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A Study of the Diurnal and Nocturnal Measurement of Polychlorinated Dibenzo-p-Dioxins (CDDs) and Polychlorinated Dibenzofurans (CDFs) in Ambient Air

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Introduction

Soils have accumulated CDDs/CDFs both from air deposition and from direct application associated with a variety of human activities. If even limited quantities of these dioxins can re-enter the atmosphere, then soil could be an important reservoir source of dioxins. The purpose of this study is to explore the potential of soils to act as a reservoir source of CDDs/CDFs through volatilization to the atmosphere. The CDDs/CDFs are semi-volatile compounds with the lower chlorinated compounds having the highest vapor pressures. In the atmosphere, the partitioning of lower chlorinated dioxins have been observed to fluctuate between particle and vapor phases as a result of changes in ambient temperatures (Bidleman, 1988). It has not been demonstrated, however, whether this same exchange occurs between soil and the atmosphere at ambient temperatures. This project measures changes in concentrations of dioxins in the atmosphere and relates them to nocturnal/diurnal and seasonal temperature variations. Such fluctuations could serve as evidence of dioxin volatilization from soils

Experimental Methods

The overall strategy for this project was to conduct simultaneous 6, 12 and 24 hour sampling of CDDs/CDFs in air, and to compare congener-specific concentrations at two locations for patterns

associated with nocturnal, diurnal and seasonal time periods. The air samples were collected using PS-1 high-volume ambient samplers. The PUF and GFF samples were harvested and prepared for shipping to the laboratory in accordance with EPA Method TO9a (USEPA, 1997). The U.S. EPA Environmental Chemistry Laboratory provided the quantification of all samples. Concentrations were determined using a modification of the isotope dilution method, EPA Method 1613, revision B (USEPA, 1994) and with HRGC/HRMS. The method detection limit for 2,3,7,8-TCDD was approximately 0.01 pg/m³ for the air samples. Sampling stations were established at both a rural and urban site. The rural site is a remote location, with no known stationary air emissions sources of CDDs, CDFs within 5km of the sampling station and is near Arendtsville, Pennsylvania. The urban site is located 10 km NE of Washington, DC (an agricultural research station in Beltsville, MD), and is ringed by a major highway and densely populated suburban residential areas. At each location, the samples were collected over 28-day periods. Individual samplers were operated 6 days per week for four weeks under the following schedule:

One 24-hr sampler. Operated continuously 24 hrs/day.

Two twelve hour samplers. One sampler operated predominantly during the daylight hours (11 am to 11 pm) and the second sampler operated predominantly during the nighttime hours (11 pm to 11 am).

Four six hour samplers. Each sampler operated for 6 hours per day. Shift changes were scheduled for 11am, 5 pm, 11 pm and 5 am.

At one location, duplicate samplers were operated as a quality assurance procedure with the 24-hr sampler and one of the four 6-hr samplers. Field sampling was conducted during the warm season (August 19 to September 16) and a cold season (November 11 to December 9) in 1997.

Findings

The following observations are made from the statistical analyses of the day-night comparison of air concentrations of CDDs/CDFs for both the urban and rural sites.

1. For all the seasons and all sites combined, the diurnal air concentration was greater than the nocturnal air concentration for all the homologue groups, with the exception of OCDD and OCDF.
2. Only TCDF had a statistically significant diurnal difference (p-value < 0.05) between the diurnal and nocturnal air concentrations. However, TCDD, PCDF, and PCDD have p-values approaching 0.05 for this day/night difference.
3. With regard to OCDF and OCDD, the diurnal air concentrations are consistently less than the nocturnal air concentrations, with ratios ranging from 0.2 to 0.3. This difference approached but did not achieve statistical significance.
4. All sampling periods (Figure 1) showed good agreement with regard to total mass of each homologue present in ambient air. This suggests sample loss did not occur when changing from a single instrument operation for 24-hr sampling period to four instruments operating at 6-hr consecutive intervals.
5. For the lower chlorinated groups, the average air concentration of the 6-hour vapor phase sampling period were less than the average air concentration of the 12-hour or the 24-hour

sampling periods. This suggests that increasing the sample time transfers the sample from the GFF to the PUF (Figure 2).

6. The ratio of particle to vapor phase air concentration (Figure 3) is lower in the diurnal than nocturnal sampling periods for the lower molecular weight compounds (Tetra and Penta CDDs and CDFs). That is, there is an increase in the vapor phase air concentration in the daytime hours relative to the nighttime hours.
7. The particle to total air concentration ratio during winter sampling at Beltsville is displayed in Figure 3. In general, the higher chlorinated congeners (Hexa to Octa CDDs and CDFs) have particle/total concentration ratios that are essentially 1, indicating that there is little or no change between daytime and nighttime sampling.
8. The mass concentrations of CDDs/CDFs in ambient air between the diurnal and nocturnal sampling periods, at the urban location, are displayed in Figure 4. The more volatile compounds (TCDD, TCDF, PCDD, and PCDF) have higher mass concentrations during the daytime relative to nighttime. However, the higher chlorinated compounds do not display such a change.
9. All of these observations are consistent with the hypothesis that soils serve as a reservoir source to the atmosphere for lower chlorinated CDDs and CDFs.

