PCDD/F CONCENTRATIONS IN REMOTE ATMOSPHERES

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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDD) and dibenzofurans (PCDF) are injected into the atmosphere as byproducts of various combustion processes. Although much is known about their environmental behavior, current estimates of PCDD/F deposition to the earth's surface exceed emission estimates by about a factor of four.[1] In this paper, we are suggesting that part of this lack of mass balance could be caused by a gross over-estimate of the deposition of PCDD/F to the world's oceans. Clearly, acquiring data on oceanic deposition will improve these mass balance estimates. The first step in determining these depositions is to measure atmospheric concentrations over the oceans. Thus, we measured the concentrations of PCDD/F in 21 air samples taken on the island of Bermuda. The average total PCDD/F atmospheric concentration in Bermuda was 110 ± 15 fg/m^3, which lead to a dry depositional rate to the world's oceans of 1,200 kg/yr and a wet depositional rate of 6,600 kg/yr. During the course of this project, another air sampling station was established at Barbados. The 10 air samples that have been analyzed from this location showed concentrations that were about a factor of two lower than at Bermuda. This result seems to indicate that flux calculations based on Bermuda data are biased high and that more representative sampling is needed.

INTRODUCTION

Despite our knowledge concerning the emission of PCDD/F into the environment, estimates of atmospheric outputs exceed atmospheric input estimates. Recent work in our laboratory focused on making a more accurate deposition estimate by using soil samples from worldwide sites including several remote locations.[1] These samples were analyzed, and depositional fluxes to land were calculated based on geographical and climatological considerations. From these data, the mass balance discrepancy was brought down to about a factor of four.

When calculating global depositional fluxes, it is important that one does not ignore the oceans which constitute 70% of the earth's surface. It is possible to calculate the flux of PCDD/F to the oceans using ambient air concentration data from representative remote islands where local contamination can be minimized. Our laboratory has established one such air sampling system in Bermuda, an island in the North Atlantic Ocean. This system uses a computer controlled air sampler that collects air only when it is coming in from the ocean. We have analyzed 21 air samples from Bermuda for PCDD/F during the 15 month course of this project. Using the average of these data, we calculated the depositional flux of PCDD/F to the oceans. A second ocean-air sampling system was established on the island of Barbados during the spring of 1996. Ten air samples covering a period of five months were analyzed from this location. These data allowed

us to investigate the possibility that PCDD/F air concentrations over the oceans vary with location. If the PCDD/F air concentrations varied significantly over the ocean, more representative sampling sites would be needed to adequately understand the behavior of PCDD/F in ocean air. For comparison, air samples were taken from five sites around the Great Lakes. These sites were selected by the Integrated Atmospheric Deposition Network (IADN) as strategic locations to study deposition of semivolatile compounds to the Great Lakes.

EXPERIMENTAL

Bermuda Sampling. A modified high volume air sampler was used to collect air samples from the top of a 23-meter tower on the west coast of Bermuda. Samples were collected using a technique known as "sectoring", where a computer controlled pump is only turned on when the wind speed is greater than 2 m/s and the wind direction is from over the ocean. Sampling media consisted of a glass fiber filter, for particulate collection, followed by a polyurethane foam plug (PUF), for gas-phase collection. Total sample volumes ranged from 2,000 and 8,000 m^3

Barbados Sampling. The sampling system employed in Barbados was similar to that used to collect samples in Bermuda. Wind sectoring was used in order to avoid local contamination, and air volumes for this site ranged from 5,000 and 7,000 m^3

Great Lakes Sampling. Samples were collected at the Great Lakes sites using a standard high volume air sampler. Two or three samples were taken from each of the Great Lakes locations during the summer of 1996. Uninterrupted 24 hour samples resulted in air volumes of about 800 m^3.

Extraction and Analysis. Samples were injected in the splitless mode on a Hewlett-Packard 5985B or 5989A gas chromatographic mass spectrometry system operating in the electron capture, negative ionization mode. Selected ion monitoring was used to enhance sensitivity, and a peak was only classified as a PCDD/F only if the mass intensities were in the correct, predicted isotopic ratios.[2]

PCDD/F were quantitated using the internal standard approach.[1] During each set of extractions either a procedural blank or a field blank was included. Typical blanks showed no detectable PCDD/F; however, occasionally contamination was found in the blanks. When this occurred, blank concentrations were subtracted from the sample, and sample peaks exhibiting lower than a 3:1 sample-to-blank ratio were not accepted. Recovery studies were conducted by spiking clean sampling media with a standard solution composed of a mixture of standard compounds representing each of the PCDD/F homologues. Typical recoveries ranged from 60-120%.

