed to SO_2. With O_3 present, an increased rate of mass gain was measured, and copper sulfite was converted to copper sulfate. NO_2 increased the mass gain to a lesser extent than O_3 and resulted in the formation of copper nitrate in addition to copper sulfate.	Aastrup et al. (2000)

Materials	Exposure Conditions	Findings	Reference
Mild Steel	Steel samples were exposed to the atmosphere in 47 marine atmospheres with varying levels of chloride and SO_2. Atmospheres were separated for data analysis based on chloride and SO_2 deposition rates.	Samples exposed at sites with moderate SO_2 and chloride deposition rates formed compact, rounded corrosion structures. Samples at sites with high SO_2 and moderate chloride exhibited cracking in the corrosion products. Samples at sites with high chloride and moderate SO_2 exhibited the highest corrosion rates of the mixed atmospheres. The 1 site with high chloride and high SO_2 exhibited a lower corrosion rate than expected.	Almeida et al. (2000)
Steel	Two types of steel were exposed to urban-industrial and rural atmospheres for 20 yrs. Avg SO_2 concentrations were 90 and <10 $\mu g/m^3$ (34 and <4 ppb) for urban and rural environments, respectively.	The corrosion rates of the two grades of steel were similar with values of 0.1 and 0.08 mm/yr for the urban and rural environments, respectively. The initial rate of corrosion was significantly faster and steady state values were approached after 4000 days exposure. The similar corrosion rates measured for the samples were thought to be due to similar time of wetness at both sites.	Damian and Fako (2000)
Copper Zinc	Samples were exposed in the field at 8 sites. SO_2, NO_2, and O_3 concentrations were monitored over a 4–yr exposure duration at each of the sites.	The highest corrosion losses for copper were observed at the site with the highest combination of SO_2 and O_3. For zinc, the highest corrosion losses were observed at the site with the highest SO_2 concentration. Both metals showed a decrease in corrosion rate with time. Runoff rates from copper were much smaller than from zinc. 90% of the corrosion products remained on the copper surface after 4 yrs; only 40% of the zinc corrosion products remained after 4 yrs.	Leuenberger-Minger et al. (2002)
Nickel	Nickel samples were exposed in the field at 3 sites (urban, industrial, and rural) for 1 yr. Concentrations of NO (41.1, 9.7, and 2.9 $\mu g/m^3$) (33, 8, and 2 ppb), NO_2 (50.1, 24.2, and 8.7 $\mu g/m^3$) (26, 13, and 5 ppb), SO_2 (22.3, 29.0, and 12.2 $\mu g/m^3$) (8, 11, and 5 ppb), and O_3 (25.8, 47.1, and 60.1 $\mu g/m^3$) (13, 24, and 30 ppb) were measured at the urban, industrial, and rural sites, respectively.	Mass loss rates of 320, 570, and 200 µg/cm2y were determined for urban, industrial, and rural environments, respectively. Mass loss was found to increase with increasing SO_2 concentration. Soluble corrosion products were formed on the surface and then removed by rainfall events. Hydrated nickel sulfates were the main corrosion products formed on the nickel surface.	Jouen et al. (2004)
Iron	Samples were exposed to humidified air in the laboratory. Samples were exposed to clean air, SO_2 (200 ppb), SO_2 and NO_2 (each 200 ppb), or SO_2 and O_3 (each 200 ppb). The same exposure conditions were used for iron samples with NaCl deposited on the surface.	No corrosion products were detected on samples exposed to humidified air alone. The addition of SO_2 alone was not enough to initiate a change in corrosion behavior of the samples. When an oxidant (NO_2 or O_3) was added to the humidified air/SO_2 system, a significant increase in corrosion rate was observed. SO_2 was found to inhibit the NaCl induced corrosion of iron, but the combination of SO_2 and NO_2 was found to accelerate NaCl induced corrosion.	Weissenrieder et al. (2004)
Aluminum	Aluminum samples were exposed to SO_2 (96 ppb) either alone or in the presence of other pollutants (NaCl, NO_2, or O_3).	SO_2 alone resulted in the loss of metallic luster. 50% of the surface had developed corrosion products after 672 h. Samples exposed to NaCl alone showed significantly larger mass gain than samples exposed to only SO_2. The combination of SO_2 and NaCl resulted in the largest mass gain (fastest corrosion rate). While the rate of mass gain was highest with a combination of SO_2 and NaCl, the pitting observed in the presence of NaCl alone was significantly reduced. O_3 was found to slightly increase the deposition rate of SO_2, no effect on SO_2 deposition rate was observed for NO_2.	Blucher et al. (2005)
Copper Zinc Steel	Samples were exposed to HNO_3 (50–180 ppb) in a laboratory exposure chamber. Tests were conducted at 65% and 85% relative humidity.	The corrosion effects of HNO_3 on carbon steel were larger than on zinc or copper. The corrosion effect of HNO_3 was found to be larger than corrosion from SO_2 alone or a mixture of SO_2 with O_3 or NO_2. No increase in corrosion was observed at 85% relative humidity compared to 65% relative humidity.	Samie et al. (2007)

Table E-2. Studies on corrosive effects of $NO_Y/NH_3/SO_X$ on stone.

Materials	Exposure Conditions	Comments	Reference

Materials	Exposure Conditions	Comments	Reference
Marble	Laboratory exposure to HNO_3 ranging from 54 to 4174 µg/m^3 (21 to 1603 ppb). Field exposures were conducted in several stages in Greece. Avg concentrations for field exposures were 1.41 µg/m^3 (0.5 ppb) HNO_3, 2.39 µg/m^3 (3 ppb) NH_3, 4.84 µg/m^3 NO_3^-, 14.61 µg/m^3 SO_4^{2-}, and 5.01 µg/m^3 NH_4+.	Marble was found to be a very good sink for HNO_3. The extent of corrosion by sulfates and nitrates were found to be of the same order of magnitude. Corrosion was found to be caused by acid and salt species (HNO_3, H_2SO_4, etc.) on the surface rather than the oxides (SO_2, NO_X).	Sikiotis and Kirkitsos (1995)
Limestone	Samples of differing thickness were exposed in the field and runoff water collected for 5 mos. The avg SO_2 concentration was 60 µg/m^3 (23 ppb).	Damage functions were developed to try to determine the ionic sulfate content in runoff water from the ambient SO_2 concentration. It was determined that the ambient SO_2 concentration alone does not determine the sulfate concentration in runoff water.	Torfs and van Grieken (1996)
Marble	Laboratory exposure to 10 ppm of SO_2 and NO_2. Field exposure to either dry deposition or dry and wet deposition in Louisville, Kentucky. Avg concentrations of 10 ppb SO_2 and 25 ppb NO_2 for field exposures.	Gypsum crust thickness of 1.9 µm for rain sheltered samples after 1 yr of exposure. SO_2 was found to be the dominant factor in crust formation. Surface recession due to rain washing was 14.5 µm/yr and due to dissolution of the gypsum crust as well as dissolution of the original marble.	Yerrapragada et al. (1996)
Marble Brick	Samples exposed in the field for 8 days with multiple fog episodes. Over 3 measurement campaigns, the mean pollutant concentrations were 17.2 µg/m^3 (7 ppb) SO_2, 265 µg/m^3 (139 ppb as NO_2) NO_X, and 131 µg/m^3 suspended particles.	For all samples, gypsum was the only stable mineral formed following exposure to fog water in a polluted environment. Exposure to fog water may be a significant cause of corrosion for materials sheltered from rainwater, but is of lesser importance if a material is exposed to rain.	Del Monte and Rossi (1997)
Marble Limestone Mortars	Samples were exposed to urban environments in both sheltered and unsheltered configurations. Pollutant concentrations were not reported.	Sulfation was the primary damage mechanism and was more intense on mortars than on stones due to higher porosity. Higher concentrations of degradation products were found on samples sheltered from rain than on samples exposed to rain.	Zappia et al. (1998)
Jaumont limestone	Samples were exposed to 340 µg/m^3 (125 ppb) SO_2 and 98 µg/m^3 (50 ppb) NO_2 in the laboratory. Samples were either exposed naked or sprinkled with fly-ash particles. Field exposure was conducted for 1 yr with samples sheltered from rainwater. Avg SO_2 concentration during the field exposure was 107 µg/m^3 (40 ppb).	Sulfation (gypsum formation) was found to proceed with greater intensity for samples sprinkled with fly-ash than for naked samples. The growth of gypsum crystals fixed the fly-ash to the surface of the limestone. Fly-ash was found to be an important factor in crust formation by facilitating gypsum crystal formation. Fly-ash particles also darken gypsum crusts from gray to black.	Ausset et al. (1999)
Calcium carbonate	Powdered calcium carbonate was exposed to 10 ppm SO_2 and 90% relative humidity for 124 days.	Reaction between calcium carbonate and SO_2 was found to take place in a liquid film on the calcium carbonate surface. The presence of several different types of airborne particles was found to increase the extent of sulfation by 20%. The SO_2 concentration used is unrealistic for ambient conditions.	Boke et al. (1999)
Mortars	A wide range of mortar and plaster samples were collected from sites throughout Europe. Pollutant concentrations over the life of the buildings were not reported.	Sulfation was the primary damage mechanism observed. Sulfite was found as an intermediate damage product in the sulfation process. Ettringite was also found as a secondary damage product due to a reaction between gypsum and calcium aluminum hydrates.	Sabbioni et al. (2001)
Mortars	Plaster and mortar samples were collected from buildings in the Old Venice Arsenal. Pollutant concentrations over the life of the building were not reported.	Gypsum was found to be the primary damage product on all of the mortars sampled. A secondary damage mechanism was found where gypsum reacts with calcium aluminum hydrates to form ettringite, an insoluble sulfate. The presence of sulfur in the damage products indicates SO_2 as the most aggressive atmospheric pollutant toward mortars.	Sabbioni et al. (2002)
Concrete	Samples were collected from the interior of a tunnel in Italy. The tunnel formerly held a railway and currently houses a road with heavy automobile traffic. SO_2 levels have declined from 350 µg/m^3 (132 ppb) in 1970 to ~10 µg/m^3 (4 ppb) in 2002. NO_X concentrations have remained relatively constant around 100 µg/m^3 (52 ppb as NO_2) over the same time period.	The urban mixture of pollutants (SO_2, NO_X, CO_2, and particles) results in formation of dendritic crusts on concrete. Nitrates were found to be present in the largely gypsum crusts. Soot particles were found embedded in the crusts as well. Low quality starting materials provide a more porous media that is more susceptible to degradation by atmospheric pollutants. The degradation of concrete is more similar to that of sandstone than of limestone.	Marinoni et al. (2003)
Marble	Samples exposed to atmosphere and sheltered from rain at 4 sites. SO_2 concentrations ranged from ~2 to 20 ppb across the sites.	Sulfation was the primary damage mechanism observed. Marble containing dolomite was less sensitive to SO_2 than calcite marble. For relative humidity greater than 72%, humidity was an important factor in determining the sulfation rate.	Lan et al. (2005)
Limestone Sandstone	Samples were collected from 3 facades of a historical building in Spain. Samples were collected from the surface as well as 5 mm below the surface to determine degradation and original compositions, respectively. Pollutant concentrations over the life of the building were not reported.	The main decay products on the surface were found to be nitrate compounds. Samples with black crusts on the surface were found to have predominantly gypsum and soot, but nitrate compounds were identified in the crusts as well. Sandstone samples were much more damaged than limestone samples due to their higher porosity.	Martinez-Arkarazo et al.(2007)

ANNEX E - References

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Annex F. Valuation of the Environmental Effects of N and S (non-materials)

F.1. Introduction

The monetary valuation of ecological effects associated with NO_X and SO_X emissions starts with natural science endpoints. These may be things that people value directly, such as loss of a particular species, or some remote effect on a resource that is not clearly understood by the general public or not valued by the public for itself, such as forest soils. Of course, damage to forest soils will affect the terrestrial ecosystem in ways that may be valuable to humans, such as tree growth, habitat, and even the aesthetics of the forest. This Annex is a review of the literature that estimates such values for various ecosystem endpoints or that provide values for effects that can be reasonably inferred from what is provided.

The purpose of this Annex is to provide an assessment of the economics literature on the effects of NO_X and SO_X emissions on terrestrial, transitional, and aquatic ecosystems.

F.1.1. Valuation in the Context of NO_X and SO_X

Figure F-1 provides a schematic representation of how economic valuation is derived from changes to NO_X and SO_X secondary standards. Starting at the upper left-hand side, the NO_X and SO_X standards are set and emissions reductions occur to change the ambient concentrations of NO_X and SO_X. Reading down from "Change in Ambient Concentrations," these reductions will lead to changes in a variety of ecological endpoints (as identified in the ISA) in terrestrial, transitional, and aquatic ecosystems. The box below, "Change in Economic Endpoints," refers to physical endpoints that people care about, in which changes can be valued (at least in principle) in monetary terms. Many times, these are referred to as ecosystem services. In a few cases, such as agricultural crop growth and yield, ecological and economic endpoints are nearly the same. Finally, at the bottom of this diagram is a box labeled "Valuation Methods," which notes alternative approaches for placing monetary values on these economic endpoints. As endpoints are discussed in detail in the ISA, this Annex focuses solely on valuation.

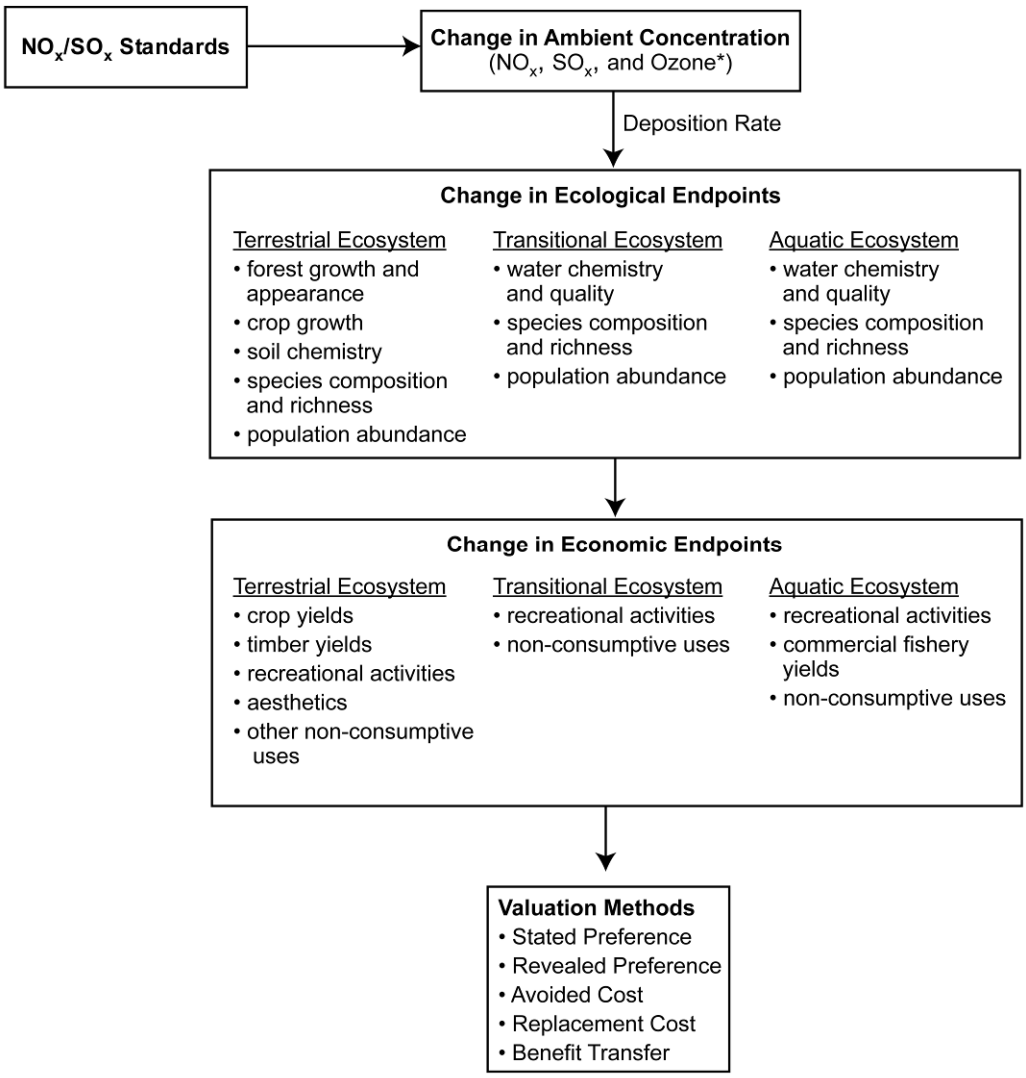


Figure F-1. Illustration chart of the assessment.

