Polychlorinated Dibenzo-p-dioxins and Dibenzo furans in the Remote North Atlantic Marine Atmosphere

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We have developed a sampling strategy that allows us to determine femtogram/cubic meter concentrations of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/F) in remote marine atmospheres. Using this sampling strategy, a total of 37 air samples were taken during two extended sampling periods at Bermuda between September 1993 and August 1997. During this time, the average total PCDD/F concentrations at Bermuda decreased from 105 ± 30 to 35 ± 10 fg/m³, giving a half-life of about 2 years for these compounds in the remote marine atmosphere. PCDD/F concentrations during both sampling periods were somewhat higher in the winter when air parcels originated from North America. A second air-sampling station was established at Barbados where 22 air samples were taken between March 1996 and August 1997: an average total PCDD/F concentration at Barbados of 15 ± 7 fg/m³ was found. This value was not significantly different than the 27 ± 7 fg/m³ found at Bermuda during this time when air arrived from the east. This indicated that the remote marine background concentration for these compounds is currently on the order of 20 fg/m³. Using these background concentrations, the dry depositional rate of PCDD/F to the world’s oceans was estimated to be 200 ± 80 kg/year, and the wet depositional rate was estimated to be 900 ± 300 kg/year. This is a total deposition rate of about 1 t/year to the oceans as compared to our previous estimate of 12 t/year PCDD/F deposition from the atmosphere to the land.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) have never been manufactured as industrial products; rather, they are byproducts from the manufacturing of chemicals such as chlorinated phenols (1, 2) and from combustion processes such as municipal waste incineration (3–15). These combustion processes form complex mixtures of PCDD/F that, once injected into the atmosphere, can be transported far from their sources (16).

To improve mass balance estimates, recent work in our laboratory has focused on estimating PCDD/F deposition to land by measuring fluxes of PCDD/F to soil, samples of which were collected from several remote locations around the world (17). These measurements indicated that the total PCDD/F deposition to land was about 12 ± 2 t/year. Clearly, it was not possible to measure deposition to the world’s oceans from soil samples. In fact, because no long-term atmospheric sampling data over the oceans were available, it was not even possible to estimate PCDD/F deposition indirectly. Thus, we now seek to fill this gap by measuring PCDD/F in oceanic air. In addition to the mass balance issue, these data also will lead to a better understanding of the background levels of PCDD/F at locations far removed from sources.

Our laboratory has established an air-sampling system on the island of Barbados (see Figure 1) (18), an island in the North Atlantic Ocean. This system uses a computer-controlled air sampler to collect air only when it is coming to the island from the ocean. Using this system, we obtained and analyzed 21 air samples from Bermuda during our first sampling period, September 1993 to November 1994, and we obtained and analyzed 16 more samples during our second sampling period, June 1996 to August 1997. In parallel with the latter sampling campaign, we also operated a second ocean-air-sampling system on the island of Barbados (see Figure 1). During this time, we obtained and analyzed 22 air samples for PCDD/F from this location.

Using these data, we have investigated the possibility that the background levels of PCDD/F are decreasing. Additionally, we have determined the variability of PCDD/F concentrations with location and with air mass origination. Using background levels, we have also calculated the flux of PCDD/F to the oceans.

Experimental Section

Bermuda Sampling. Air samples were collected at Tudor Hill on the west coast of Bermuda. The Atmospheric Ocean Chemistry Experiment (AEROCE) operates a 23-m tower connected to a small laboratory facility located approximately 50 m inland (19). Samples were collected at this site using a modified high-volume air sampler (General Metal Works, model GS2310) that was mounted on the north side of the tower about 3 m from the top. The sample head was connected with aluminum tubing to a pump and flow meter at the bottom of the tower. The flow rate of the air sampling...
system was calibrated prior to the start of sampling in 1993 and then recalibrated in March 1998. Sample volumes, using both calibration curves, differed by less than 3%.

Polyurethane foam plugs (PUF; Olympic Products Corp.), 10 cm high × 10 cm in diameter, were precleaned by Soxhlet extraction (6 h) with a 50% acetone in hexane solution. All solvents used in this study were HPLC grade (OmniSolv, EM Science). The PUF plugs were then allowed to dry in a clean hood. PUF plugs were stored and shipped to and from Bermuda in a glass sleeve, which had been placed inside a sealed aluminum container. Glass fiber filters (GFF; Whatman, EPM2000), 20 cm long × 25 cm wide, were cleaned by heating them at 450 °C for 8 h to remove organic material adsorbed onto the filter. GFF media were wrapped in aluminum foil and sealed in Ziplock bags for shipping.