In order to study the breakthrough volume on PUF, two samples ranging from 4,000-5,000 m^3 of indoor laboratory air were collected. Indoor lab air was used so that the load of PCDD/F on the PUF would be large enough to determine whether breakthrough was occurring. The PUF was then cut in half, and the front and the back halves were extracted and analyzed separately. Analysis of the indoor air breakthrough samples showed that all of the PCDD/F were contained in the front half of the PUF. The back half of the PUF showed levels of PCDD/F on the order of the blank. Thus, we are confident that breakthrough did not occur with the sampling volumes used in this study.

RESULTS AND DISCUSSION

Bermuda Air Concentrations. Bermuda was selected because it is located far enough away from the large industrialized areas of North America and Europe to diffuse any of the direct inputs from these sources. Bermuda also has a unique climate, which is influenced by a pressure system known as the Bermuda high.[3] When this high-pressure system shifts southward, air comes to Bermuda from North America, and this typically occurs during the months of November through April. During the summer, when the Bermuda high shifts north, air parcels arriving at Bermuda originate primarily from Western Europe and North Africa. Thus, the atmosphere in Bermuda can show inputs, depending on the season, from two of the most industrialized continents in the world. In addition, the temperature in Bermuda is relatively constant, which eliminates the large concentration variations that might occur because of temperature fluctuations.

The concentrations of PCDD/F in 21 air samples taken from Bermuda between September, 1993 and November, 1994 were measured and blank corrected. PCDD/F concentrations ranged from 270 fg/m^3 in December of 1993 to 20 fg/m^3 in May of 1994.

Knowing the general flow climatology at Bermuda, we compared the concentration data by dividing it into two sets: (a) data acquired during the months of November through April when air arrives from the west, and (b) data acquired during the rest of the year when air arrives from the east. An average of 125 ± 20 fg/m^3 was found for air arriving from the west, and an average of 90 ± 15 fg/m^3 was found for air arriving from the east. The *t*-statistic for these data was 1.9, which indicates that these two averages were significantly different at the 85% confidence level. Thus, it is possible that the PCDD/F load in the Bermudan atmosphere is higher during the winter months when the air is originating from North America.

Figure 1 shows the average homologue profile for PCDD/F in the air sampled at Bermuda. Standard error bars are given for both particle- and gas-phase PCDD/F. These data show an average total PCDD/F air concentration of 110 ± 10 fg/m^3 in Bermuda. We also see a high fraction of PCDD/F in the vapor phase due to the warm temperatures and low particulate content in Bermuda air.[4,5]

Dry Deposition to the World's Oceans. The initial purpose of this study was to determine the depositional flux of PCDD/F to the oceans. Assuming that Bermuda is a representative location for making background atmospheric PCDD/F concentration measurements, it is possible to determine a dry particle flux to world's oceans by using the following equation:

$$F(dry) = C_p V_d \quad (1)$$

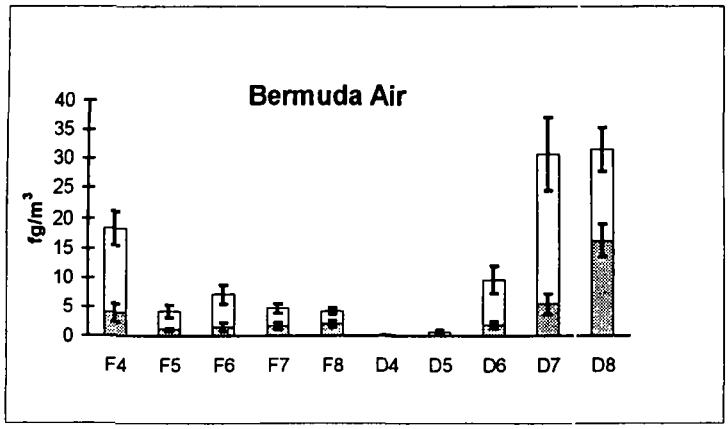

Figure 1. Homologue profile for the average PCDD/F concentrations in Bermuda air. The dark portions of the graph represent particle-phase concentrations, and the white portions represent vapor-phase concentrations. Standard error bars are given.