F.1.1.1. Ecosystem Services

Broadly defined, ecosystem services are the benefits that people obtain from ecosystems (Millennium Ecosystem Assessment, 2003). In the Millennium Ecosystem Assessment (MA), ecosystem services are classified into provisioning, regulating, supporting, and cultural services. Provisioning services denote the products people obtain from ecosystems; regulating services are associated with the ecosystem functions that regulate climate, nutrient cycle, water filtration, and so forth; supporting services are ecosystem functions, such as primary productivity and production of O_2, that support the provision of ecosystem services; and cultural services are the non-material benefits ecosystems provide to people through spiritual enrichment, cognitive development, reflection, recreation, and aesthetic experiences.

Ecosystems are productive systems in which various biological and physical factors, as well as their interactions, serve various functions in the production of ecosystem services. However, economic valuation of the environment has focused mostly on the contributions of individual goods and services to human well-being. Alternately, ecosystem services valuation is based on the various benefits generated by the ecosystem (Polasky et al., 2005). In this case, benefits include both marketed and non-marketed services, and their valuation considers the environment as a natural capital asset that generates returns on investment in ecosystem protection and management.

For example, wetlands constitute a form of natural capital. They serve as flood barriers, soaking up excess water and slowing and preventing floodwaters from spreading uncontrollably. Wetlands help replenish groundwater and improve both ground and surface water quality by slowing down the flow of water, and absorbing and filtering out sediments and contaminants. They also provide spawning habitat for fish, supporting the regeneration of fisheries. In addition, wetlands provide habitat for many wildlife species and support commercial and sport fishing, as well as hunting and other forms of recreation.

Though different functions and processes of ecosystems, such as water filtration, may be economically important, they need to be viewed as inputs of or mechanisms for the production of economically valuable services, such as drinking water, timber, or recreational benefits. The end products, not the elements of the production process, ultimately generate economic well-being. Along these lines, Boyd and Banzhaf (2007) advocate defining ecosystem services as "components of nature, directly enjoyed, consumed, or used to yield human well-being." In other words, ecosystem services are the end products of nature to which ecosystems contribute as intermediate inputs or production technologies. Though this distinction may at first seem unimportant, it is crucial for the accurate valuation of ecosystem services. Regarding the incorporation of ecosystem services into the measurements of national income and the value of goods and services produced in an economy, such as gross domestic product (GDP) accounts, Boyd and Banzhaf (2007) note that:

If intermediate and final goods are not distinguished, the value of intermediate goods is double-counted because the value of intermediate goods is embodied in the value of final goods. For example, clean drinking water, which is consumed directly by a household, is dependent on a range of intermediate ecological goods, but these intermediate goods should not be counted in an ecosystem service welfare account. Also important is that ecosystem services are attributed only the incremental value they contribute to the production of valuable end products. Using the above example, the value of ecosystem services associated with drinking water denotes the marginal contribution of ecosystems in the production of drinking water, not the full value of the final product.

Given the complexity and variety of ecosystems and their services, their valuation poses several challenges. According to the National Academy of Sciences' Committee on the Valuation of Ecosystem Services, the importance of ecosystem functions and services is often taken for granted and overlooked in

environmental decisionmaking. Moreover, the key challenge in the valuation of ecosystem services lies in the difficult integration of economic valuation and ecological production theory. This is no straightforward task, because many ecosystem goods and services are not quantifiable using available methods, and the application of economic valuation methods may be subject to judgment, uncertainty, and bias (Heal, 2005).

A study by Costanza et al. (1997), seeking to determine the value of global ecosystem services, exemplifies the problems and pitfalls in the valuation of ecosystem services. Deriving and summing value estimates from the existing literature for a wide range of ecosystem attributes and services, this study suggested that the total value of global ecosystem services likely ranges from $16 to $54 trillion annually, or roughly one to three times global GDP. The study has been influential and widely quoted and used, especially among scientists and environmentalists. Economists consider it fundamentally problematic both conceptually and methodologically, preferring to focus on the value of changes to ecosystem services, which is relevant for policy, or what is termed the marginal value of ecosystem services. More profoundly, the entire concept of the value of global ecosystem services is problematic; without the global ecosystem we would all perish. The estimate of the value of global ecosystem services by Costanza et al. (1997) has therefore been characterized as a "serious underestimate of infinity" (cf. Toman, 1998; Smith, 2007).

F.1.1.2. Use of the Valuation Literature to Define Adversity

A secondary standard, as defined in Section 109(b)(2) of the Clean Air Act, must "specify a level of air quality the attainment and maintenance of which, in the judgment of the Administrator, based on such criteria, is required to protect the public welfare from any known or anticipated adverse effects associated with the presence of [the] pollutant in the ambient air." One way to quantify adverse effects is through monetary valuation.

Adversity is difficult to quantify and measure, and there are several challenges to using a monetary valuation approach. A major effect that is geographically extensive might be considered to be more adverse than a more severe effect limited to one geographic location. Another problem is aggregation. Any change in pollution may have multiple effects (i.e. effects on many types of ecosystem services) leading to difficulty in aggregating in a consistent way.

Monetary values on any service or resource degradation reflect human preferences about what is a severe effect. Larger unit values correlate with more severe effects, other things equal. Also, more extensive effects, will contribute to larger welfare loss (or gain). In addition, since monetary units can be added, the aggregation issue can be addressed by "simply" summing the welfare losses (or gains). Although this is not strictly true (e.g., values for improvements in water quality and fish populations may

not be additive), in principle the differences in how people conceptualize ecosystem improvements can be captured in the way resource improvements are valued in monetary terms.

Clearly, there are many practical problems associated with using monetary value as a way of defining adversity. First, many resources and services have not been valued and efforts to credibly transfer the results of valuation studies to other areas and resources have been minimal. Second, studies addressing multiple effects are particularly difficult to transfer and few in number. Finally, even with the first two problems addressed, a judgment would still need to be made on whether the air quality standard was the contributing factor for eliminating adverse (highly monetarily valued) effects.

F.1.1.3. Methods for Selecting Literature for this Assessment

Assessing the economics literature on the effects of NO_X and SO_X emissions on terrestrial, transitional, and aquatic ecosystems requires identifying and reviewing relevant studies addressing these effects. Multiple methods were used for this Annex: searching existing databases of this valuation literature; conducting systematic searches of the economics literature; reviewing a large number of key articles, reports, authors, and journals; and identifying studies based on the expertise and familiarity with the relevant literature of lead researchers.

Two existing databases on environmental valuation studies – the Environmental Valuation Reference Inventory (EVRI) and the Beneficial Use Values Database (BUVD) – were particularly useful for this assessment. The EVRI database, which includes nearly 1,900 valuation articles/studies on environmental and human health effects, was screened according to criteria regarding the potential relevancy of geographical location (U.S.), types of environmental goods and services valued (ecological functions, extractive uses, non-extractive uses, passive uses); and environmental stressor. This resulted in over 200 articles/studies of interest. BUVD is a relatively small database (131 articles/studies), so it was imported into the literature review database in its entirety, with unrelated articles/studies later excluded on an individual basis.

A large number of additional journals and literature databases were identified that publish and cover research potentially relevant to this assessment. The selected peer-reviewed journals[1] and library databases[2] were then reviewed using search engines and a range of key words developed to find studies addressing relevant ecological endpoints (aquatic, transitional, terrestrial) and their economic values. The

[1] American Economic Review, American Journal of Agricultural Economics, Canadian Journal of Economics, Canadian Journal of Forestry, Contemporary Economic Policy, Ecological Economics, Environment and Development Economics, Environmental and Resource Economics, Environmental Science and Technology, Forest Science, Forestry Chronicle, Journal of Agricultural and Applied Economics, Journal of Applied Econometrics, Journal of Agricultural and Resource Economics, Journal of Agricultural Economics, Journal of Environmental Economics and Management, Journal of Forest Economics, Journal of Forestry, Journal of Political Economy, Journal of Risk and Uncertainty, Land Economics, Marine Resource Economics, Resource and Energy Economics, Review of Agricultural Economics, Review of Economics and Statistics, Water Resources Research.

[2] AgEcon Search, Agricola, BioOne, CSA Illumina, EconLit, GeoRef, Google Scholar, SciSearch/Science Citation Index (Web of Science), SCOPUS, Sportfishing Values Database, SSRN.

tables of contents of those journals that could not be searched electronically were reviewed in hard copy and relevant articles were added to the literature review database. These searches were augmented by reviews of the bibliographies of the following EPA reports: *EPA Report to Congress: The Benefits and Costs of the Clean Air Act 1990–2010* (November 1999); *Air Quality Criteria for Ozone and Related Photochemical Oxidants* (February 2006); *Air Quality Criteria for Particulate Matter* (October 2004).

The results from these searches were checked for duplicates and clearly irrelevant studies, after which over 500 potentially relevant articles/studies were identified for initial assessment. Relevancy of each study for this assessment was determined according to the following key criteria.

- Does the study address an ecological endpoint sensitive to reductions in NO_X and SO_X emissions?
  - Does the study value quality changes in the ecological endpoint, which is actually or potentially attributed to reductions in NO_X and SO_X emissions?

- Is the study peer-reviewed and preferably, published in an academic journal?
  - Very few, if any studies fully satisfy all above criteria. For this reason, studies that at least partially satisfy these criteria were deemed potentially relevant for this project. Finally, reviews and meta-analyses were included in the assessment whenever they were available and dealt with potentially relevant ecological endpoints.

In the initial assessment, each record's potential relevancy to the assessment was rated on a scale of 1 to 4, with 1 indicating that the record appears directly relevant to this assessment (the study addresses quality change of an ecological endpoint, which is actually or potentially attributable to NO_X/SO_X). Records rated 2 only partially satisfied the "relevancy criteria," but were considered important to be referenced in this report. Records rated 3 were to be reviewed more closely to determine their usefulness, and those rated 4 were found not relevant for the purposes of this assessment. Because our goal in the initial assessment was to avoid missing potentially relevant studies, we classified borderline cases to the lower number category.

All studies rated 1 through 3 were next reviewed using several attributes, including ecological endpoints, valuation techniques, geographical area, use vs. non-use value category, and other details of interest. Of those studies, about half addressed aquatic ecosystems (Figure F-2). The reviewed studies addressed many different ecological endpoints, such as sport fishing, commercial fisheries, aquatic recreation (e.g., swimming and boating), general water quality, ecosystems services provided by aquatic ecosystems, and coral reefs (Figure F-3). Nearly one third of the studies addressed terrestrial ecosystems (e.g., forestry/commercial timber, outdoor recreation, and agriculture); the rest dealt with transitional ecosystems (e.g., ecosystems services provided by wetlands and wetlands recreation).

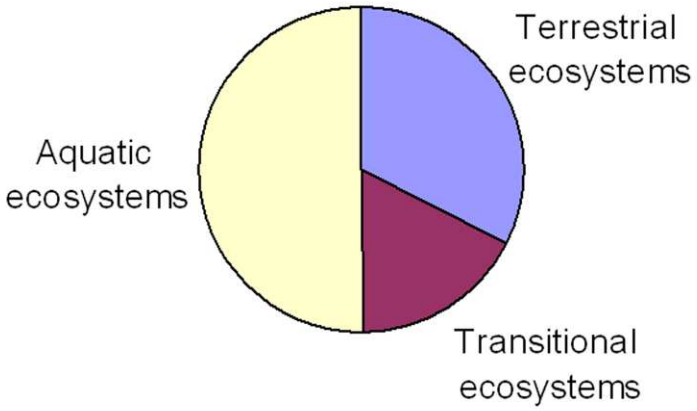


Figure F-2. Reviewed studies by ecosystem addressed.

F.2. Conceptual Framework

F.2.1. Taxonomy of Values for Environmental Goods and Services

The economic value derived by society from these ecological goods and services can be categorized as either "use" or "non-use" values. Use values comprise values for those goods and services that can be used either directly or indirectly. Non-use values denote the characteristics of the ecological goods and services that are not used at all but still hold economic value. The schematic in Figure F-4 illustrates these divisions of values for environmental goods and services.

Direct use values are held for those goods and services which can be directly consumed or utilized by individuals or society. Some direct use goods, such as fish caught or timber cut are sold in markets and thus valued using market data. Other direct uses, such as recreational use of ecosystems for fishing, hunting, and sightseeing, are usually not bought or sold through a market and are therefore more difficult to value. Similarly, changes in their value are more difficult to quantify. Thus, direct use can be subdivided into directly used market and non-market goods or services.

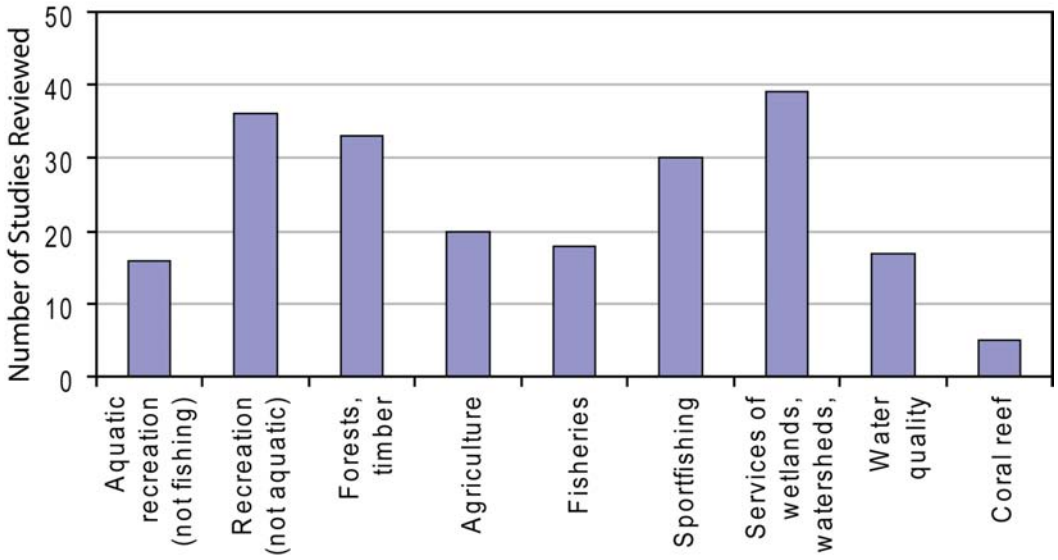
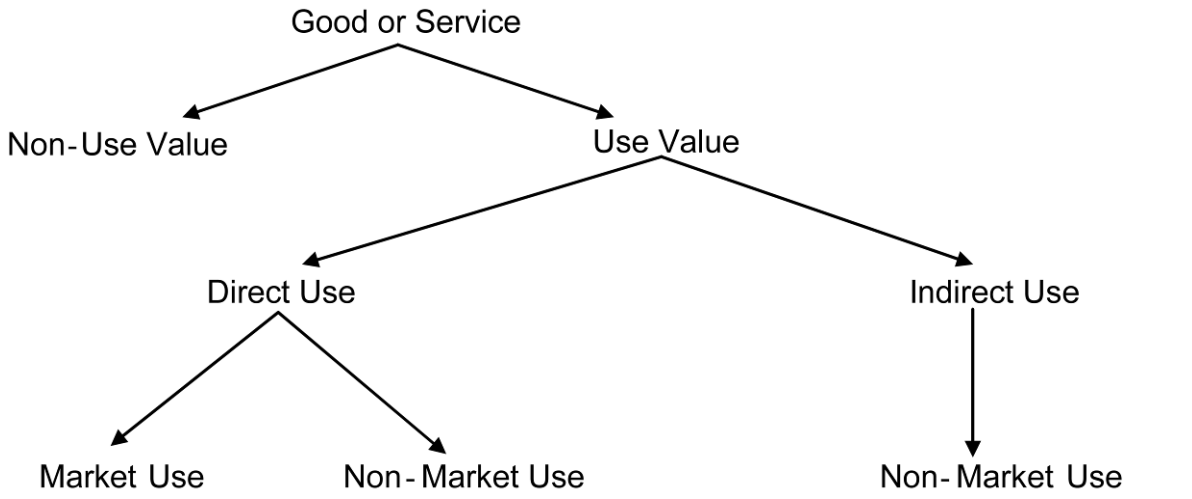


Figure F-3. Reviewed studies by ecological endpoint.