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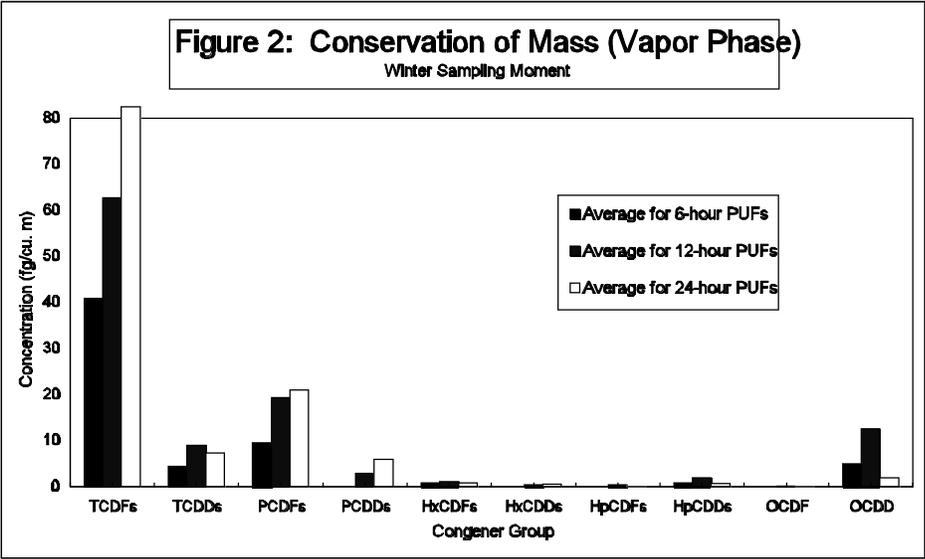
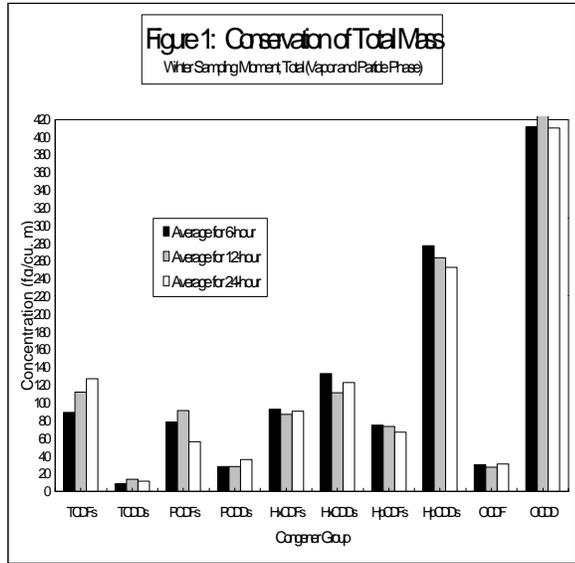
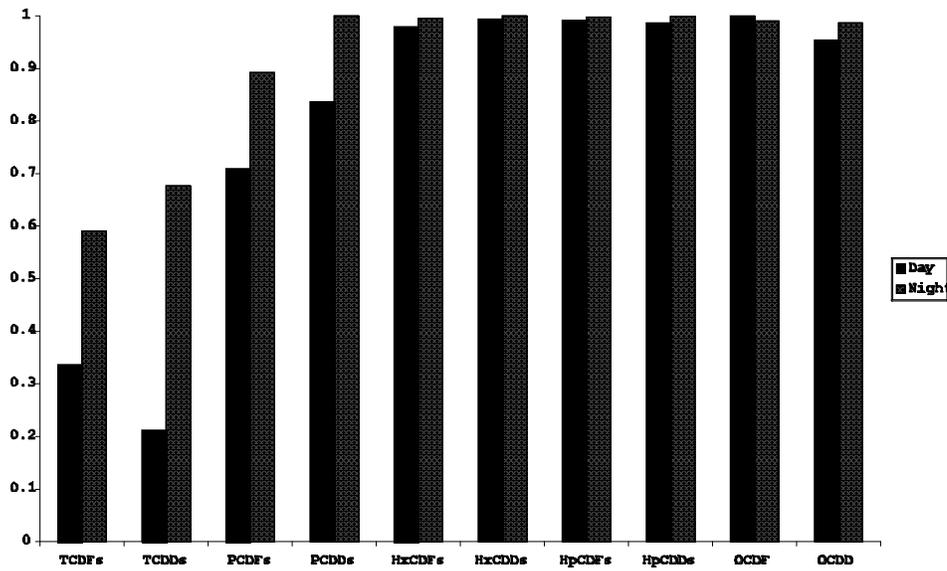


Figure 3: Ratio of Particle to Total Air Concentration



**Figure 4: Diurnal/Nocturnal Behavior in 12-Hour Samples
Winter Sampling Moment, Total (Vapor and Particle Phase)**