where *F(dry)* is the dry particle flux of PCDD/F to the oceans in fg/cm^2 yr, C_p is the PCDD/F concentration in the average atmospheric particle phase (35 fg/m^3 in this case), and V_d is the dry particle deposition velocity (0.3 cm/sec).[6] Total PCDD/F dry deposition to the world's oceans per year was calculated by multiplying *F(dry)* by the total surface area of the oceans and converting to kg/yr. In this experiment, the flux was found to be 320 fg/cm^2 yr. Using the total ocean surface area of 3.6 x 10^{14} m^2, we find that 1,200 ± 160 kg of PCDD/F are deposited to the world's oceans each year.

Wet Deposition to the World's Oceans. The calculation of a wet depositional flux is straightforward when rain concentration data are available. This flux is simply:

$$F(wet) = C_{rain} P \quad (2)$$

where C_{rain} is the concentration of PCDD/F in rain, and P is the rainfall rate. We know that the average rainfall rate to the surface of the earth, and to the oceans, is about 1 m/yr. Unfortunately, we do not know the concentration of PCDD/F in this rain; thus, we need to calculate it.

A parameter that is commonly used to describe the wet depositional process is known as the washout ratio (W). It is defined by the following equations:

$$W = C_{rain}/C_{air} \quad (3)$$
$$W = W_p f + W_v(1-f) \quad (4)$$

where *C* is the concentration of the compound in rain and air on a mass/volume basis; W_p and W_v are the washout ratios for the particle and vapor phases, respectively; and *f* is the fraction of PCDD/F bound to particles in the atmosphere. Values for W_p and W_v have been calculated using data from rain samples taken in Indianapolis, Indiana.[7] Using these data and our *f* values from Bermuda air, we can calculate *W*. Finally, by rearranging Equation 3, we can calculate the con-

centration of PCDD/F in rain and the wet depositional flux to the oceans. The gives a rate of 6,600 ± 900 kg/yr, which is about 5 times the dry depositional flux.

Barbados Sampling. Although Bermuda is representative of typical background ocean air, we must be sure that we have reliable data before we can extrapolate deposition estimates based on concentrations found in this one data point to 70% of the earth's surface. For this reason, we decided to expand our data set to include another island in the North Atlantic that has unique qualities of its own: the island of Barbados.

Sample to sample concentrations in Barbados varied from 10-80 fg/m^3 and did not show any observable trends. Figure 2 shows the average homologue profile observed at Barbados. Average PCDD/F concentrations found in Bermuda were about twice as high as those found in Barbados. Barbados is a remote island, and the nearest PCDD/F sources are on the African continent nearly 5,000 km to the west. Since Bermuda is both closer to and receives inputs from North America and Europe, it is expected to receive the more contaminated air. These results lead us to believe that Bermuda may exhibit consistently higher contamination than more remote islands, and therefore deposition estimates based on these concentrations will need to be revised after more representative sampling is conducted.

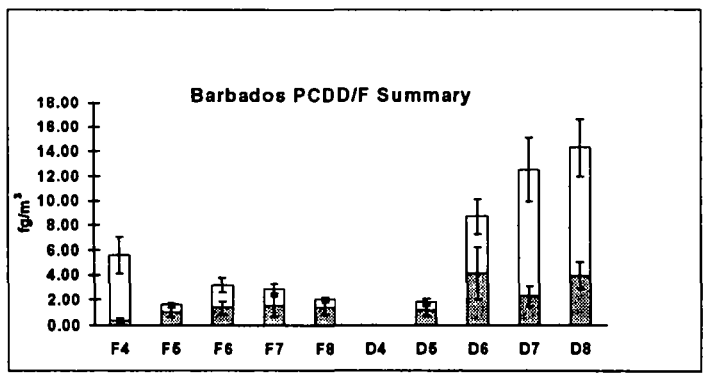

Figure 2. Average PCDD/F concentrations in Barbados air.