Source: EPA (2002).

Figure F-4. Taxonomy of values for environmental goods and services.

Examples of direct, market uses of ecological goods and services include commercially sold food sources (fish, crops, other animals); building materials (wood, stone); fuel sources (wood, coal, oil); drinking water (groundwater, surface water); chemicals; and minerals (EPA, 2002). Examples of direct, non-market uses of ecological goods and services include recreational fishing and hunting; beach use (sunbathing, swimming, and walking); boating; hiking; camping; wildlife watching; and sightseeing (EPA, 2002).

Indirect use values capture those ecological services that are not used directly but still provide benefits of economic value to society. These services include flood control, storm water treatment, ground

water recharge, climate control, pollution mitigation, wave buffering, soil generation, nutrient cycling, habitat value, and biodiversity (EPA, 2002).

Non-use values denote the characteristics of the ecological goods and services that are not used at all but still hold economic value. These non-use values include what are known as existence and bequest values–the value of simply knowing that certain ecosystems exist and of ensuring that they continue to exist for future generations, respectively. These services are also not traded in a market and quantifying their value is a challenge.

Importantly, empirical methods for addressing non-use value generally estimate the total value of a resource. Distinguishing between the use and non-use values often is not possible, and the valuation results including non-use values should therefore generally be considered total valuation rather than non-use valuation studies. Examples of non-use values of ecological goods and services include existence value, cultural/historical value, intrinsic value, bequest value, and altruistic value (EPA, 2002).

In this Annex, the focus is on the potential incremental benefit that might be realized from reducing levels of SO_X or NO_X by a relatively small amount, rather than the total value of the affected ecosystems. Therefore, the term "total value" in this Annex generally denotes total marginal benefits that contain both use and non-use values, not the total value of the entire resource. This notation is consistent with the principles of economic valuation of the environment, which generally focus on predicting damages or benefits from marginal changes in environmental conditions.

F.2.2. Welfare Economics

Any environmental goods or services that somehow contribute to human well-being are economically valuable. Their economic value reflects the capacity of the environment to satisfy different human needs, which is related to the direct consumption of different goods and services derived from the environment. It also includes different indirect, passive, and non-use values for environmental goods and services, such as recreational benefits, enjoyment of natural landscape, purity of air and water, and provision of habitat for species other than humans.

Economic valuation is rooted in the basic principle of consumer sovereignty. Rather than judging whether an individual's choices are right or wrong, each person is considered able to make rational choices that advance his or her well-being, given the possibilities available. The principle of consumer sovereignty extends also to the valuation of environmental goods and services. Even in the absence of markets for environmental benefits, each individual is considered able to assess the importance of changes in environmental quality on personal well-being or, as economists commonly refer to it, utility.

Consumer (CS) and producer surpluses (PS) are the basic monetary measures of well-being (or welfare) in economics. They denote the "excess utility" consumers and producers enjoy when consuming

or producing specific goods or services after paying for them. Producer surplus is measured by profit, the value of production after accounting for all costs. Consumer surplus, which is a more subtle concept, can be thought of as the difference between the price and the maximum value that an individual holds for a good or service. However, it generally is not an exact measure of changes in welfare because CS does not fix the baseline level of utility, thereby ignoring the income effects of a changing baseline

CS has two exact (Hicksian) measures: willingness-to-pay (WTP) and willingness-to-accept (WTA). In the context of environmental valuation, WTP denotes an individual's maximum willingness to pay for an environmental good or service. WTA, on the other hand, stands for the minimum compensation an individual is willing to accept to forgo an environmental good or service. Though WTP and WTA both are exact measures of CS, they generally are not equal, meaning that the CS in general does not have a unique measure. WTP and WTA for usual marketed goods and services are similar and within narrow bounds of income effects (Willig, 1976). Similar findings can be expected with environmental goods and services only when they have close substitutes (Shogren, 1994; Hanemann, 1991).

Since many environmental goods and services cannot be easily substituted, WTP and WTA are expected to differ, sometimes substantially. In fact, the WTP-WTA divergence can range from zero to infinity, depending on the substitutability of an environmental good and other market or non-market goods (Hanley et al., 1997). Using WTA to measure welfare changes might often be justified on the grounds of economic theory and property rights, but many studies choose to estimate WTP for its practicality. In addition, WTP generally is lower than WTA and therefore is conservative, providing another justification for using WTP for valuing the environment. Finally, both WTP and WTA can be difficult to measure, and valuation studies therefore sometimes estimate the ordinary CS. It approximates WTP and WTA and is between these two exact measures of welfare. In the special case of no income effects, all different measures of consumer welfare coincide.

Various methods have been developed to determine the value of different ecological goods and services by estimating the change in social welfare or WTP for changes in the quantity or quality of a given environmental resource (see Table F-1). Some valuation techniques obtain WTP from observing people's actions (revealed preferences or RP) while others rely on people's responses to hypothetical situations (stated preferences or SP). Yet another set of valuation methods relies on other studies, either by transferring their estimates into another context (benefits transfers) or by conducting statistical meta-analyses of earlier studies to examine their systematic findings. See Section F.2.3 for details about these approaches.

As noted by Kramer et al. (2003), several forest protection valuation studies also considered the sensitivity of contingent valuation estimates to various preference elicitation methods, including dichotomous choice, payment card, and open-ended techniques. Haefele et al. (1992) used payment card and dichotomous choice techniques in a contingent valuation survey measuring the WTP of Southern

Appalachian residents for protecting high-elevation spruce-fir trees from exotic insects and air pollution. Estimates for mean WTP were $20.86 per year using a payment card method, and $99.57 per year using a discrete choice method. Sample sizes for each method were relatively small (232 and 236 respondents, respectively). Another limitation concerns the wide span between the two valuation statistics, which despite a large difference in the mean estimates showed no overlap of the 95% confidence intervals. Similar studies have been performed by Loomis et al. (1996) and Kramer and Mercer (1997).

F.2.3. Benefit Estimation Approaches

Table F-1 introduces different valuation techniques and indicated which type of value (direct use, indirect use, total value) each can be used to estimate. Studies addressing non-use values are referred to in this Annex as total valuation studies. This is because non-use valuation methods in fact generally estimate the total value of a resource, including both its use and non-use components.

Travel cost (including site choice models) and hedonic pricing methods are perhaps the most regularly applied revealed preference (RP) methods for valuing the environment, whereas contingent valuation and choice experiments are the most popular stated preference (SP) methods. One of the key differences between the RP and SP methods is that RP methods can only fully address direct and indirect use values, whereas SP methods are required for the estimation of total values of environmental resources, including their non-use value component.

Travel cost studies predict use values for ecological resources, such as natural parks, by examining individuals' travel expenditures to utilize that resource (most often at a park or some other recreational site), including the opportunity cost of work time missed while traveling to and utilizing the resource. Travel cost studies commonly use a random utility framework, which infers individuals' WTP for an ecological resource (again usually a recreational site) by observing their choice from among one or more alternatives. While the travel cost method uses changes in the quality of one resource to ascertain its value, the random utility model uses individuals' choices among various options of various qualities at various prices to do the same.

Hedonic price studies predict the value of ecological resources by examining their effect on property values. Assuming that all the benefits from living in a specific location and house are capitalized into the market value of the property, hedonic models estimate the independent effects of different housing characteristics on housing prices. Controlling for all observable housing and location characteristics, hedonic pricing models examine environmental values for, for example, proximity to forests or particular watersheds by estimating the implicit incremental price people are willing to pay for that proximity. Hedonic pricing relies on assumptions such as efficiently functioning housing market and

perfect information and mobility by individuals. However, because WTP is not necessarily tied to ecosystem changes, this Annex does not consider property values as a method of valuation.

Other market or RP-based approaches to valuing changes in ecological goods and services include the alternative/replacement cost method; avoidance expenditures/averting behavior method; referendum method; user fee method; market price and market simulation method; and a host of different variations of these and other valuation approaches. See, for example, Freeman (2003) for the theory and applications of different methods for valuing environmental quality.

The RP methods have the advantage of gleaning their value estimates from individuals' real world actions. However, because they do not include the non-use value of ecological resources, none of them capture total value. This problem has given rise to the development of a variety of non-market valuation methods that use surveys to elicit preferences for public goods. Because these methods are generally based on eliciting "stated" rather than "revealed" preferences, they are broadly categorized as SP methods.

The contingent valuation method is the most common SP method. It involves developing and administering surveys, in which respondents are presented with a scenario or a program with specified environmental outcomes and costs. Each respondent is asked to indicate approval or disapproval of the proposed environmental scenario and its monetary cost. Researchers vary the proposed costs across different survey respondents and use their choices to estimate how much people on average are willing to pay for different scenarios to improve the environment. Because some of the respondents may use a public good also for direct enjoyment, say viewing an endangered bird, the surveys actually capture total value for the improvements, rather than just their non-use value.

Choice experiment methods (including contingent ranking, contingent choice, and conjoint analysis) separate an environmental good into its constituent attributes, recombine those attributes into different bundles, and elicit respondents' preferences for those bundles. Often a monetary value can be assigned to those attributes and thus the process allows researchers to determine WTP for the bundle and each attribute. Conjoint analysis usually is performed by choosing the most preferred attribute bundle from a group (choice experiment, contingent choice) or via ranking a series of attribute bundles (contingent ranking). Using conjoint analysis, researchers may be able to simultaneously value various relevant goods or services that an environmental resource provides. For example, improving a public body of water provides improved recreational opportunities, drinking water, and support of aquatic ecosystems.

Valuing the environment as a factor of production monetizes the incremental benefits from using the environment as an input to production. In other words, this method treats the environment as a production input comparable to other raw materials and infrastructure, such as land, capital, labor, and so forth. This method is appropriate for valuing environmental effects that have direct value as a factor of

production. Examples of such cases include the effects of water quality on the productivity of commercial fisheries, or the impact of soil characteristics on agricultural productivity. However, this method is limited to market goods and services and can only address their role as part of the production process. This method does not address non-market environmental goods and services or non-use values.

Benefits transfer approaches translate the entire estimated demand function from one application to another. Sometimes the function is adjusted to meet the specific criteria of the target site, and then new WTP value estimates are generated for the environmental good/service at the new site using the demand function. Using the transferred demand function, both changes in the level of use and the unit value benefits for the new site can be estimated (EPA, 2002). There are four general types of benefits transfer technique: mean unit value transfer/ adjusted unit value transfer, benefit/demand function or model transfer, meta-function transfer, and structural benefits transfer. The first three methods dominate the literature (Smith et al., 2006).

Mean unit value transfer/adjusted unit value transfer entails taking the value of a specific environmental good or service (such as recreational hunting), sometimes from a single study of the same good and sometimes estimated by averaging a range of value estimates from various primary studies, and transferring that value to the same good or service at a new site.

Benefit/demand function or model transfer is the translation of the entire estimated demand function from one site to another. Sometimes the function is adjusted to meet the specific criteria of the target site, and then new WTP value estimates are generated for the environmental good/service at the new site using the demand function. Using the transferred demand function, both changes in the level of use and the unit value benefits for the new site can be estimated (EPA, 2002). *Meta-function transfer* involves the use of meta-regressions to combine the results of numerous valuation studies and allows researchers to account for influencing factors, thus enabling them to create value estimates for new policy sites. *Structural benefits transfer*, also known as preference calibration, requires selection of a preference model which can describe individual choices over a set of market and associated non-market goods to maximize utility when faced with budget constraints (Rosenberger and Loomis, 2001; Smith et al., 2006).

Meta-study review provides a useful way of summarizing the literature on the valuation of ecological endpoints from reductions in NO_X and SO_X, though there are few studies exactly on this topic. But there are studies summarizing monetary valuation efforts for particular sets of endpoints, such as the economic valuation of fresh water ecosystem services. Where such studies are available, they are summarized in the appropriate section of this Annex.

Even more valuable are **meta-analyses**, which perform statistical analyses of the results of original studies. Such studies explain variation in monetary value estimated for various endpoints using features of the original studies' methodologies as well as the characteristics of the site being studied and other factors.

Smith and Pattanayak (2002) defined meta-analysis as the practice of using a collection of formal and informal statistical methods to synthesize the results found in a well-defined class of empirical studies.

In general, the three uses of meta-analysis are: (1) synthesize or "take stock" of the literature on a particular valuation topic; 2) test hypotheses with respect to the effects of explanatory variables on the value construct of interest; and (3) use the estimated meta-analysis model to predict estimates of the value construct across time and space (Bergstrom and Taylor, 2006). Bergstrom and Taylor (2006) provided a review of the techniques and theory behind the use of meta-analysis for benefits transfer. They noted that to conduct a successful meta-analysis for benefits transfer, it is important to be as comprehensive as possible in terms of the studies to be included. Excluding a study would be equivalent to applying a zero weight to the information in that study. The authors list some additional criteria to be considered when identifying studies for inclusion in a meta-analysis, including controlling for the valuation method and estimated welfare measure, as well as addressing the temporal and spatial scales of the valued commodity.

Extensive evaluation of the relative merits of, and issues with, different environmental valuation methods is not within the scope of this Annex. Vast amounts of research have been conducted to develop and evaluate alternative environmental valuation methods. For example, the Handbook of Environmental Economics recently dedicated an entire 1,100–page volume to addressing methods for valuing environmental changes (Mäler and Vincent, 2005).

The validity of environmental valuation methods is sometimes questioned, in particular that of SP methods. Because survey-based valuation methods are based on what people say rather than what they do, there is a tendency to question the credibility of the results. For this reason, nonmarket valuation researchers, following the lead of the National Oceanic and Atmospheric Administration (NOAA) Expert Panel that reviewed the highly publicized studies valuing damages from the EXXXXXXXXXon Valdez oil spill, often build into their surveys a series of validity tests, such as testing for the sensitivity of WTP to the scope of resource being valued (Federal Register, 1993). Additionally, SP surveys are vulnerable to a variety of issues dealing with the design and administration of surveys, as well as analyzing their data (e.g., Carson and Hanemann, 2005).

Though examining actual choices lends credence to RP methods, they are not free of problems. For example, hedonic pricing studies of housing markets rest on the assumptions that the housing market is at equilibrium and that housing choices accurately reflect the attributes of interest, such as air pollution or environmental amenities associated with the residential location. Hedonic studies and other RP studies, such as recreation trip demand analysis, are also susceptible to potential biases. These include the omission of important variables, which may thwart the efforts to accurately value environmental quality.

