

A Global Mass Balance for Chlorinated Dioxins and Dibenzofurans

Louis P. Brzuzy and Ronald A. Hites

School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana, USA, 47405.

Introduction

Chlorinated dioxins and dibenzofurans (PCDD/F) are well-known environmental contaminants that have received prolonged attention by the scientific community and by environmental regulators. They enter the atmosphere primarily as byproducts from industrial combustion, waste incineration, metals production, and automobile emission.¹⁻⁵⁾ PCDD/F are semivolatile, hydrophobic compounds; hence they accumulate in organic rich media such as soils, sediments, and biota.

In spite of our knowledge about the environmental behavior of PCDD/F, a significant problem remains: Deposition from the atmosphere is estimated to be roughly 10-25 times higher than estimated inputs from known sources.^{6,7)} There are three explanations for this mass balance discrepancy: (a) The depositional fluxes are overestimated because of sampling bias. (b) The input estimates are low because

of unrecognized sources. (c) Both the sources are underestimated and the deposition is overestimated.

We believe that depositional fluxes are overestimated. Most PCDD/F measurements have been made in places of significant human industrial activity; 54% of such measurements are from northern and central Europe, 21% are from Canada, and 14% are from the United States east of the Mississippi River. Deposition estimates may only apply to these regions, and they may not be representative of parts of the world less impacted by industrial activity. Clearly, an expanded database of PCDD/F measurements from many geographical regions must be established before a realistic assessment of their mass balance can be made.

Measuring PCDD/F deposition directly is difficult, and there are few such measurements in the literature.^{8, 9)} Instead deposition is estimated from concentration measurements in other environmental matrices.¹⁰⁻¹⁴⁾ For example, concentrations of PCDD/F in air and precipitation (usually rain) are used to estimate dry and wet deposition, respectively. Atmospheric deposition can also be estimated from PCDD/F concentrations in lake sediments. A sediment-derived flux yields a sum of both wet and dry deposition.

Each of these techniques has limitations. Using air and rain to estimate deposition requires that a large number of measurements be made over an extended period of time (at least one year) to obtain an average deposition estimate. Sampling for shorter periods can result in substantial errors due to the climatic factors that influence air and precipitation concentrations. In addition, transporting, operating, and maintaining air and precipitation sampling equipment at remote locations is not practical. A major limitation in using lake sediments to estimate global deposition is that lakes are not uniformly distributed worldwide. Collecting undisturbed sediment cores from lakes in remote regions is also difficult and expensive.

In order to estimate fluxes on an expanded geographical scale, we need a technique that will overcome the limitations described above. Estimating flux from PCDD/F concentrations in soils may

be such a technique. Soils are uniformly distributed and they are relatively easy to collect and handle, but it is not clear if they are a conservative matrix for PCDD/F deposition. Therefore a series of studies were done to investigate using soils as a matrix to determine PCDD/F deposition. Measuring the concentration of PCDD/F in soil as a function of depth was undertaken in order to evaluate their mobility in the soil. Soils and lake sediments were collected in similar geographical areas or soils were collected in areas where lake sediment data were available in order to compare flux estimates. Field duplicates were collected and analyzed to determine the variability of the soil matrix itself and to test the reproducibility of our sample collection protocol.

Converting a soil concentration to a deposition estimate is straightforward. First, we assume all the PCDD/F are in the organic material in the soil, and the entire organic layer of the soil has been collected. Second, the surface area from which the soil was collected is known. Third, the mass of the entire sample collected has been determined. Once a soil concentration of PCDD/F has been measured, the deposition is calculated by the following equation:

$$\text{Flux (ng m}^{-2} \text{ y}^{-1}) = c \ m \ A^{-1} \ t^{-1}$$

where c is the PCDD/F concentration (ng g^{-1}), m is the mass of soil collected (g), A is the area of sample collected (m^2), and t is the time of accumulation (years). From previous studies using sediment cores we are confident that there was very little accumulation of PCDD/F in the environment before about 1935,¹⁰⁻¹¹⁾ so t is set at 60 years.

Results and Discussion

Soil core studies. Figure 1 shows the soil PCDD/F concentrations as a function of depth for three soil cores collected near Shingleton, Grayling, and Verona, Michigan, USA and for one core collected on the island of Guam. In all the Michigan cores, PCDD/F concentrations approach detection limits at about 25 cm in depth. The Guam core was only collected to a depth of 18 cm, and concentrations are near detection limits at this depth. Cumulative inventories of PCDD/F can be computed by multiplying the PCDD/F concentrations by the total weight of each core section. In all cases, greater than 80% of the total PCDD/F inventory is found in the upper 15 cm of soil.

Comparison of soil and lake sediment-derived fluxes. Soil-derived and lake sediment-derived flux estimates from four regions were compared. They were the northwest United States, the Michigan Lower Peninsula, the Michigan Upper Peninsula, USA, and the Lake District of the United Kingdom.

Table 1 shows the soil and sediment flux estimates for each region, their average, and the percent relative standard deviation (RSD) between the values. For all the regions the percent RSD is within our measurement error of $\pm 30\%$, with an

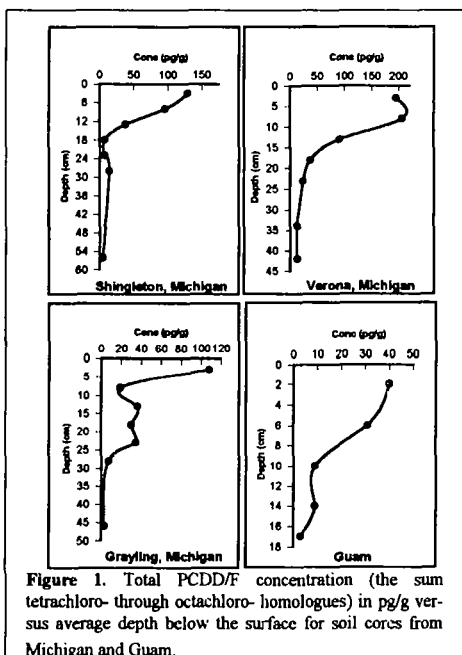


Figure 1. Total PCDD/F concentration (the sum tetrachloro- through octachloro- homologues) in pg/g versus average depth below the surface for soil cores from Michigan and Guam.

overall percent RSD of $\pm 19\%$. This good agreement indicates that soils and sediments produce comparable flux estimates for the same geographic region.

