Concentrations of PCDD/F in Air and Particulate at a Rural Site in West Germany

M.S. McLachlan and O. Hutzinger

Chair of Ecological Chemistry and Geochemistry
University of Bayreuth, 8580 Bayreuth, FRG

Introduction

Food, primarily animal fat, is the main vector of human exposure to PCDD/F (Environment Ontario, 1988). This is due to the accumulation of these compounds in terrestrial food chains. The primary pathway of PCDD/F into the terrestrial environment is through the atmosphere. Most exposure models have assumed that deposition of atmospheric particles is the dominant phenomenon (Stevens and Gerbec, 1988). However, recent studies have shown that plant surfaces strongly accumulate lipophilic organic compounds present in the gas phase (Bacci et al., 1990). In order to evaluate the significance of these processes for PCDD/F entry into the terrestrial food chain, a knowledge of the atmospheric concentrations and air/particle distribution of PCDD/F during the growing season is necessary. In this paper we present the results of a sampling program conducted in the summer and early autumn of 1989 at a rural location in West Germany, in which 12 consecutive air samples of a weeks duration were analysed for PCDD/F.

Experimental

The air sampler developed at our institute over the last several years was employed (Umlauf et al., 1989). It uses a glass fibre filter to capture the air particles and XAD resin to trap the PCDD/F in the gas phase.

The sampling train consists of a brass ring supporting a brass sieve plate ($\varnothing = 7.5$ cm), two glass cartridges ($\varnothing = 6$ cm) with imbedded glass frits, and a bell-shaped glass fitting equiped with a vacuum meter and connected to a vacuum hose. The glass parts are flanged, and the four components are assembled using three silicon O-rings and three spring clamps. The two cartridges are filled with XAD and serve as the primary and backup traps for contaminants in the gas phase. A filter is placed on the sieve plate, and the pressure drop across it during sampling seals it against the supporting ring.

The sampler was set up on a meadow belonging to a government training farm southwest of Bayreuth (pop. 70,000). The prevailing winds are westerly, and there are no known major sources of PCDD/F such as municipal waste incinerators or highways in the area. The site was exposed, with the nearest building 30 m away.

The sampling train was installed so that the surface of the sieve plate was 1.8 m above the ground. A 50 cm x 50 cm stainless steel roof with 20 cm high sides was mounted 25 cm above the sieve plate to prevent rain from interfering with the sample. The sampling train was connected to a vacuum pump (Rietschle TLD 10) with an 8 m long 1" vacuum hose. A flow meter and a thermometer were installed at the pump outlet. Before sampling the system was checked for leaks by sealing the sampler entry and measuring the vacuum and flow.

Sampling began on July 12, 1989, and continued until October 4, 1989. With the exception of one 24 hour power failure (Sept. 12-13), sampling was continuous. The XAD traps were changed weekly, which corresponded to an average sampling volume of 1500 m^3. The filter was changed each morning at approximately 7:30 to minimize blow-off effects. The used filters were stored in glass petri dishes at -16°C until the end of the week.

The ambient temperature and the metering temperature were recorded periodically. It was found that the latter was on average 27°C higher, and all sampling volumes were corrected using this difference.

Organohalogen Compounds 1 441

Analysis

XAD-2 (Serva) was the absorbent selected for this study. The technical grade product was cleaned in 500 g batches. It was first rinsed with deionized water while stirring in a 200 L sieve until the rinse water was no longer milky. This was followed by rinsing with 1000 ml methanol (tech. grade), 500 ml acetone (tech. grade), 500 ml toluene (tech. grade) and 500 ml n-hexane (nanograde). The final step was a 24 hour soxhlet extraction in n-hexane:acetone (3:1, nanograde). The resin was stored in glass bottles in n-hexane.

Approximately 20 g of dry XAD was used in each sampler cartridge. The moist XAD was spooned into the cartridges and then rinsed with a small quantity of acetone to reduce the electrostatic adhesion. The contents of each cartridge were dried under a nitrogen stream prior to assembly for transport to the field.

Glass fibre filters were purchased from Schleicher & Schuell (No. 8, $\varnothing = 90$ mm). After analysis of 7 filters showed PCDD/F levels at the laboratory background level, it was decided to use the filters as delivered.