A number of studies have compared SP analyses with RP analyses, such as hedonic property value studies. Generally, these comparisons have suggested that when similar environmental values are examined, RP methods generally yield somewhat higher value estimates than SP methods. For example,

Carson et al. (1996) reviewed over 80 studies which included comparisons of SP and RP methods, and concluded that SP methods are on average about 75% to 90% of corresponding RP values.

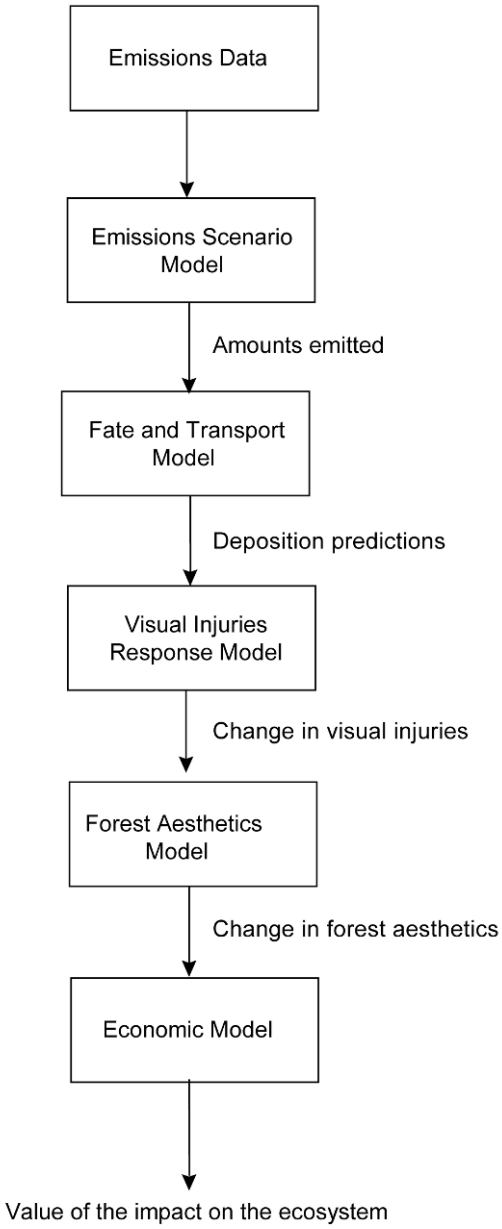
F.3. Valuation of forests and terrestrial ecosystems

F.3.1. Use Values

The impacts of NO_X and SO_X can occur over many different terrestrial ecosystems and use-value efforts must look at each of these ecosystems individually. One serious threat to agriculture from NO_X emissions comes from ambient ozone (O_3), which is a byproduct of atmospheric reactions between Volatile Organic Compounds (VOCs) and NO_X. In commercial forests, air pollution effects have not been addressed in economics beyond evaluating the potential effects of O_3. Unlike in agriculture, the scientific understanding of O_3 effects on trees is more limited and related mostly to visual injury to leaves in young saplings, an indicator that is difficult to link to tree growth in mature forests. However, the valuation of O_3 has already been evaluated in detail in the *Air Quality Criteria Document* (AQCD) *for Ozone* (EPA, 2006), and will not be covered in this Annex or the ISA (see also Tables F-2 and F-3).

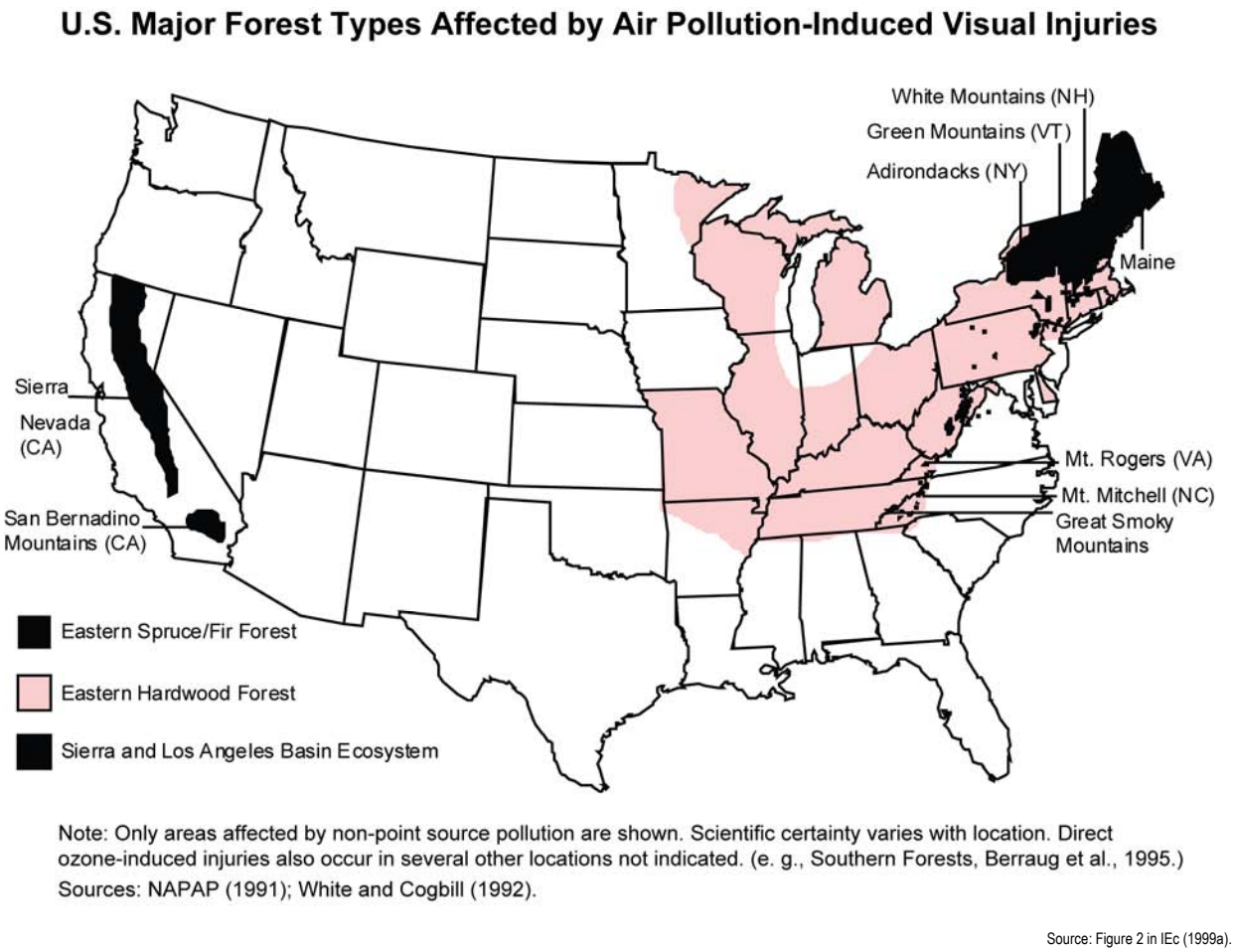
Some studies have attempted to specifically measure use values associated with forest quality, without regard to the factor that is altering forest quality. For example, an early study by Leuschner and Young (1978a) considered the effects of crown density changes due to insect infestation around 19 lakeside campgrounds in east Texas. A travel-cost model estimated the CS losses from a 10% reduction in crown density to fall between 0.69% and 6.5%, depending on the number of substitute recreation sites available. More studies that look at how forest quality affects various uses are listed in Table F-4. Also, Table F-5 lists value estimates from a meta-analysis but does not reflect the considerable variation of value estimates across underlying studies.

Figure F-5 depicts the linkages between aesthetic welfare benefits and air pollution. One such linkage that is shown is the visual quality of forests. Changes in woodland appearances are monitored using scientific indicators of ecosystem change, such as crown condition, mortality, foliar damage, vegetation structure, and plant diversity (McLaughlin and Percy, 1999). However, in comparison to valuation of changes in commercial timber, measuring the economic value of aesthetic changes in forests and natural ecosystems can be more directly based on scientific information regarding the effects of pollution on forest health. Although the scientific linkages between air pollution and visual forest quality include large degrees of uncertainty, historic examples of air pollutant effects on forest aesthetics facilitate their empirical valuation. Figure F-6 shows the regions and species that have been identified as historically affected by air pollutants.



Source: Exhibit 1 in IEc (1999a).

Figure F-5. Linkages from emissions to forest aesthetics.



Source: Figure 2 in IEc (1999a).

Figure F-6. Geographic distribution of forested areas historically affected by air pollution.

When the aesthetic quality of forests is important to people, visible injuries to trees can affect consumer welfare. Loss of or damage to foliage, changes in tree density, changes in species composition, and changes in vegetation structure can all affect the enjoyment that people derive from forests, and are therefore appropriate for economic assessment. Estimation of the aesthetic value of forest condition uses RP or SP methods and often focuses on long-term outcome stressors, rather than current intermediate situations. Nevertheless, there are few scientific studies that relate changes in pollution concentrations to these endpoints, and that make a direct linkage between science and economics. A memorandum by Industrial Economics, Inc. (IEc) (1999b) produced for *Benefit-Cost Analysis of the Clean Air Act 1999*, provided a comprehensive review of early forest aesthetics valuation literature. A recent literature review by Kramer et al. (2003) also summarized several key studies described in this report. Table F-5 lists and describes studies which have estimated monetary value for the types of non-consumptive use and non-use values for forests and natural ecosystems which may be affected by N and sulfur emissions.

F.3.2. Total Values

Several studies were reviewed by Kramer et al. (2003), and measured the total WTP of the general public for forest aesthetics and attempted to separate contributions of use values and non-use values. Most of these studies indicated that in the aggregate, non-use values (including option, bequest, and existence value) were significantly greater than use values (recreation).

Walsh et al. (1990) employed a contingent valuation study using an iterative bidding technique to estimate WTP of Colorado residents for protecting ponderosa pine (*Pinus ponderosa*) forests from the mountain pine beetle (*Dendroctonus ponderosae*). Presented with pictures of mid-level forest quality representing current conditions (100 to 125 live trees measuring more than 6–inches in diameter per acre), respondents were asked their WTP to prevent the lowest forest quality (0 to 50 trees per acre) and to attain the highest forest quality (125 to 175 trees per acre). Overall mean WTP for changes in forest quality was estimated at $47 per household. In addition, respondents decomposed total value into four categories of value (recreational use, option, existence, and bequest). Results showed that use values accounted for 27.4% of total value, and non-use values accounted for 72.6% of total value. The study was limited by small sample size (200 respondents) and possible bias from framing the scenario as "one of the most important issues facing Colorado residents."

A study by Haefele et al. (1992) that measured WTP to protect Southern Appalachian spruce-fir forests, used a decomposition approach to determine dominate influences on total values. The authors found that non-use values (bequest and existence values) overshadowed use values as reasons to protect forests. Holmes and Kramer (1996) relied on results from Haefele et al. (1992) to compare WTP between recreational forest users and members of the general public. Mean household estimates for forest-users ($36.22) were substantially larger than estimates for nonusers ($10.37).

Kramer et al. (2003) used a dichotomous-choice, contingent-valuation format to determine WTP of Southern Appalachian residents for protecting spruce-fir forests from insects and air pollution. The study measured incremental levels of forest protection using two scenarios: the first increment occurred along road and trail corridors, a scenario that would appeal to people valuing the ecosystem primarily for recreational use; the second level was for the entire ecosystem, a scenario that would appeal to people valuing the continued existence of the entire threatened ecosystem. Using randomly assigned values between $2 and $500 dollars, respondents were asked if they would pay a certain tax amount for each scenario. Results suggested that preferences for forest ecosystem protection created a well-behaved demand curve, with incremental WTP increasing at a decreasing rate.

F.3.3. National-Scale Valuation

An EPA-contracted valuation study by IEc (1999b) developed a benefits-transfer model using results from Holmes and Kramer (1996), Peterson et al. (1987, and Walsh et al. (1990) to estimate national benefits from the 1990 Clean Air Act Amendments (CAAA). Calculations applied WTP values from these previous studies across all households in the affected states. (See Table F-6 for more information on the underlying original studies, and Table F-7 for benefits transfer results.) Estimates for the total value of avoiding air pollution-induced damage to forest aesthetics in the U.S. during the period 1990–2010 were found to range from $3 to $17 billion. Due to limitations in the original studies and the simplicity of the benefits-transfer model, the authors warned that the estimates should only be used to consider the general magnitude of benefits to forest aesthetics (in the range of billions of dollars) rather than as precise values.

F.3.4. Valuation of Degrees of Injury

A few studies—Hollenhorst et al. (1993, Ruddell et al. (1989, Hammitt et al. (1994, Buhyoff et al. (1982) —measured general preferences for forest aesthetics without estimating changes in welfare. Hollenhorst et al. (1993) considered the effect of tree mortality on perceived forest aesthetics. On a 1 to 10 scale for visual and recreational appeal, 400 respondents ranked pictures of 25 sites with tree mortality ranging from 6% to 98% from gypsy moth (*Lymantria dispar*) damage. The results produced a hill-shaped function, whereby site appeal increased with mortality at levels as high as 40% but then declined. The authors speculated that respondents had a general distaste for tree mortality but valued light penetration to the forest understory, which allows for the growth of wild flowers and lower-level vegetation.

Other studies confirmed this visual preference for light penetration, including Ruddell et al. (1989) and Hammitt et al. (1994, who observed positive responses to forest edges and open middle grounds without light-obstructing tree canopies. Buhyoff et al. (1982) tested how awareness of environmental damages affects perception of aesthetic losses. The study compared aesthetic rankings of photographs between a control group and a group that is informed about the cause of forest damage prior to the ranking session. Results show a heightened level of sensitivity to forest damage by the “informed” group of subjects.

Several other studies investigated the notion of aesthetic thresholds, or discontinuous jumps in aesthetic preferences across small changes in visual injuries. Of particular interest to early studies were thresholds at the lower limit of visual perceptibility.

Contingent valuation studies by Vaux et al. (1984) and Flowers et al. (1985) assessed aesthetic preferences at recreational areas with fire damage and found that small differences in site appearance can

produce large changes in recreation preferences. This finding is generally consistent with the results from two early studies by Buhyoff et al. (1979) and Buhyoff and Wellman (1980, which asked respondents to rate various levels of insect damage. The authors found that preferences seemed to be most affected by the presence or absence of insect damage, as opposed to the degree of damage.

Crocker (1985) surveyed 100 recreationists for their WTP for recreational experiences at forested sites with slight injury, moderate injury, or severe injury. Mean WTP estimates for the environment with slight injury were three times higher than WTP for environments with moderate and severe injury, suggesting that people are willing to pay a premium for recreational access below the lower limit of perceptibility. As a group, respondents did not indicate a clear preference ordering between the moderate and severe injury environments.

Holmes et al. (2006) use a hedonic method to predict the impact of forest damage due to the hemlock woolly adelgid (*Adelges tsugae*), an invasive insect, on the value of residential properties. Examining 3,379 residential property sales in New Jersey between 1992 and 2002, the study analyzed how the appearance/health of the forest on the home's parcel and within 0.1, 0.5, and 1 km buffers around it affects the housing market. Controlling for other relevant variables, the study estimated that hemlock health status had a statistically significant effect on property values. The estimation results suggest, for example, that a 1–point increase (e.g., from 10% to 11%) in the percentage of healthy hemlocks (less than 25% foliar damage) of all forests on the home's parcel was associated with a 0.66% sales price increase. Similar changes in the hemlock forests and their health status in the home's near proximity are predicted to be associated with yet larger increments in the sales price.