Great Lakes Sampling. It seemed likely that PCDD/F concentrations over the oceans would be much lower than anything previously sampled. We can see that this is true when we compare the concentrations found over the oceans with typical concentrations found elsewhere (see Table 1). Urban concentrations are 50-300 times higher than ocean air. Even Trout Lake, Wisconsin, which was one of the most remote locations sampled before this study; showed PCDD/F concentrations 4-8 times higher than concentrations measured at Bermuda or Barbados.

We have also collected air samples from five sites around the Great Lakes to provide a North American continental comparison of near-water PCDD/F air concentrations. Each of these sites is part of the Integrated Atmospheric Deposition Network (IADN). The purpose of IADN is to determine the loading of persistent toxic contaminants to the Great lakes; thus, these sampling sites have been strategically selected to provide these estimates. For our purposes, these sites

provide a qualitative comparison of near-water PCDD/F concentrations in remote as well as urban atmospheres.

Homologue profiles from these samples are shown in Figure 3, and total PCDD/F concentrations are given in Table 1. These data show that PCDD/F air concentrations at the remote locations of Brule River/Eagle Harbor and Sleeping Bear Dunes are on the order of 3-6 times higher than ocean air. Higher concentrations at IIT and Sturgeon Point are due to the influences from Chicago and Buffalo, respectively. It is interesting to note that these concentrations are much lower than the typical urban concentrations seen in Table 1. This may indicate that range of PCDD/F transport in air is relatively short.

The homologue patterns (see Figure 3) for the IADN sites are typical of PCDD/F in air, and they resemble those shown earlier for Bermuda and Barbados. PCDD/F in these samples are found to a greater extent in the particulate phase compared to ocean air due to a cooler climate and more suspended particles at the IADN sites. An exception is the Eagle Harbor/Brule River profile, which is the most remote IADN site. Its higher V/P ratio is likely a result of the lower particle content in the air compared to the other IADN sites.

ACKNOWLEDGMENTS

We like to thank Tom Snowden and Hal Maring of AEROCE for their assistance in setting up the air sampling stations in Bermuda and Barbados. We also thank Megan Mckay and Cornelius Shea, the technicians at these two sites. Ilora Basu and Matt O'Dell were especially helpful in organizing IADN sampling. Finally, I would like to thank the National Science Foundation (Grant No. BES9321274) for funding this work.

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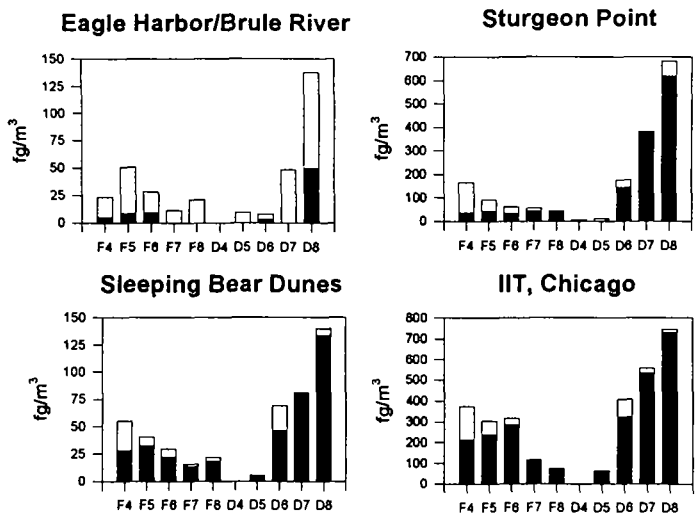

Figure 3. PCDD/F air concentrations at each of the IADN sites.

Table 1. Comparison of Bermuda air concentration measurements with those from prior studies.

Location	Total PCDF (fg/m^3)	Total PCDD (fg/m^3)
Kobe, Japan[7]	8,800	8,600
Indianapolis[4]	2,600	2,500
Bloomington[7]	780	1,100
Trout Lake, Wisconsin[7]	180	240
IIT, Chicago	1,200	1,800
Sturgeon Point	420	1,260
Sleeping Bear Dunes	160	260
Brule River/Eagle Harbor	130	200
Bermuda	40	70
Barbados	15	40