



Project Summary

Atmospheric Transport and Deposition of Polychlorinated Dibenzo-*p*-Dioxins and Dibenzofurans

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Polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) are toxic compounds which are dispersed through the environment by atmospheric transport and deposition. It has been previously shown that there is a varying mixture of these compounds produced by combustion (the source of these compounds). Conversely, sedimentary sinks have been shown to have a constant pattern. Therefore, the goal of this project was to study PCDD/F in ambient air and rain samples (the transport media linking source to sink) in an effort to enhance our understanding of the physical/chemical parameters controlling the transformations which take place during atmospheric transport and deposition. Analytical methods included high-volume air sampling, wet-only rain sampling, column chromatographic cleanup, and an electron capture, negative ionization form of gas chromatographic mass spectrometry. Air and rain samples were divided into vapor-phase and particle-bound or dissolved and particle-bound fractions, respectively. The results showed that total PCDD/F concentrations in Bloomington, Indiana, had a geometric standard deviation range from 1.4 to 4.4 pg/m³ in air and from 63 to 220 pg/L in rainwater. The vapor-to-particle (V/P) ratio for individual congeners ranged

from 0.01 to 30. This ratio is controlled by the individual congener's vapor pressure and the ambient air temperature. Estimates of washout and the Henry's law constants were obtained using average ambient air and rain data. Total washout ranged from 10,000 to 90,000 for the tetra- through octa-homologues; Henry's law constants ranged from 1.3×10^{-5} to 8.9×10^{-8} atm⁻³/mole. Atmospheric concentrations were shown to be consistent with previously observed sediment fluxes. Principal component analysis was used to compare the observed air and rain data with literature data for sources and sinks. This analysis indicates that the observed homologue profiles bridge the gap between source and sink profiles. The underlying characteristics of individual PCDD/F congeners (such as vapor pressure and Henry's law constant) show trends with level of chlorination. When transport and depositional processes act on those trends, the varying mixture in the sources becomes the consistent pattern in the sinks.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).



Introduction

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/F) are ubiquitous in the environment and are of concern because of the high toxicity of certain congeners. PCDD/F are discharged daily into the environment in low concentrations by industrial and municipal waste incineration, car exhaust, and pulp and paper mill effluents. Chlorophenol-based herbicides and insecticides contain trace amounts of PCDD/F. Once PCDD/F are released into the environment, they become distributed throughout various environmental compartments, including the atmosphere, which transports PCDD/F long distances.

While PCDD/F are transported through the atmosphere, transformations may occur. The differences between homologue profiles of typical PCDD/F sources and sinks suggest that transformations of PCDD/F do, in fact, occur. For example, a typical homologue profile of PCDD/F produced by incineration, the major source of PCDD/F, shows a random distribution of PCDD/F. However, sediments, the ultimate sinks for PCDD/F, have a PCDD/F homologue profile that is enriched in octachlorodioxin. Also, the PCDD/F homologue profiles of air and rainwater show an enhancement of octachlorodioxin. Therefore, we conclude that PCDD/F undergo transformations while they reside in the atmosphere.

To understand the environmental transport and fate of PCDD/F, it was important to study the factors that control their atmospheric transport and deposition and to examine possible degradational pathways for PCDD/F. Specifically, the questions we addressed included: (a) What are PCDD/F concentrations in ambient air? (b) How are atmospheric PCDD/F partitioned between the vapor and particle phases? (c) Do concentrations of PCDD/F show seasonal variations? (d) Do PCDD/F concentrations change from rural to urban areas? (e) How are PCDD/F deposited from the atmosphere? To answer these questions, we performed a detailed, 3-year study of PCDD/F in the ambient air of Bloomington, Indiana.

Procedure

To accomplish our study goals, both air and rain samples were collected. Air

samples were collected using a high-volume air sampler equipped with a glass fiber filter; vapors were collected on polyurethane foam plugs. A total of 95 air samples was taken over a 3-year period. Subcooled-liquid vapor pressures for PCDD/F were measured using a gas chromatographic retention time correlation method; these vapor pressures were used in analyzing the air data. Fourteen rain samples were collected using a wet-only rain sampler. Particles in the rain sample were separated from dissolved PCDD/F using a glass fiber filter.

All samples were either Soxhlet- or liquid-liquid extracted and subjected to silica and alumina column chromatographic cleanup. All analyses were performed by electron capture, negative ionization, low resolution mass spectrometry. All PCDD/F were quantitated as congener classes.

Results and Discussion

Typical PCDD/F concentrations measured in Bloomington air ranged from 1-4 pg/m³. All air samples showed a predominance of octachlorodioxin. Total PCDD/F concentrations showed no seasonal variations, but the vapor-to-particle ratios changed. These ratios varied from 0.01 to 30 and were dependent on the compound's subcooled-liquid vapor pressure and the ambient temperature. Heats of adsorption for PCDD/F were calculated and ranged from 11-32 kcal/mole. Heats of adsorption increased with increasing level of chlorination, indicating that the vapor-to-particle ratio for more chlorinated PCDD/F has a greater temperature dependence than for the lesser chlorinated compounds. Total PCDD/F concentrations in Indianapolis, Indiana, an urban location, were found to be higher (tens of pg/m³) than total PCDD/F concentrations at Trout Lake, Wisconsin, a rural location (tenths of pg/m³). In addition, the homologue profile of PCDD/F in rural air was determined to be closer to that of sediments than was the homologue profile of urban air.

The homologue profiles of PCDD/F in rain were similar to those of sediments. Total concentrations of PCDD/F in rain were 10-84 pg/L in the dissolved-phase and 37-320 pg/L in the particle-phase. Using the accumulated air data, vapor scavenging ratios were calculated and ranged from 7.7×10^3 to 2.7×10^6 ; particle

scavenging ratios ranged from 1.2×10^4 to 7.2×10^4 . Particulate scavenging is the major wet removal process affecting PCDD/F, and total overall scavenging efficiency of PCDD/F increases with increasing level of chlorination. Depositional fluxes of PCDD/F were calculated, and dry deposition was determined to be five times more efficient than wet deposition.

Conclusions and Recommendations

Our data support the following scenario. A broad range of PCDD/F are introduced into the atmosphere by numerous sources, forming a uniform, urban, ambient air mixture. As the air mass moves away from the sources, it is diluted with cleaner air and starts to "age." Less chlorinated congeners are found to a greater extent in the vapor phase, and thus, they may undergo vapor-phase photodegradation; particle-phase photodegradation probably does not occur. This enhances the relative concentrations of the more chlorinated congeners. The particles, with their enhanced load of the more chlorinated congeners, are deposited by both wet and dry processes. Although the dry process dominates, the efficiency of the wet method improves for the more chlorinated congeners. Once in the water column, Henry's law constants predict greater vaporization of the less chlorinated congeners. This further enhances the relative proportion of the more chlorinated congeners that pass through the water column to the sediment. All of these processes favor a homologue profile enriched in the more chlorinated congeners. Therefore, octachlorodioxin is most predominant in the sediments. Our data suggest that only the most chlorinated PCDD/F congeners are environmentally persistent. This finding may be of interest to policymakers because these congeners tend to be the least toxic.

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Robert L. Harless is the EPA Project Officer (see below).

The complete report, entitled "Atmospheric Transport and Deposition of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans," (Order No. PB91- 144 667/AS; Cost: \$23.00, subject to change) will be available only from:

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