After sampling the particle fraction (7 filters) and the XAD (primary and backup) were soxhlet extracted for 48 hours in n-hexane:acetone (1:1). Prior to commencing the extraction a mixture of ^{13}C-labelled internal standards was added to the solvent including 200-600 pg of one isomer from each PCDD/F homologue group.

The extract was divided 4:1, and the smaller fraction was reserved for the analysis of other compounds. The PCDD/F fraction was first sent over an acid-silica/basic-silica column and subsequently isolated on an alox chromatographic column. The sample was evaporated to dryness and taken up in 20 μL toluene.

The PCDD/F were measured on a Finnigan MAT 8230 double focussing mass spectrometer equiped with a Gerstel cold injection system using an HP Ultra II column. A resolution of 2000 was selected.

Sampling System Tests

In an initial experiment the absorption efficiency and extractability of the sampling system was investigated. The sampling train was assembled in the normal fashion, except that glass wool was laid on top of the primary XAD trap. The labelled standard mixture of 10 PCDD/Fs normally used for the cleanup was then applied to the glass wool. The sampler was switched on and 1500 m^3 were collected over a week. Prior to extraction four other ^{13}C labelled PCDD/F isomers were added to the soxhlet solvent as clean-up standards.

The recoveries of the initial standard isomers in the different sample materials are given in Table 1. While one third of the Cl_8DD was still present on the glass wool, virtually all of the remaining standard had been carried onto the XAD trap by the air stream as intended. A small amount of the standard was found on the filter. Due to the proximity of the glass wool to the filter, it is possible that some of the standard was transfered between them during transport of the sampling train to the measuring station (The absorptive capacity of the filter is particularly high when it is new). The remainder of the standard was found on the first trap. No material was found on the back-up cartridge. The overall standard recoveries ranged from 93-116% with the exception of Cl_8DF. The low recovery in this case likely occured during the cleanup on the alox column which is susceptable to losses of this one isomer. These results indicated that the resin both effectively absorbed gaseous PCDD/F and that the subsequent extraction was quantitative. On the strength of these results it was decided to operate the sampler without a pre-applied internal standard mixture.

Following the first extraction in n-hexane/acetone, the samples above were subjected to a further 24 hour extraction in toluene. Neither the filter nor the XAD extracts yielded any detectable quantities of environmental PCDD/F. Thus it was concluded that the n-hexane/acetone mixture, which offered handling advantages over toluene, provided a complete extraction.

Substance	Filter	Glass Wool	Recovery (%) XAD #1	XAD #2	Total
2.3,7,8-Cl_4DD	8	< 1	99	< 1	107
1.2,3,7,8-Cl_5DD	4	< 1	96	< 1	100
1.2,3,6,7,8-Cl_6DD	3	2	92	< 1	97
1.2,3,4,6,7,8-Cl_7DD	3	14	76	< 1	93
Cl_8DD	1	34	66	< 1	101
2.3,7,8-Cl_4DF	12	< 1	104	< 1	116
1.2,3,7,8-Cl_5DF	4	< 1	95	< 1	99
1.2,3,4,7,8-Cl_6DF	3	< 1	98	< 1	101
1.2,3,4,6,7,8-Cl_7DF	3	9	88	< 1	100
Cl_8DF	1	17	57	< 1	75

Results of the Sampling Program

The back-up traps of the first five air samples were analysed, but no PCDD/F could be detected in any of them. It was concluded that breakthrough of the primary XAD trap was not a concern.

The average concentration of the PCDD/F over the measuring period was 1400 fg/m^3 ambient air. This is comparable with the levels measured by Buck and Kirschmer (1988) at two rural sites in northwestern Germany, but about 15 times less than the most contaminated of the 18 sites sampled by these authors. It lies at the lower end of the ranges of 610-79,000 fg/m^3 measured in Hamburg, FRG (Päpke et al., 1989), and 740-12,000 fg/m^3 measured in Bloomington, Indiana (Eitzer and Hites, 1989).