At least one study seems to provide evidence against the concept of thresholds at the lower limit of perceptibility. A referendum-type contingent valuation survey by Jenkins et al. (2002) used two sample populations to value a forest protection program. The initial forest condition was described as "pristine" for one group and already "somewhat damaged" for another group. The degree of forest damage incurred in the absence of a forest protection program was the same for both sample groups. Regressions for the entire sample population showed no statistically significant difference in WTP for forest protection between the two groups.

Further analysis of Jenkins et al. (2002) suggested that aesthetic preferences and thresholds differ between recreational groups. Comparisons among recreational groups revealed that consumptive forest users (hunters and anglers) held values that were sensitive to change in forest condition, while non-consumptive forest users (hikers and campers) held values that were insensitive to the same amount of change. Overall, however, non-consumptive forest users expressed higher values than consumptive forest users. Aesthetic thresholds also seem apparent for recovering forests. Paquet and Belanger (1997) found that the aesthetic effects of clear cutting were largely removed once re-growth reached a height of 4 m.

Finally, there is substantial literature related to the amenity value of urban/suburban forests and open space. McConnell and Walls (2005) recently reviewed this literature, evaluating more than 60 published articles that have attempted to estimate the value of different types of open space. Two lines of research emerge in this literature: studies that estimate the hedonic value of open space proximity to residential properties, and studies that use SP methods to value preservation of open space. Unfortunately, neither line of research generally comprises studies that provide information on the WTP for quality changes to open space that might be caused by changes in NO_X and SO_X emissions. In most cases, the proximity or preservation of open space or urban/suburban forest is valued without reference to the quality or even the type of open space or forest. Although this literature demonstrates the value of the availability and preservation of open space, its relevancy for the purposes of this assessment is at best limited.

F.3.5. Limitations and Uncertainties

Shortcomings in the air pollution terrestrial valuation literature have been well documented in recent reviews (Adams and Horst, 2003; EPA, 2006). In existing economics literature, the effects of O_3 on terrestrial endpoints overshadow assessments of other effects of NO_X and SO_X pollution, such as acid deposition and N fertilization. The latter effects have been well documented in the scientific literature, but the lack of valuation studies related to them limits full assessments of terrestrial damages from NO_X and SO_X pollution. Incomplete scientific understanding of the effects of air pollutants on ecosystems and economic endpoints extends to many valuation studies. Even in the valuation of O_3 effects, which have been relatively thoroughly studied, improvements in noneconomic input data could play an important role in evaluating the magnitude of vegetation damages from O_3.

Economic models should incorporate more specific temporal (dynamic) and spatial data regarding terrestrial effects of air pollution to reflect more realistic situations. For example, the O_3 effects valuation literature analyzes air pollution effects across a period of time using only two or three scenarios that represent large, static changes. In the real world, however, these changes would occur gradually and incrementally. Future studies should try to consider more dynamic models that can describe effects of marginal air quality changes. From a spatial perspective, previous studies often assumed that producer responses are similar across large geographic areas. However, regional factors may be important, suggesting a possible need for finer-scale agricultural and forestry data that would allow models to consider micro-level physical and economic factors (Adams and Horst, 2003).

With regards to the effects of air pollution on agricultural crops, most economics studies date from the 1980s and many focus on O_3. Therefore, there is a general need for updated valuation studies that consider agricultural damages from air pollution, especially with regards to the roles played by NO_X and

SO_X. Specific issues include the need to develop new exposure-response functions for sensitive crops and the effects of air pollution on crop yields under actual farm conditions.

Assessments of welfare losses in commercial forestry from air pollution are mainly limited by scientific uncertainty regarding the extent of ecological damage. Restrained by the large size and slow growth of trees, scientific research has primarily considered O_3 effects on seedlings and has little transferability to mature trees.

Existing literature on valuation of changes in forest aesthetics has focused primarily on historical cases of acute air pollution or insect infestation and may be overly simplistic. Although these valuations are useful, no existing assessments have examined the effects of reduced air pollution on forest aesthetics. Understanding the effects of marginal changes in air pollution would require the collection of long-term high-quality data about forest health, as well as improved casual linkages between air pollutants and visible injuries to trees. Scientific advancements at this scale would require a sophisticated monitoring network operating over several decades. Until the impacts of pollution on the foundational services of terrestrial ecosystems are better understood, valuation assessments may be premature. Additionally, most studies also fail to distinguish between marginal values of forest health and average values of forest health, an oversight that may create bias in final estimates.

A major limitation of both non-economic and economic forest health assessments concerns the limited extent of documented ecosystem-level changes. Most forest health surveys focus on average forest conditions that allow for modeling of near-term trends in economic value, but fail to detect fundamental changes in ecosystem processes that sustain natural capital in the long run (McLaughlin, 1999). Quantifications of impacts on species effectively conform to existing valuation methods; however, these effects may be overshadowed by long- term or irreversible reductions in ecosystem structure and function (EPA, 1999). Assessing ecosystem-level changes presents new challenges to both science and economics as they include a large degree of uncertainty in the scale and nature of effects. In particular, economic assessments of ecosystem impacts may require regional- to national-scale modeling of numerous ecosystem functions rather than analyses of specific service flows that directly contribute to human welfare (EPA, 1999). In spite of these challenges, the relationship between air pollution and forest health has enormous implications for policy development and should be addressed in future research.

More advanced methods to address uncertainty and irreversibility are essential to future modeling of complex ecosystem-level impacts. Several alternative methods to address ecological uncertainties are currently being developed and should play a central role in future models (EPA, 1999).

F.4. Valuation of Transitional Ecosystems

The economic analysis of the benefits on wetlands (transitional ecosystems) from reduced emissions are limited in this Annex to three recent and comprehensive meta-analyses. Brander et al. (2006) provided a comprehensive review and meta-analysis of the wetland valuation literature. This study improved upon previous similar studies (Brouwer, 1999) (Brouwer et al., 1999; Woodward and Wui, 2001) by including tropical wetlands estimates from other valuation methodologies, other wetland services, and estimates from more countries.

It is well known that wetlands serve a variety of potentially valuable ecological functions, including flood and flow control, storm buffering, sediment retention, groundwater discharge, and habitat for plant and animal species. Wetlands also contribute to climate stabilization, carbon sequestration, and the overall quality of the natural environment. Brander et al. (2006) (Table F-8) described these functions and their associated goods and services, as well as their values as determined by common valuation methods.

F.4.1. Use and Non-Use Values

The Brander et al. (2006) meta-analysis included 191 different wetland valuation studies from 25 different countries. Eighty of those studies, half of which were from North America, provided useful empirical data for the meta-analysis. A total of 215 individual observations were gleaned from those studies for use in meta-regressions. The study reviewed the literature, discussed valuation techniques, calculated average wetland values using the results from the combined data set, and then performed a meta-regression of the data to determine which explanatory variables had the greatest effect on wetland value. Non-market use values of wetlands, as well as non-use/existence values, were also included in the analysis. Because not all of the studies generated WTP value estimates, wetland size and population statistics were used to convert estimates from the diverse valuation methodologies to 1995 dollar values per hectare per year, following the example of Woodward and Wui (2001), which is described below.

The results of the Brander et al. (2006) meta-analysis showed an average value for wetlands of $2800/ha/yr (1995 dollars), and median value of $150/ha/yr. Individual values were calculated by wetland type, the wetland service provided, contingent, and valuation method used. The meta-regression also revealed that studies using the contingent valuation method consistently returned the highest wetland values. It is noted that this may have been due to the type of wetland values that this method was applied to, rather than something intrinsic to the methodology.

To look at the value differences from a reduction specifically in N emissions, there is a focus on Brander et al.'s (2006) analysis of wetland value changes that resulted from a small change in water

quality or some other ecosystem service. These results are valuable because they may be related to changes in acid deposition as a result of changes in the concentrations of NO_X or SO_X. In the meta-regression results of Brander et al. (2006), the only such ecosystem service which was shown to have a statistically significant effect on wetland value was hunting. Hunting had an unexpected negative influence on wetland value. Although not statistically significant, water quality, habitat and nursery service (specifically support for commercial fisheries and hunting), fishing, and biodiversity all had positive effects on wetland value. The accuracy of the value transfer exercise in Brander et al. (2006) seems to be in line with other similar efforts, with an average transfer error of 74%. Overall, the value transfer function from Brander et al. (2006) produced higher-value transfer error for less valuable wetlands (and systematically over-predicted their value) and lower value transfer error for more valuable wetlands (and slightly under-predicted their value).

Woodward and Wui (2001) found 39 studies that contained sufficient data for inter-study comparison, including peer-reviewed and gray literature. Similar to the approach of Brander et al. (2006), Woodward and Wui (2001) assumed that a wetland's value is a function of its ecological characteristics and socio-economic environment, and that there exists a true public WTP at a given moment for a particular wetland. With these assumptions, they attributed variability in wetland value to two principal sources: differing characteristics of the wetland and error in the estimation of the true value (Woodward and Wui, 2001).

Brouwer et al. (1999) analyzed the WTP of 30 CV studies addressing ecosystem functions of wetlands, providing a total of 103 estimates. The studies were mostly conducted in the U.S., but were not in any way comprehensive spatially. They ranged from 1981 to 1997 and covered a wide range of commodity definitions, including preserving wetlands threatened by flooding, maintaining or improving current catch levels and fish populations, saving the bald eagle (*Haliaeetus leucocephalus*), improving/maintaining habitat, water quality ladder changes, preventing shellfish bed closures, increasing the number of protected rivers, and explicitly preserving a measure of water quality. No attempt was made to standardize the degree of change being valued. Instead, the authors attempted to address differences in the studies through the use of dummy variables and some degree of sub-setting.

Based on all of the included studies, Brouwer et al. (1999) estimated that the average WTP for the addressed ecosystem functions was about $90 per household per year. These studies covered types of wetlands (primarily fresh water systems), ecosystem functions (water quality and biodiversity, and to a lesser extent water quantity and flood control), and wetlands size. Cutting across types of systems, location, and function enhanced, the WTP for salt and fresh water improvements was about the same. Within fresh water wetland systems, riverine wetland improvements appeared to be more highly valued than palustrine wetland improvements. Across ecosystem function, flood control was more highly valued than biodiversity, water quality and water generation, in that order. Improvements to larger wetlands

appeared to be somewhat more highly valued than to improvements to smaller wetlands. Improvements in use values averaged slightly more than $100 per household per year, whereas improvements in non-use values only showed values about half this size. Spatially, values were higher in California, followed by Georgia and Louisiana.

The review of outdoor recreation valuation studies by Rosenberger and Loomis (2001) included 13 studies and 59 value estimates associated with waterfowl hunting, a popular activity in transitional ecosystems. On average, these studies estimated that the value of waterfowl hunting is about $32 per person per day (1996 dollars). However, different value estimates ranged from about $2 to over $160 per person per day. In their meta-analysis, Rosenberger and Loomis (2001) predicted a $40 value per person for a day for waterfowl hunting (Table XXXXXXXXXX). These results demonstrate potential benefits from waterfowl hunting, but do not address changes in the quality of transitional ecosystems that may possibly be associated with reduced NO_X/SO_X emissions.

F.4.2. Limitations and Uncertainties

Meta-analyses of wetland value (and the underlying original studies) are not directly useful because they do not measure changes in ecosystem services that would follow from some tightening or loosening of the standard for NO_X or SO_X. Nevertheless, they have indirect use by pointing out the importance of various methodologies, the overall values commonly assigned to wetland improvement, and types of ecosystem services that might be affected by air pollutants. For example, both Brander et al. (2006) and Woodward and Wui (2001) found that CV studies generally yielded greater value per acre than travel cost studies. This is not surprising, as the former would generally include non-use values. Furthermore, Woodward and Wui's (2001) meta-analysis showed that the availability of bird hunting, bird watching, and amenity services affect wetland value. For example, bird watching (which could be affected by bird populations which, in turn, could be affected by nutrient enrichment) contributes more value to an ecosystem than any of the other ecosystem services. This is mainly due to the popularity of bird watching and the large numbers of people who engage in this recreational activity.

F.5. Valuation of Aquatic Ecosystems

As discussed in the ISA and the preceding annexes, acidification and eutrophication are the two main effects of NO_X and SO_X on aquatic ecosystems. In economic valuation of the effects of NO_X and SO_X deposition on aquatic ecosystems, these effects are reflected partly in the WTP for recreational fishing (with effects on the catch rate and fishing quality in a particular aquatic ecosystem) and partly on aesthetic and non-use (and total) values. Valuation methods used to assess the value of aquatic ecosystems

include contingent valuation (CV) (open-ended, discrete choice, etc.), choice experiments, hedonic-pricing valuation, travel cost (TC) (hedonic travel cost and traditional travel cost), cost-effectiveness analysis, avoided-damage cost, replacement cost, market analysis, and so forth. The CV method has gained popularity for total (use plus non-use) value estimation, whereas the travel cost method plays an important role in deriving use values. Currently, there is also a tendency to use stated and RP techniques together for the valuation of recreational activities. Supplemental to the below discussions about valuation of acidification and eutrophication on aquatic ecosystems, Table F-9 describes different aquatic valuation studies according to the ecological effect examined (acidification, eutrophication) and lists their relevant details.

An extensive literature review by Wilson and Carpenter (1999) provides an excellent starting point to the valuation literature on aquatic ecosystems. This paper examined 30 studies published between 1971 and 1997 that estimated the value of nonmarket ecosystem services provided by fresh water bodies in the U.S. Sixteen were SP studies, with the rest split between travel cost and hedonic pricing approaches. The travel cost studies covered very specific water bodies and stressors, such as a boatable to swimmable change in water quality for 13 recreation sites along the Monongahela River in Pennsylvania (Smith and Desvousges, 1986), and a change in water quality measured by the Uttormark's Lake Condition Index for recreational use of Pike Lake in Wisconsin (Bouwes and Schneider, 1979). Beyond spatial and stressor differences, the studies differ in their units for expressing value. The Monongahela River study used benefits per household, with the largest value expressed for a change from boatable to swimmable ($51). The Bouwes and Schneider (1979) study concluded that the total (aggregate) annual mean CS was almost $86,000.

There are several additional meta-analyses that describe methods of valuation for aquatic ecosystems, but not specifically relating to effects caused by NO_X or SO_X. Van Houtven et al. (2007) analyzed WTP for fresh water quality improvements, covering 131 valuation estimates from 18 SP studies that used or could be transformed to use the water quality ladder (boatable, fishable, swimmable) modified into a 10–point scale. The analysis started with 90 studies but found that most were not sufficiently comparable for statistical analyses. The studies ranged from 1977 to 2003 and covered rivers, lakes and estuaries.

A meta-analysis by Johnston et al. (2005) examined the value of fish catch based on a total of 48 studies published in the U.S. and Canada between 1977 and 2001. The study statistically examined WTP for fish relative to variations in resource, context, angler, and policy attributes, as well as methodological attributes of the studies themselves. The attributes examined included species targeted, geographic region, water body type, catch rate, angler demographics, and fishing method. Among 391 WTP observations, 122 were estimated using CV methods, 59 using TC methods and the remaining from discrete choice models.

Johnston et al. (2005) found that SP studies have generally resulted in lower WTP estimates than RP studies, which is consistent with earlier multiple study reviews and meta-analyses. Dichotomous choice CV also has produced lower WTP estimates than choice experiment or conjoint surveys, compared to the default of open-ended surveys (including payment cards and iterative bidding). However, these findings were not robust across all regression model specifications. The study supported previous findings (Poe et al., 2000) that WTP is systematically associated with variations in resource, context, and angler attributes. The study also concluded that WTP per fish varies systematically across study methods, but the variation due to methodology accounted for a relatively small proportion of total WTP variation. Again, these results demonstrate the value of recreational fishing, but do not address changes in water quality that may be associated with reduced NO_X/SO_X emissions.

F.5.1. Acidification

The Adirondack Park in New York is the best documented of all areas affected by acidic deposition in the U.S. Due to air pollution that largely originated from power plants and other sources to the west and southwest of the park, many watersheds in the park have experienced slow acidification of water and soil since the late 18th century. This park has been the subject of numerous valuation studies in recent decades.