Comparison to fluxes calculated from air measurements. We can also compare our soil-derived fluxes to flux estimates made from air concentrations. Broman *et al.* reported an atmospheric depositional

flux of PCDD/F to the Baltic Sea of $38 \text{ ng/m}^2 \text{ y}^{12}$. A series of flux estimates we made from soils collected in the Baltic Republics yielded a geometric average flux for this area at about $28 \text{ ng/m}^2 \text{ y}$, which is in good agreement with Broman *et al.*

Field Duplicates. As an additional check on the reliability of using soils to estimate fluxes, we collected a series of field duplicates from various regions of the world, estimated fluxes from both samples, and compared the values. These field duplicates were collected either at the same time by the same individual, or at different times by different individuals. In this way we test both the collection protocol, and the variability in the soil matrix itself. Table 3 shows the results of the field duplicate estimates. Note that these samples represent several geographical regions worldwide. Relative standard deviations range from 2 to 54% with an average RSD of 25%. This is well within an acceptable range of error given the magnitude of the differences between emissions and deposition.

We conclude from these studies that soils can be used to reliably estimate atmospheric deposition of PCDD/F.

Global Mass Balance for PCDD/F. Soil samples were collected over a three year period from several areas of the world covering both the Northern and Southern Hemispheres. Over 300 samples were collected, and approximately 150 of these samples have been analyzed to date and fluxes have been estimated.

Atmospheric measurements of PCDD/F concentrations worldwide show that concentrations are within a fairly narrow range between approximately 0.5 and 35 pg/m^3 . This indicates that they are fairly well mixed in the ambient atmosphere. Soil and sediment concentration values show greater variability. Sediment concentrations from the Great Lakes and Siskiwit Lakes range from 23 to 1500 pg/g . Literature values for background soils concentrations range from about 25 to 10000 pg/g .

Since PCDD/F are removed from the atmosphere by dry and wet deposition, then climatic factors that influence deposition might be controlling their concentrations in environmental sinks. We

suggest that the deposition of PCDD/F from the atmosphere may exhibit some correlation to the various climatic zones of the world. If we consider these climatic zones as different depositional environments for atmospheric PCDD/F, we can estimate fluxes for each of these zones and revise or mass balance based on the flux and the geographical area of each zone.

Table 3 shows the major climatic zones of the world based on the

Table 1: Soil-derived and sediment-derived fluxes (in $\text{ng m}^{-2} \text{ y}^{-1}$) from similar geographical regions.

Region	Sediment	Soil	Average	RSD
Northern Rocky Mountains, USA	175	183	179	3%
Lower Michigan, USA	850	663	756	17%
Upper Michigan, USA	183	264	223	26%
Lake District, United Kingdom	1190	795	993	28%
Mean % RSD				19%

Table 2: Total PCDD/F flux, (in $\text{ng m}^{-2} \text{ y}^{-1}$), mean value, and relative standard deviation for field duplicates measurements.

Region	Dup 1	Dup 2	Mean	% RSD
Flaming Gorge, Wyoming, USA	2.1	1.9	2.0	7%
Ruby Lake, Nevada, USA	6.3	11.8	9.1	43%
Stockholm, Sweden	438	508	473	10%
Black Forest, Germany	227	551	389	59%
La Curina, Spain	70	89	80	17%
Ponta-de Pedroz-PA, Brazil	41	44	43	5%
St. Croix, Virgin Islands	14	16	15	9%
Eagle, Colorado, USA ^(a)	12	14	13	14%
Mean %RSD				21%

(a) collected by two different individuals approximately one year apart.

designation of Trewartha,¹⁵ the areas of those zones, the flux and the deposition of PCDD/F to those zones. Total deposition to these zones is about 6000 kg per year. However, this designation of climatic zones does not take into account the area of the global oceans. If we use a conservative depositional flux estimate of 15 ng/m² y, then the output rate to the global oceans is about another 6000 kg/yr. We estimate a total global deposition of PCDD/F at about 12,000 kg/yr.

Based on current emission factor data from known combustion sources,¹⁶ we estimate global emissions of PCDD/F at about 5000 kg per year, which is only about 2 times lower than our estimate of deposition.

We conclude from this study that the global deposition of PCDD/F has been overestimated in the past. When deposition is estimated based on geographical regions, the mass balance between emissions and outputs improves. This indicates that most of the major sources of PCDD/F are known, and that PCDD/F contamination to the environment can be limited by controlling the emissions from these sources.

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Table 3. Area of the major climatic zones of the world, PCDD/F flux to, and estimated deposition to those areas.

Climatic Zone	Area (10 ¹² m ²)	Flux (ng/m ² y)	Deposition (kg/yr)
Tropical Rainy	34.4	25	900
Dry	46.6	15	700
Humid Mesothermal NH	8.8	100	900
Humid Mesothermal SH	1.1	15	17
Humid Microthermal	16.4	70	1000
Polar	25.5	15	400
Undifferentiated Highlands	7.1	250	1800
Flux to Land			6000
Oceans	396.4	15	6000
Global Deposition			12000