The average homologue distribution is illustrated in Figure 1. The majority of the Cl_4- and Cl_5-isomers and about 25% of the Cl_6-isomers were present in the gaseous phase, while the Cl_7- and Cl_8-isomers were almost totally particle bound. This is in agreement with the observations of Eitzer and Hites (1989).

Figure 1
Average Homologue Distribution

Figure 2
PCDD/F Concentrations vs Time
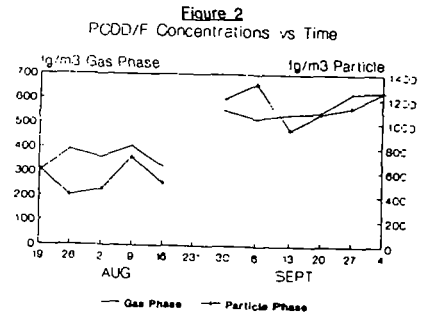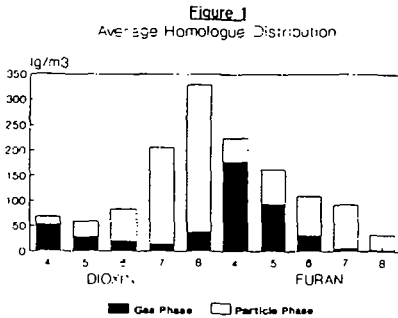
The concentrations of PCDD/F in the gaseous and particulate phases over time are plotted in Figure 2. In the first five weeks of the study the gas phase concentrations were quite constant. The PCDD/F measured could have represented the contribution from small mobile sources (automobiles) and more distant major sources. Alternatively, the air concentration could have reflected an equilibrium state between the atmosphere and the surrounding terrestrial environment. The average temperatures over the sampling periods were stable, ranging from 15.3-18.6 °C, and hence the air-earth equilibrium state would also have been stable.

This period was followed by a step increase in the PCDD/F level in late summer (the Aug. 23 sample has not yet been measured due to analytical difficulties), followed by a slight increasing tendency through the cooler weather of early fall. While one would normally expect a decrease in the air concentrations of ubiquitous lipophilic organic contaminants when the temperature decreases (Manchester-Neesvig and Andren, 1989), the opposite was observed. The step increase corresponded to a cold snap at the end of August, which signalled the beginning of the heating season. Coal and wood fired space heaters are still very common in this area, and high concentrations of PCDD/F have been found in their chimney soot (Thoma, 1988). We suspect that the increase in the PCDD/F levels are due to emissions contributed by these sources. The magnitude of the increase (factor 1.5, against the temperature trend) suggests that household heating is a significant PCDD/F source in this area.

The PCDD/F concentrations in the particle fraction are more variable. This is in large part due to the fluctuation in the particle load, which depends on many factors such as the stability of air masses, precipitation events, and particulate emissions. For instance, the first sampling period was very dry, while 11.4 cm of rain fell in the next two weeks. The fourth and fifth sampling periods were again relatively dry. This is reflected in the PCDD/F levels, which were significantly lower in weeks 2 and 3 than in weeks 1, 4 and 5. An increase in the PCDD/F levels at the end of August was also observed for the particle fraction. This supports the hypothesis presented above, namely that other PCDD/F sources came into play at this time.

Discussion

These observations have several implications for air-plant transfer of PCDD/F. The high proportion of the lower chlorinated PCDD/F in the gas phase indicate that gaseous diffusion could play an important role in the accumulation of these compounds in plants. The uniform gas phase concentrations in summer indicate that crops are subject to a relatively constant atmospheric PCDD/F fugacity during this period (on a weekly time scale). The increase in fugacity combined with a decrease in ambient temperature at the beginning of the heating season likely result in a significant upward shift in the plant equilibrium concentration. Thus plants such as corn which are harvested late could contain relatively high levels of PCDD/F. The dry deposition of particle bound material is higher during periods of dry stable weather. Rain events serve to cleanse the atmosphere of particulate. While there is then a considerable wet deposition flux to the plant, the rain also serves to rinse deposited matter from the leaves. The net impact of this process as well as the relative importance of gas phase diffusion and particulate deposition on plant accumulation of PCDD/F have yet to be clarified.

Acknowledgements

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