Morey and Shaw (1990) applied the travel cost model and estimated recreational fishing values associated with water quality change resulting from acidic deposition in the Adirondack Park area. The results showed that the aggregate expected conditional compensating variation for a 50% increase in catch rate of two trout species at four sites was $3,863 (1977 dollars; $13,175 in 2007 dollars), based on 607 survey respondents with an estimated standard deviation of $89 ($304 in 2007 dollars).

A travel cost model was also applied by Mullen and Menz (1985) to link acidic deposition and recreational fishing in the Adirondack Park. A net average economic value per angler day was calculated to be $20 (1976 dollars; $73 in 2007 dollars) for lakes, ponds, and streams in the Adirondacks, with an estimated total loss in net economic value of $1.07 million (1976 dollars; $3.89 million in 2007 dollars) per year for a 5% reduction in fishable area. These estimates excluded streams because limited knowledge existed to assess the effect of pH fluctuations on aquatic life in streams. Shaw (1989) questioned the reliability of these results, arguing that the demand equation was not compatible with economic theory and that aggregating separate CS measures from different equations was inappropriate.

Englin et al. (1991) assessed the economic impact on recreational fishing in four upper northeastern states resulting from acidic deposition control. Biological effects of acidification were linked with hedonic travel cost and random utility models through the acid stress index (ASI) and fish catch per unit effort (CPUE). The analysis was based on multiple data sources and yielded positive social welfare for

2030 under a scenario of reducing by 50% the ambient deposition in 1989. This level of decline in acidic deposition was expected to occur on the basis of analyses conducted by the National Acid Precipitation Assessment Program (NAPAP).

Cameron and Englin (1997) measured welfare under an assumption that people are not certain about participation in fishing. Based on WTP results from a survey and a random utility model, surpluses were estimated for preventing a 20% loss in the availability of high-elevation lakes for fishing in northeastern states.

Randall and Kriesel (1990) employed a SP method to value a National Pollution Control Program, which led to improved air and water quality by 25% within 5 years. A nationwide survey conducted in multiple modes found an estimated annual willingness to pay of $694 ($1,098 in 2007 dollars) per household. The researchers concluded that the estimated value was lower than their multimarket hedonic estimates.

Banzhaf et al. (2006) conducted a CV survey, which was designed to estimate the total value (use plus non-use values) of reducing acidification by liming the lakes and forests in the Adirondack Park to a degree matching recent SO_X and NO_X reductions under emissions trading programs. The mean WTP for improving 600 lakes "of concern," and small increases in populations of two bird species and one tree species was $48 (2003 dollars; $54 in 2007 dollars) per year per New York household. The mean WTP for improving 900 lakes "of concern," four bird species and three tree species was $54 (2003 dollars; $61 in 2007 dollars) per year per New York household.

Sequential implementation of several regulations, including in particular the CAA, has substantially reduced acidic deposition, especially in the eastern part of the U.S. Burtraw et al. (1997) conducted a benefit-cost analysis for the NAPAP program. Besides improving public health and visibility, emissions controls contributed to decreased lake acidification which was projected to have economic benefit associated with improved recreational fishing in the Adirondack Park. The ASI and CPUE approaches were used in the Tracking and Analysis Framework (TAF) model to capture the response of three recreationally fished species to water quality improvement in 33 statistically selected Adirondack lakes. The per capita recreational fishing benefits in 2010 were estimated to be $0.62 (1990 dollars; $0.98 in 2007 dollars) annually per angler fishing in the Adirondack area.

F.5.2. Eutrophication

As is the case for acidification, the endpoints most studied in the valuation literature for nutrient enrichment concern fishing and non-use (or total) values. Change in aquatic recreational behavior is another endpoint for looking at valuation of such ecosystems, although it is difficult to link those changes due to ambient NO_X or SO_X concentrations.

F.5.2.1. Recreation

Bockstael et al. (1989a) measured the benefits of improvements in water quality of the Chesapeake Bay using travel cost and SP methods. A telephone survey with 959 respondents revealed an aggregate WTP for water quality improvement from current level to a level acceptable for swimming and/or other water activity of about $91 million (1987 dollars; $166 million in 2007 dollars) for households in Maryland. Based on three other surveys, a travel cost model yielded aggregate use values of about $34.7, $4.7, and $1.4 million ($63.1, $8.6, and $2.6 million in 2007 dollars) for a 20% water quality improvement for beach use, boating, and sport fishing, respectively.

Morgan and Owens (2001) simulated water quality change under a baseline (without additional pollution control) and a scenario with pollution control in the Chesapeake Bay watershed and then calculated aggregate benefits for beach use, boating, and striped bass sport fishing by transferring the benefits from Bockstael et al. (1989a). Lower bound aggregate benefits for beach use, boating, and sport fishing were $288.8, $6.7, and $288.8 million (1996 dollars; $380.4, $8.8, and $380.4 million in 2007 dollars), respectively for a 60% improvement in Chesapeake Bay water quality.

Lipton (2004) mailed out an open-ended contingent valuation survey to 2,510 randomly selected Maryland boaters regarding willingness to pay for one unit improvement in the water quality of the Chesapeake Bay. The boaters ranked their perception of water quality on a scale of one to five. The median WTP for a one step improvement in water quality was $17.50 ($19.66 in 2007 dollars) per year and the mean was $63 ($71 in 2007 dollars), with 38% of respondents expressing a zero WTP. It was found that the boaters who keep their boats in the water would pay more than those who keep them on trailers. Individuals who ranked ambient water quality lower and had more concern for the health effects from water quality degradation would likely pay more for water quality improvement. The aggregated WTP for the Chesapeake Bay boaters in Maryland was approximately $7.3 million ($8.2 million in 2007 dollars) per year with a $146 million ($164 million in 2007 dollars) present value (a 5% discount rate).

Smith et al. (1991) estimated the recreational fishing value of Albemarle-Pamlico Estuary in North Carolina using a hedonic travel cost model. The analysis was based on an intercept survey with 1,012 interviews at 35 boat sites and 44 bank sites in 1981 and 1982. The estimated benefit derived from the application of a conventional demand model to the boat site sample ranged from $1.49 to $2.58 (1982 dollars; $3.19 to $5.53 in 2007 dollar), and for the bank site sample ranged from $0.65 to $1.11 ($1.39 to $2.38 in 2007 dollars) for an increase in catch rate of one fish per hour per person.

Four years later, Kaoru (1995) and Kaoru et al. (1995) used the information collected from the same survey to estimate the recreation value from improvements in Albemarle and Pamlico Sounds using a household production model and a random utility model. They linked the effluent loading and quality of sport fishing with the fisherman's decision on site selection. Instead of fish availability being estimated as the average number of fish caught per person per hour for each entry point, Kaoru et al. (1995) used total

catch per trip per person as their key measure of fishing success. They included not only the estimated N loadings but also the effect on biochemical O_2 demand as an influence on fishing quality. The results suggested that depending on aggregation methods, CS ranged between $7.05 and $36.19 ($9.56 and $49.08 in 2007 dollars) for a 5% increase in total catch. The CS was $1.27 to $6.52 ($1.72 to $8.84 in 2007 dollars) for a 36% decrease in N loadings at all sites.

Whitehead et al. (2000) used a joint stated and RP model to estimate recreation value of improvements to Albemarle and Pamlico Sounds in terms of CS per trip and per season. A telephone survey was conducted in 1995 to learn how North Carolina residents would value improvements of water quality resulting in a 60% increase in fish catch and a 25% increase in open shellfish beds. The analysis was based on 765 completed responses. The CS per trip was estimated at $64 (1995 dollars; $87 in 2007 dollars) for current quality and $85 ($115 in 2007 dollars) for improved quality and the CS per season was $121 ($164 in 2007 dollars) for current and $155 ($210 in 2007 dollars) for improved quality.

The Catawba River in North and South Carolina is used for electric power generation, recreation, drinking water, and wastewater assimilation. With population growth and land use change, the health and vitality of the river system are declining as the river flows downstream. Through a mail-phone survey of 1,085 residents randomly selected from 16 counties of Catawba River Basin, Kramer and Eisen-Hecht (2002) presented a management plan designed to maintain the water quality at the current level over time. The water quality in the entire watershed was classified as good, fair or poor on maps to illustrate the distribution of the tributaries with different water quality. The mean WTP was estimated to be $139 ($160 in 2007 dollars) for protecting current water quality from deterioration.

A site choice model applied jointly with a trip frequency model was used by Needelman and Kealy (1995) to assess the relative benefits of eliminating eutrophication, fecal bacteria, and oil and grease in New Hampshire lakes. The site choices analysis was based on 53 individuals and 1,021 trips, while the trip frequency model was based on a total of 519 individuals including the responses for the site choices model. The mean seasonal benefits were valued at $1.40 ($1.90 in 2007 dollars) for eliminating eutrophication from all sources ($1.33; $1.80 in 2007 dollars) for eliminating nonpoint source pollution alone and $0.09 ($0.12 in 2007 dollars) for eliminating point source pollution alone) with an aggregate seasonal benefit of $1.16 million ($1.57 million in 2007 dollars), with $1.11 million for nonpoint source and $0.08 million for point source pollution. However, the economic benefit estimates were exclusively for swimming and day trips. The measures of water quality were not from the year of the survey (1989) but from a range of years from 1976 to 1991.

The Tar-Pamlico River has experienced declining fish catches, disease in fish and shellfish beds, algae blooms, and aquatic grass losses. More than half of the pollution impairing one third of the river was estimated to come from agricultural nonpoint sources. Whitehead and Groothuis (1992) proposed a management program in which farmers used best management practices (BMPs) to significantly improve

the water quality of the Tar-Pamlico River such that recreational anglers would be able to catch twice as many fish per trip. A mail survey was sent to 179 households in four counties in Tar-Pamlico River basin (with a 61% response rate). The mean WTP for doubling fish catch was estimated at $25 ($38 in 2007 dollars), which was bounded from above by a $35 use value ($53 in 2007 dollars) and from below by a $21 ($32 in 2007 dollars) non-use value. The benefits of water quality improvement in the study area were aggregated at $1.62 million (1991 dollars; $2.46 million in 2007 dollars) each year. The researchers believed that non-use value could account for as high as 84% of the estimate. However, the study suffered from small sample size and relatively high non-response rate (11%) to the WTP questionnaire.

Some portions of the coastal coral reefs in the Florida Keys are projected to disappear within 10 to 25 years. In 2000, the U.S. government announced a long-term plan to save coral reefs proposing that 20% of all coral reefs in American-controlled waters would become ecological preserves by 2010. Park et al. (2002) investigated the WTP to preserve current water quality and health of the coral reefs in the Florida Keys. Based on 460 responses to a CV survey and 4,035 respondents to a travel cost survey (460 responses used in the analysis), the annual use value was estimated at $481 per person per snorkeling trip ($553 in 2007 dollars). The mean predicted WTP per trip from a Tobit model was $735 ($844 in 2007 dollars). Over 85% of the predicted WTP value was within plus or minus $50 ($57 in 2007 dollars) of the total trip expenses from the contingent valuation scenario.

F.5.2.2. Commercial Fisheries

As one of six background studies for the National Science and Technology Council (NSTC), Diaz and Solow (1992) used a time series estimation approach to examine the effects from hypoxia[1] in the Gulf of Mexico. The study failed to confirm the relationship between the annual occurrence of hypoxia and commercial fishery health, based on catch rate per unit effort of three major species from the 1960s to 1990s. Although the benefit assessment did not detect effects attributable to hypoxia, this does not necessarily mean that the economic effects would not occur. NSTC (2000) identified alternatives for reducing the adverse effects of hypoxia and examined the costs associated with reduction of N and P inputs. A net cost estimated by the U.S. Mathematical Programming Model for Agriculture was about $0.8 per kilogram ($0.36 per pound; $0.96 per kilogram/$0.36 per pound in 2007 dollars) for a 20% edge-of-field N loss reduction on agricultural lands, whereas restoring 5 million acres of wetland would have a net cost of $1.00 per kilogram ($0.45 per pound) ($1.2 per kilogram/$0.54 per pound in 2007 dollars) of N removal.

[1] Hypoxia (DO depletion) is a phenomenon resulting from the overloading of nutrients (usually N or P) in water. Most fresh waters are P-limited, and therefore added N from atmospheric deposition does not have a substantial effect on productivity. In contrast, marine and estuarine waters tend to be N-limited, and are therefore expected to respond to additional N inputs by increasing algal productivity. Excessive production of algae can deplete the water of oxygen when those algae die and are decomposed by oxygen-consuming microorganisms. If the concentration of DO decreases to very low levels, fish, and other life forms can die.

The Neuse River in North Carolina is important to the commercial blue crab (*Callinectes sapidus*) fishery in the eastern U.S. It accounted for about a quarter of the blue crab harvest from 1994 to 2002. Smith and Crowder (2005) simulated the progress of eutrophication in the Neuse River using a series of ordinary differential equations, which linked changes in the quantity of nutrients, algal growth, spatial population distribution of blue crab and its prey species with fishing efforts. Results suggested that a 30% reduction in N loading in the Neuse River watershed over a 50–year period would result in about a $2.56 million ($2.71 million in 2007 dollars) discounted present value generated in fishery rent (the difference between fishing revenues and costs including fixed and opportunity cost).

F.5.2.3. Water Clarity

In addition to effects on fish populations, eutrophication reduces water clarity due to excessive growth of algae. Boyle et al. (1999) studied the social welfare related to water clarity of four lakes in Maine employing a two-stage hedonic demand model. Based on data from 1990 to 1995 on property sales for 25 lakes, tax records, mail survey, and water clarity data from the Maine Department of Environmental Protection (DEP), the CS for water clarity improvement from the average ambient level (3.78 m) to 5.15 m was estimated to be $3,677, $3,765, and $12,870 ($4,562, $4,671, and $15,967 in 2007 dollars) for differently specified demand systems (Cobb-Douglas, semilog, and linear demand models, respectively). Social welfare loss for visibility deterioration from an average level to 2.41 m ranged from $25,388 to $46,750 ($31,497 to $57,989 in 2007 dollars). One of the interesting findings in the study was that the slope of the Cobb-Douglas demand model increased to 3.0 m, a threshold used by the Maine Department of Environmental Protection to indicate improved water quality and public preferences for it.

Poor et al. (2006) evaluated water quality in a small watershed of Maryland using a hedonic property valuation model. The watershed is located in a peninsula surrounded by the Potomac and Patuxent Rivers and the Chesapeake Bay. Due to nonpoint source pollution runoff, water quality has deteriorated, which might have negative impacts on residential housing prices, especially for those close to the river. To estimate the possible extent of the impact, total suspended solids (TSS) and dissolved inorganic nitrogen (DIN) were averaged by year and included in the model as indicators of ambient water quality. The estimates showed that a marginal increase in TSS reduced average housing prices by $1,086 ($1,113 in 2007 dollars), and a marginal increase in DIN decreased housing prices by $17,642 ($18,087 in 2007 dollars).

F.5.3. Avoided Costs

Based on a model projection, IEc (1999c) estimated the benefits of decreased N deposition to the estuaries in the eastern U.S. using the avoided cost method. According to their results, the annual avoided cost in 2010 would range from $26 to $102 million if 12.8 million pounds of N loading was reduced annually in Long Island Sound. An annual reduction of 58 million pounds of N loading into Chesapeake Bay would avoid an annual cost of $349 to $1,278 million. Uncertainty associated with model assumptions and the inappropriate use of avoided cost estimates to value benefits or damages are two major sources of potential error in generating such estimates. In addition, the avoided costs method generally does not measure values conceptually accurately, and these values also are not linked to benefits from reduced pollution.

F.5.4. Limitations and Uncertainties

Several general limitations apply to the valuation of water quality changes. First, the definition of water quality is too ambiguous to quantify comparisons across studies. Second, the degree of water quality improvement is not often clear. A common obstacle in any environmental economic valuation is the availability of data. Problems stemming from lack of data extend from biological data on the populations of target species to limitations of the available economic data on the value of commercial and recreational fisheries to small samples of survey respondents (Smith and Crowder, 2005).

The geographical focus of valuation studies is another limitation. The studies reviewed here largely focused on the eastern part of the U.S., represented by the Adirondacks, Chesapeake Bay, and Albemarle and Pamlico Sounds. Several studies investigated the total value of aquatic ecosystems and the majority of the studies calculated recreational values of water quality improvement. Only a few studies addressed the economic value of commercial fisheries. There is considerable uncertainty in the estimates of benefits as they vary significantly even for studies in the same area, with similar changes in the commodity, and use of the same valuation methodology.

Almost every study reviewed here mentioned the problem of uncertainties about the natural science (Diaz and Solow, 1992; NSTC, 2000). For example, the processes involved in the development of hypoxia are not fully known. There is also no clear connection between a decrease in pollution level and an increase in catch rate (Bockstael et al., 1989b). Additionally, uncertainty arises from the selection of parameter values (Smith and Crowder, 2005) and models (Burtraw et al., 1997). Due to the uncertainty about water quality improvement in tributaries of the Chesapeake Bay, the estimates provided by Morgan and Owens (2001) excluded benefits from water recovery in the tributaries.

Study coverage also affects benefit estimates. For example, Morey and Shaw (1990) only included those fishermen who could make day trips to one or more of the study sites, fishermen with complete

records, and fishermen whose distance to the farthest site was less than 200 miles. Morey and Shaw (1990) evaluated four sites and two kinds of trout in the Adirondacks while Englin et al. (1991) valued only one trout species and lakes in four states.

Many studies relied on information from surveys, which may suffer from various biases. For example, several studies reviewed here used intercept surveys, which are not necessarily representative of the target population (Bockstael et al., 1989b; Smith et al., 1991). Double counting of values may also introduce errors into value estimation. For example, people who are boating may also go fishing (Bockstael et al., 1989b).

F.6. Summary

Previous ecosystem valuations presented in AQCDs were very limited because they considered only studies that could directly attribute monetary values to changes in emissions. The assessment of the literature in this Annex has a different approach: the voluminous literature that values various ecosystem services affected by emissions is included, whether or not the actual linkages all the way from emissions to those effects have been quantified. This approach nevertheless necessitates that the natural science underpinnings be examined in the context of preferences, that is, descriptions of damages (or benefits) from NO_X and SO_X emissions (or reductions in those emissions) from the natural sciences that translate into things that the public cares about. These include, for example, whether the water is boatable or swimmable, the marketable yield associated with changes in a forest or a crop, and effects on aesthetics of wetlands.

The physical endpoints and their corresponding valuation studies are divided into different ecological and value endpoints applicable to terrestrial, transitional, and aquatic ecosystems. There is significant valuation literature on the effects of O_3 on crops (and to a far lesser degree on forest yield), but this topic is beyond of the scope of this assessment. Beyond the O_3 effects, there is little quantification of the science describing the effects of pollution related to NO_X and SO_X on ecosystems. Valuation studies are themselves classified into meta-analyses and original studies, the latter into market studies (e.g., commercial fishing), RP studies (e.g., those related to recreation behavior, property values, etc.), and SP studies (those that ask people survey questions about their WTP for hypothetical ecosystem improvements).

For valuation of terrestrial effects, survey methods are most common. Supplemented by travel cost approaches, this literature leads to a variety of estimates of WTP for improved forest quality that could prove useful for estimating benefits of N and S reductions (provided a number of linkages can be made), even though some of the endpoints valued are related to insect damage. One meta-analysis is available that summarizes this valuation literature.

For wetland valuation, three meta-analyses are available that summarized the valuation literature. This literature is problematic because it focuses on values per wetland acre rather than WTP for changes in services provided by a wetland affected by deposition of N and S pollutants. However, some of the available studies provide WTP for discreet ecosystem services, which is helpful in matching these values to services affected by reductions in N and S deposition. Nevertheless, because there is a very poor understanding of the scientific basis for linking NO_X and SO_X emissions to ecosystem health endpoints, the ability to make the necessary linkages to estimate benefits of pollution reductions is very limited.

The aquatic service valuation literature is the most voluminous of the three categories reviewed. It contains many recreation value studies, a number of property value studies, some total (use plus non-use) value studies, some studies on commercial fishery damages and several good meta-analyses of primary valuation studies, which provide estimates of the WTP of households for improvements in the aquatic ecosystem related to N and S changes. Again, however, there is little focus on NO_X or SO_X as the cause of alterations to the aquatic ecosystem.

Overall, there is a robust literature valuing a variety of ecosystem services that could be related to reductions in N and S emissions. Therein addition, issues affecting the credibility of any individual study and even the studies grouped by technique, such studies can only be used for general valuation purposes. The most important limitation is establishment of the linkages between the physical, chemical, and biological effects of air pollutants on natural ecosystems and changes in exposure to NO_X and SO_X.

Table F-1. Commonly adopted environmental valuation methods based on revealed or state preferences.

Methods	Description	Direct Use	Indirect Use	Total Value
Revealed Preference Methods	Observing individual choices and behavior to predict their preferences for environmental goods and services.			
Avoided expenditure method	Predicting the cost of mitigating the effects of reduced environmental quality.	X	X	
Derived demand functions	Estimate the value of environmental goods and services by deriving the demand functions of households or firms for them (e.g. water use)	X	X	
Hedonic valuation method	Estimating an implicit price for the environmental quality attributes of marketable goods, such as housing.	X	X	
Market analysis	Used for valuing market goods using data on prices and quantities of outputs and inputs. May use prices of close substitutes, methods of deriving shadow prices, or simulation of changes in market conditions.	X	X	
Referenda	Examining voting results related to environmental resources to predict values for them.	X	X	
Replacement cost	Measures expenditures incurred in replacing or restoring environmental good or service lost (e.g. water filtration). Provides accurate valuation only under strict assumptions usually not met.	X	X	
Travel cost method	Values the environmental attributes of recreational sites by examining visitation frequency and cost differential incurred in reaching site with different attributes.	X	X	
User fee	Examine user fees paid to gain access to an ecological resource such as a park to estimate the lower bound of society's value for that resource.	X	X	

Methods	Description	Direct Use	Indirect Use	Total Value
Stated Preferences Approach	Directly surveying individuals to predict their preferences for environmental goods and services.			
Choice experiments, conjoint analysis	Elicits individuals' choices from several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to contingent ranking).	X	X	X
Contingent valuation	Elicits data on individuals' willingness to pay for environmental goods and services (hypothetical setting, limited by potential biases). Often implemented using a hypothetical referenda.	X	X	X
Contingent ranking	Elicits data on the ranking of several alternatives associated with different environmental and cost outcomes. Elicits data on WTP indirectly (by eliciting cost-environmental outcome tradeoffs, similar to choice experiments, conjoint analysis).	X	X	X

Table F-2. Economic effects of ozone and other pollutants on agriculture, as reported in the 1996 ozone criteria document.

Study	Region	Pollutant and Concentration	Model Features				Results (Annual 1980 U.S. Dollar)			
			Price Changes	Output Substitutions	Input Substitutions	Quality Changes	Crops	Consumer Benefits	Producer Benefits	Total Benefits (Costs)
Adams et al. (1986a)b	U.S.	Ozone, 25% reduction from 1980 level for each statec	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, barley	1160×106	550×106	1700×106
Kopp et al. (1985)b	U.S.	Ozone, universal reduction from 53 ppb to 40 ppba	Yes	Yes	Yes	No	Corn, soybeans, wheat, cotton	Not reported	Not reported	Not reported
Adams et al. (1986b)	U.S.	Acid deposition, 50% reduction in wet acidic deposition	Yes	Yes	Yes	No	Soybeans	172×106	–30×106	142×106
Adams and Crocker (1989)	U.S.	Ozone, seasonal standard of 50 ppb with 95% complianced; Includes adjustments for 1985 Farm Bill	Yes	Yes	Yes	No	Corn, soybeans, cotton, wheat, sorghum, rice, hay, barley	905×106	769×106	1674×106

[a] Seven-h growing season geometric mean. Given a long-normal distribution of air pollution events, a 7–h seasonal ozone level of 40 ppb is approximately equal to an hourly standard °f 80 ppb, not to be exceeded more than once a year (Heck et al., 1983).

[b] Reported in 1986 criteria document.

[c] Reported All studies except Garcia et al. use NCLAN data to generate yield changes due to ozone.

[d] Seven- and twelve-h growing season geometric mean. Analysis includes both fixed rollbacks (e.g., 25% and seasonal standards (with variable compliance rates).

Source: Adams and Horst (2003)

Table F-3. Economic effects of ozone on marketable benefits from forests.

Reference	Pollutant/Coverage	Response and Air Quality Data	Economic Model	Annual Damages or Benefits of Control
Callaway et al. (1986)a	All pollutants. Forest products (hardwood and softwood) in the eastern U.S.	Assumes three arbitrary growth reductions (10%, 15%, and 20%) for hardwood and softwood tree species.	Spatial equilibrium models of softwood and hardwood stumpage and forest products industries in the U.S.	$340 to $510 million; damage in 1984 dollars for assumed reductions in growth levels.
Crocker (1985)	Acid deposition. Forest products and forest ecosystem service flows for eastern U.S.	Assumes a 5% reduction in products due to acid deposition: assumes a pristine background pH of approximately 5.2.	Naive; assumed changes in output multiplied by avg value of those goods or services.	$1.75 billion damage in 1978 dollars from current levels of acid deposition.
Crocker and Forster (1986)	Acid deposition. Forest products and forest ecosystem services for eastern Canada.	Assumes 5% reduction in forest productivity for all eastern Canadian forests receiving $10 kg/ha/yr sulphate deposition.	Naive; assumed changes in output multiplied by avg value of goods or services.	$1.5 billion damage in 1981 Canadian dollars from current levels of acid deposition.
Haynes and Adams (1992)	Air pollutants, including acid precipitation. Losses estimated for eastern U.S. softwoods.	None; paper demonstrates a methodology for assessing economic effects of yield (growth and inventory) reductions due to any course. Assumes losses from 6% to 21% for softwoods.	Econometric model of U.S. timber sector (TAMM).	Damages of $1.5 to $9.0 billion in 1988 dollars.b
Bentley and Horst (1998)	Ozone. All hardwoods and softwoods except western hardwoods.	Dose-response based on survey of experts scaled to partial attainment of secondary standard relative to the current primary standard. SUM06 exposure metric is based on a cumulative daytime exposure during the growing season.	Econometric model of U.S. timber sector (TAMM).	Benefits of $14 million in 2010 (1990 dollars) for partial attainment of 0.08 ppb 3rd max secondary standard. This standard was considered during the standard development process.

[a]We used the updated version of Crocker et al. from 1986, while Adams and Horst cited a prior version, from 1985.

[b]We drew different numbers from the Crocker and Forster study than those reported by Adams and Horst.

Source: Adams and Horst (2003), exceptions: Table 2 in Bentley and Horst (1998).

Table F-4. Forecasted average values for select activities, per day per person in 1996.

Activity	Northeast	Southeast	Intermountain	Pacific Coast	Alaska	USA
Swimming	14	9	19	9	14	14
General recreation*	30	25	34	25	30	30
Fishing	37	32	41	32	37	37
Waterfowl hunting	40	35	44	34	40	39
Big game hunting	45	40	50	40	45	45

*The activity category includes camping, picnicking, sightseeing, hiking, small game hunting, wildlife viewing, and other general recreation. In the meta-analysis, values for these activity categories do not differ statistically significantly. Source: from the meta-analysis benefit function by Rosenberger and Loomis (2001), Table 6.

Table F-5. Typical impacts of specific pollutants on the visual quality of forests.

Pollutant	Geographic Extent	Injury Type	Major Types of Visual Injuries	Notes
Ozone	Area or regional effects	Direct injuries	Foliar injuries (e.g., pigmented stipple), increased needle/leaf abscission, premature senescence of leaves. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for ozone.	

Pollutant	Geographic Extent	Injury Type	Major Types of Visual Injuries	Notes
		Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as insect attacks. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	
Acidic Deposition	Area or regional effects	Indirect Injuries	Increased susceptibility to visual injuries may result from other adverse environmental factors, such as climatic factors. For example, increased needle/leaf abscission, elevated mortality rates, and/or changes in species composition.	Acidic deposition can also cause direct foliar injuries. Acids are, however, more likely to indirectly affect the visual appearance of forest trees, unless exposure levels are very high.
Sulfur Dioxide	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Sulfur dioxide may also cause indirect injuries. Indirect injuries, however, are not well documented.
Hydrogen Fluoride	Point source pollution	Direct Injuries	Foliar injuries including leaf/needle discoloration and necrosis. Pattern, size, location, and shape of foliar injuries to indicator species can be specific for sulfur dioxide. At high concentrations, elevated mortality rates of sensitive species and changes in species composition may occur.	Hydrogen fluoride may also cause indirect injuries. Indirect injuries, however, are not well documented.

Source: Exhibit 2 Industrial Economics (IEc) (1999a)

Table F-6. Economic valuation studies related to forest aesthetics.

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Crocker (1985)	CV (open ended)	Southern California	Evaluating visits to recreational sites with slight, moderate, and severe O_3 induced damages to ponderosa and Jeffery pine stands.	Household WTP (per trip)	Slight damage: $2.09 Moderate damage: $0.66 Severe damage: $0.74
Haefele et al. (1992)	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution	Household WTP (per yr)	PC: $21 DC: $100
Holmes and Kramer (1996)a	CV (payment card, dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insect and air pollution. Analysis compared forest users and non-users.	Household WTP (per yr)	Forest users: $36 Non-users: $10
Holmes et al. (2006)	Hedonic pricing	New Jersey	Evaluate the effects of hemlock forest health status on housing prices. Hemlock health status is potentially deprived by hemlock woolly adelgid; an exotic forest insect.	Housing price	Hemlock forest health status is positively associated with housing prices. For example, a 1–point increment in (e.g., from 10% to 11%) in the % of healthy hemlocks of all forests on the home parcel was associated with a 0.66% sales price increase. Similar changes in home's near proximity are associated with yet larger price increments.
IEc (1999b)b	Benefits transfer	National	Protect trees from various different types of damage (see description of source studies)	Welfare Loss (1990–2010)	$3 to $17 billion
Jakus and Smith (1991)	CV (dichotomous choice)	Maryland and Pennsylvania	Protect private homeowner property and surrounding public lands from gypsy moth damages (reduce tree defoliation by 25%)	Household WTP (for entire program)	Private Property Prgm (only): $254 to $420 Private and Public Prgm: $314 to $527
Jenkins (2002)	CV (open ended)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout ecosystem	Household WTP (per yr)	$153

Study	Method	Study Area	Description	Economic Endpoint	Economic Value
Kramer et al. (2003)	CV (dichotomous choice)	Southern Appalachian Mountains	Protect high-elevation spruce firs from insects and air pollution along roads and throughout the entire ecosystem	Household WTP (per yr)	Road side only: $18 Entire ecosystem: $28 Non-use: 87% of total value Use: 13% of total value
Kramer and Mercer (1997)	CV (payment card and dichotomous choice)	National (USA)	Protect 10% of tropical rainforests as national parks or forest reserves.	Household WTP (per yr)	PC: $31 DC: $21
Loomis et al. (1996)	CV (dichotomous choice, open ended)	Oregon	Protect old growth forests of Pacific Northwest from fires.	Household WTP (per yr)	DC: $98 OE: $33
Leuschner and Young (1978b)	TCM	Texas	Reduce crown density in recreational areas.	Consumer Surplus (losses)	–0.69 to –6.5% (depending on level of substitute sites)
Miller and Lindsey (193)	CV (dichotomous choice)	New Hampshire	Protect private homeowner property from gypsy moth damages (reduce tree defoliation by various amounts)	Household WTP (per yr)	$55 to $86 (depending on level of reduction in tree defoliation)
Peterson et al. (1987)	CV, hedonic property	Los Angeles area	Avoid O_3 induced damages to trees in local national forests for recreationists (in greater LA area) and homeowners (with property bordering forest).	Household WTP (per yr) Consumer Welfare	Recreationist: $43 Homeowner: $131 $31 to $161 million
Treiman (2006)	CV (dichotomous choice)	Missouri	Improve residential tree care and maintenance in different sized cities.	Household WTP (per yr)	Urban areas: $14 to $16
Walsh et al. (1989)	TCM	Colorado Rockies	Reduce tree density in recreational areas.	Consumer Surplus (losses)	–8.5 to –23.2% (for reductions in tree density ranging between 10 to 30%)
Walsh et al. (1990)	CV (iterative bidding)	Colorado	Protect ponderosa pine forests from damages caused by the mountain pine beetle.	Household WTP (per yr)	$47 Non-use: 73% of total value Use: 27% of total value

[a]Holmes and Kramer study applies same results found in Haefele et al. (1991)

[b]Benefits transfer was based on results from Holmes and Kramer (1996), Peterson et al. (1987), Walsh et al. (1990).

Table F-7. Summary of the monetized estimates of the annual value of forest quality changes

Reference	Aesthetic Change Valued	Value of Change per Household (Current Dollars)	Value of Change per Household (1990 Dollars)i	Total Value of Change for Region (Current Dollars)	Total Value of Change for Region (1990 Dollars)i
Peterson et al. (Peterson, 1987)	Ozone damage to San Bernardino and Angeles National Forests	$6.31 - $32.70ii	$7.26 - $37.62	$27 - $140 million	$31 - $161million
Walsh et al. (1990)	Visual damage to Colorado's Front Range	$47	$61.68	$55.7 million	$73.09 million
Holmes and Kramer (1996)	Visual damage to spruce-fir forests in southern Appalachia	$10.81 nonusers $36.22 users	$10.37 nonusers $34.76 users	NA	NA

Source: Exhibit 4 Industrial Economics (IEc) (1999a).

Table F-8. Estimated value of avoiding forest damage in the U.S.

Affected System	States Included	Value per Household	Householdsi	Total Annual Value	Cumulative Value (1990–2010)ii
Sierra Nevada and Los Angeles Basin	CA	$7.26 - $37.62	10.4 million	$75.5 million - $391.2 million	$1.02 billion - $5.27 billion
Eastern Spruce Fir and Selected Eastern Hardwood	ME, VT, NH, MA, NY, PA, WV, TN, KY, NC, VA	$7.26 - $37.62	23.2 million	$168 million - $872.8 million	$2.27 billion - $11.75 billion

Source: Exhibit 5 Industrial Economics (IEc) (1999a)

Table F-9. Ecological wetland functions, economic goods and services, types of value, and applicable valuation methods.

Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Methods (s)a
Flood and flow control	Flood protection	Indirect use	Replacement cost Market prices Opportunity cost
Storm buffering	Storm protection	Indirect use	Replacement cost Production function
Sediment retention	Storm protection	Indirect use	Replacement cost Production function
Groundwater recharge/discharge	Water supply	Indirect use	Production function NFI Replacement cost
Maintenance/Nutrient retention	Improved water quality Waste disposal	Indirect use Direct use	CVM Replacement cost
Habitat and nursery for plant and animal species	Commercial fishing and hunting Recreational fishing and hunting Harvesting of natural materials Energy resources	Direct use Direct use Direct use Direct use	Market prices, NFI TCM, CVM Market prices Market prices
Biological diversity	Appreciation of species existence	Non-use	CVM
Micro-climate stabilization	Climate stabilization	Indirect use	Production function
Carbon sequestration	Reduced global warming	Indirect use	Replacement cost
Ecological Function	Economic Goods and Services	Value Type	Commonly Used Valuation Methods (s)a
Natural environment	Amenity Recreational activities Appreciation of uniqueness to culture/ heritage	Direct use Direct use Non-use	HP, CVM CVM, TCM CVM

a Acronyms refer to the contingent valuation method (CVM), hedonic pricing (HP), net factor income (NFI), and the travel cost method (TCM).

Source: Table 1, Brander et al. (2006).

Source: with modifications adapted from Barbier (1991); Barbier et al. (1997); Brouwer et al. (1999); and Woodward and Wui (2001).

Table F-10. Economic valuation studies related to acidification and eutrophication in aquatic ecosystems.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Acidification						
Banzhaf et al. (2006)	Injured lakes in Adirondacks, NY	CV	Fish, bird species, and tree species	WTP (total value)	1. The mean WTP for base version was $48 per yr per household in New York State while the mean WTP for scope version was $54 per yr per household in New York State (discounting rate =3%)	1. Base version: improvement in fish population of 600 lakes, small improvements in the populations of two bird and one tree species. 2. Scope version: improvement in fish population of 900 lakes, improvement in the population of four bird and three tree species.
Bockstael et al. (1989a)	Chesapeake Bay, MA and DC	CV and TC	Fish	Aggregate benefit/ consumer surplus (recreational value)	1. 20%water quality improvement resulting in aggregate benefits for beach use, boating, and sportfishing were about $34.7, 4.7, and 1.4 millions. 2. aggregate WTP for water quality improvement from current to a level acceptable for water activity was about $91 million (1987 dollars)	1. TNP, product of N and P, was included in the model. 2. WTP was aggregated for households in Maryland.
Cameron and Englin (1997)	Northeast U.S.	CV and RUM	Trout fishing (uncertain about use)	Consumer surplus (recreational value, existence value)	1. For passive user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was $218 for S model and $215 for OP model. 2. For active user, surplus for preventing a 20% loss in currently fishable high altitude lakes in the Northeast was $283 for S model and $439 for OP-I model and $436 for OP-D.	1. S model: Surplus interpretation of the WTP responses 2. OP model: Option price interpretation of the WTP responses. 3. I: complete independence between yr-to-yr decisions 4. D: complete dependence on previous decisions
Englin et al. (1991)	ME, NH, NY (excluding New York City) and VT	HTC and RUM	Catch per unit effort (number of fish caught in an h)	Consumer surplus (recreational value)	1. Under baseline scenario (1989), welfare loss was estimated at $0.27 m (HTC) and $1.75 (RUM) 2. Under NAPAP scenario 1, welfare loss was occurred in 2010 at $13.7 m (HTC) and $1.2 m (RUM) but social welfare would gain in 2030 at $3.5 m (HTC) and $5.5 m (TCM) 3. Under NAPAP scenario 4, welfare would gain in 2010 at $3 m (HTC) and $7.4 m (TCM) and also gain in 2030 at $4.4 m (HTC) and $9.7 m (TCM)	1. Acidic stress index (ASI) measuring fish biological tolerance to acidity was included in the model. 2. The benefits were valued in 1989 dollars 3. Multiple datasets were used in the analysis. 4. Only trout species fishing was included. 5. The benefit estimates were aggregated for four states by accounting income increase and population change resulting from baby boom.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Kaoru et al. (1995)	Albemarle and Pamlico Sounds, NC	CV and RUM	Fish	Consumer surplus (recreational value)	1. 35–site model: $36.19 for 5% increase of total catch at all sites (full-wage) 2. 35–site model: $6.52 for 36% decrease in N loadings at all sites (full-wage)	1. Estimated N loadings and biochemical O_2 demand, were used in household production models to measure fishing quality. 2. The paper also estimated benefit based on opportunity cost at 1/3 wage for 23−site and 11–site models.
Morey and Shaw (1990)	Four fishing sites in Adirondacks, NY	CV and TC	Brook and Lake Trout	Consumer surplus (conditional compensating variations) (recreational value)	1. $475.87 for 5% increase in catch rates for trout (1977 dollars) 2. $2162.04 for 25% increase in catch rates for trout (1977 dollars) 3. $3862.94 for 50% increase in catch rates for trout (1977 dollars)	1. Economic values were aggregate CCV for 607 survey respondents. 2. Catch rate, as an indicator of acid deposition, was included as a variable in the model.
Morgan and Owens (2001)	Chesapeake Bay	Water quality model and Benefit transfer	Water quality	Aggregate benefit (recreational value)	1. Lower bound total benefit for beach use was $288.8m from a 60% improvement in Chesapeake Bay water quality. 2. Lower bound total benefit for trailered boating was $6.7m from a 60% improvement in Chesapeake Bay water quality. 3. Lower bound total benefit for striped bass sport fishing was $288.8m from a 60% improvement in Chesapeake Bay water quality.	1. The study also provided aggregate benefits at avg and high level for three recreational uses. 2. Benefit transfer was based on the results in Bockstael et al. (1988).
Mullen and Menz (1985)	Adirondack, NY	TC	Fish	Net economic value per angler day/ Consumer surplus (recreational value)	1. Net economic value per angler day was avgd at $19.90 for entire waterbody including lakes, ponds, and streams. 2. Total angler value was estimated $31.3 million for entire water body. 3. The loss in net economic value was estimated at $1.07 million for lakes and ponds due to reduction in angler visitation.	1. The values were in 1976 dollars. 2. Total value was aggregated by number of trips.
Randall and Kriesel (1990)	Nationwide, U.S.	CV	Water/air quality	WTP (total value)	1. The estimated annual willingness to pay was $694.42 per household.	1. The study valued a National Pollution Control Program, which improved air and water quality by 25 percent in 5 yrs.
Smith et al. (1991)	Albemarle and Pamlico Sounds, NC	HTC and demand function	Fish	Benefit/ consumer surplus (recreational value)	1. Conventional demand model: $2.58 for boat, $1.11 for bank fishing 2. Simple inverse demand model: $0.79 for boat, $0.62 for bank fishing 3. Detailed inverse demand model: $0.88 for boat, $0.79 for bank fishing	1. Benefit was calculated for an one-fish increase in catch rate per h per person 2. Catch rate was included in the model. 3. The paper also estimated benefit based on opportunity cost at 1/3 wage.

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Whitehead et al. (2000)	Albemarle and Pamlico Sounds, NC	CV and TCM	Fish catches and shellfish beds	Consumer surplus per season/ per trip (recreational value)	1. The consumer surplus per trip is $64 for current quality and $85 for 60% increase in fish catch and 25% more open shellfish beds. 2. The consumer surplus per season is $121 for current quality and $155 for 60% increase in fish catch and 25% more open shellfish beds.	1. The consumer surplus per trip difference between two baseline and scenario was not significant at the 0.10 level while the consumer surplus per season difference between two situations was. 2. The studies also estimated annual aggregate consumer surplus per season for 41 counties within the watershed.
Eutrophication						
Boyle, et al. (1999)	Four lakes, ME	HTC (two stages, hedonic demand model	Water clarity (visibility)	Consumer surplus (recreational value)	1. The consumer surplus (+) for an avg visibility improvement from 3.78m to 5.15m was $3,765 and $3,677 for semi-log and Cobb-Douglas model. 2. The welfare losses (–) for an avg visibility decrease from 3.78m to 2.41m was $25,388 and $46,750 for semi-log and Cobb-Douglas model.	1. The welfare was also measured in linear demand model. However, the own price of water clarity is not significant.
Diaz and Solow (1992)	Gulf of Mexico	Time series	Brown shrimp, white shrimp, and Menhaden	Mean catch rate per unit effort	1. The study failed to quantify economic effects of hypoxia based on past data.	1. Hypoxia was measured in terms of area (zone) and index in the model to calculate correlation.
Kramer and Eisen-Hecht (2002)	Catawba River, NC and SC	CV	Water quality	WTP (total value)	1. A mean willingness to pay was revealed at $139 for maintaining current water quality over time.	1. Phone-mail-phone and mail-phone survey formats applied.
Lipton (2004)	Chesapeake Bay, MA	CV	Water quality	WTP (use value)	1. The median WTP for a one scale improvement in water quality was $17.50 per boater per yr and the mean was $63, with 38% expressing a zero WTP.	1. The aggregate WTP for the Chesapeake Bay boaters in Maryland was about $7.3 million per yr, total improvement gets a $146 million present value.
Needelman and Kealy (1995)	Lakes, NH	Site choice model and a trip frequency model	Water quality	Benefit (recreational value)	1. The mean seasonal benefits estimates were $1.4 for eliminating eutrophication from all sources ($1.33 for nonpoint source and $0.09 for point source) and the aggregate seasonal benefits were estimated at $1,163,000 for eliminating eutrophication from all sources ($1,105,000 for nonpoint source and $75,000 for point source).	1. The study also reported mean and aggregate seasonal benefits for eliminating bacteria, oil and grease, eutrophication problems, and all pollution from all sources. 2. The benefit estimates address exclusively swimming and day trips.
vNSTC (2000)	Gulf of Mexico, Mississippi-Atchafalay River Basin	Cost effective, simulation model (US Mathematic Programming Model in Agriculture)	Fish, shrimp, and marine ecosystem	Social cost for reduction/ restoration	1 For 20% edge-of-field N-loss reduction, the net cost was estimated at $0.8/kg ($0.36/pound), while restoring 5 million acres of wetland would have net cost of $1.00/kg ($0.45/pound).	1. The benefit to reduce N loadings to the Gulf was difficult to calculate because economic analysis failed to show direct effects on Gulf fisheries, which was a background study conducted by Diaz and Solow (1992).
Park et al. (2002)	Florida Keys, FL	CV	Water quality and health of coral reefs	WTP per trip expenses (recreational value)	1. The annual avg use value was $481.15 per person per snorkeling trip.	

Reference	Study Area	Method	Ecological Endpoint	Valuation Endpoint	Economic Value	Note
Poor et al. (2006)	St. Mary's River watershed, MA	HPVM	Ambient water quality	Avg housing price within the watershed (commercial value)	1. One unit (mg/L) increase in TSS resulted in a $1,086 loss on avg housing prices within the watershed. 2. One unit increase in the dissolved inorganic N resulted in a $17,642 loss on avg housing prices.	1. Total suspended solids and dissolved inorganic N included as indicators of ambient water quality.
Smith and Crowder (2005)	Neuse River, NC	Bio-economic model	Blue crab	Fish rent (commercial value)	1. A 30% reduction in N loadings over a 50–yr time period increases present value rents by 2.56 million, total catch by 12.4 million pounds, and total trips by 91,000.	1. Discounting rate was 2.5%.
Whitehead and Groothuis (1992)	Tar-Pamlico River, NC	CV	Catch rate	WTP (total value, use, and non-use value)	1. The mean WTP resulting from a 61% response rate was estimated at $25, which was bounded from above by a $35 use value, and from below a $21 nonuse value. 2. The aggregate benefits from water quality improvement estimated at $1.62 million each yr.	1. The study proposed a program in which farmers are required to use BMPs to improve the water quality of the Tar-Pamlico River so that anglers would catch twice as many fish per trip. 2. A mail survey was sent to 179 households in four counties in Tar-Pamlico River basin.
Various Effects						
Johnston et al. (Johnston, 2005)	U.S. and Canada	Meta-analysis	Catch rate	WTP (recreational use)	1. WTP per fish over the sample ranged from $.048 to $612.79, with a mean of $16.82	1. This study supports previous findings that WTP is systematically associated with resource, context, and angler attributes.

ANNEX F - 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 vapour (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 sulphur hexafluoride (SF_6), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs).

Gross primary production

The total carbon fixfixed by plant 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: $pH = {}^-\log_{10}[H^+]$, 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 fixfixation 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 exposureand 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.

ANNEX F - References

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