Sampling media were shipped overnight to the Bermuda Biological Station and placed in a freezer until they were used for sample collection. To eliminate local contamination, samples were collected using a technique known as “sectoring,” in which the computer-controlled pump is only activated when the wind speed is greater than 2 m/s and when the wind is coming from the sampler over the ocean (headings of 180°–330°, in this case). At the end of each sampling cycle, the sampling head was taken down from the tower to a clean room. The collected samples were removed from the sampling head, placed in their original packaging, and stored in a freezer until shipment. At this point, new PUF and GFF media were installed to begin another sampling cycle. A computer was used to monitor and record wind speed, wind direction, temperature, and rain data (19). Every 24 h, a site technician recorded ambient temperature, flow speed, wind direction, temperature, and rain data (19).

Samples were then extracted with hexane for 24 h. The extracts were rotary-evaporated, solvent-exchanged three times with 75 mL each of hexane, and reduced to a volume of approximately 200 μL for alumina cleanup.

A 5 × 95-mm Pasteur pipet was dry loaded to a height of 6.5 cm with neutral alumina (Brockman Activity I) that had been activated by heating at 160 °C for 24 h and topped with 0.5 cm of anhydrous sodium sulfate. The 200-μL extract from the silica cleanup was loaded onto the column eluted with 8 mL each of hexane, 2% dichloromethane in hexane, and 40% dichloromethane in hexane. The PCDD/F were contained in the 40% fraction, so this fraction was reduced to a volume of less than 25 μL under a gentle stream of nitrogen before analysis by gas chromatographic mass spectrometry.

Samples were injected (splitless) into a Hewlett-Packard 5979A gas chromatographic mass spectrometer operating in the electron capture, negative ionization mode. Chromatographic separation was achieved using a 30-m, DB-5MS, capillary column (250-μm i.d., 0.25-μm film thickness; J&W Scientific, Folsom, CA). Helium was used as the carrier gas. Temperature programming was as follows: isothermal for 2 min at 40 °C, 30 °C/min to 210 °C, 2 °C/min to 280 °C, isothermal for 10 min. The pressure of the reagent gas, methane, in the mass spectrometer’s ion source was maintained at 0.43 Torr. The ion source temperature was held at 175 °C. Two ions from each homologue group were monitored using selected ion monitoring to enhance sensitivity, and a peak was only classified as a PCDD/F if its mass spectral intensities were in the correct, predicted isotopic ratio (16).

PCDD/F were quantitated using the internal standard approach. A standard solution composed of the five carbon-13-labeled standards and at least one standard compound representing each of the PCDD/F homologues was used to develop response factors relative to the five carbon-13 standards used in the spiking of the sample. Each PCDD/F was grouped in its respective homologue class, and the total peak areas of these homologues were used for response factor calculations. Responses of each homologue were calculated relative to the internal standard containing the same number of chlorine substitutions. These calculations were applied to each of the samples and the blanks. Samples were blank-corrected, and the total volume of air that had been sampled divided into the resulting value.

Quality Control in Sample Preparation. During each set of extractions, either a procedural blank or a field blank was included. A procedural blank consisted of a Soxhlet thimble loaded only with glass wool. Field blanks were sample media that had only passive contact with the sampling system as described earlier. Field and procedural blanks were extracted, cleaned, and analyzed in the same manner as real samples. Typical blanks were clean compared to real samples. Little or no PCDD/F were detected in the blanks about 50% of the time. The other half of the time, procedural blanks, GFF field blanks, and PUF field blanks contained averages of 50 ± 40, 70 ± 60, and 60 ± 50 pg, respectively (N = 5, 6, and 5). These values are not significantly different from one another; therefore, we assumed that when contamination...
was found, it occurred primarily during the extraction and clean up processes. OCDD was the most prevalent contaminant in the blanks, followed by a few TCDF congeners. These two homologue groups comprised >50% of the total PCDD/F found in the contaminated blanks. Occasionally, other PCDD/F congeners were detected in the blanks at or above the levels found in air samples; however, most blanks contained PCDD/F at levels that were at least 10 times lower than those of the samples. When a PCDD/F congener was detected in the blank for a set of extractions, its total mass was calculated and compared to mass in the air samples from that set. If the sample-to-blank ratio for that congener was less than 3 to 1, then that congener was considered to be not detected and given a value of zero.

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. These samples were extracted and cleaned in the same manner as real samples; however, they were not spiked with the isotopically labeled internal standard until just before injection into the mass spectrometer. Typical recoveries ranged from 60% to 120%.

To study the breakthrough volume of PCDD/F on PUF, two samples of indoor laboratory air, ranging from 3500 to 5500 m³, were collected. Because indoor laboratory air was used, the load of PCDD/F on the PUF was 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. Air temperatures in Bermuda and Barbados stay relatively constant year around. Daily records taken during sampling showed that the temperature never exceeded 30°C and rarely dipped below 20°C at these two locations. Thus, we performed this breakthrough study using indoor air at 25°C.

Results and Discussion

Breakthrough. Due to the large atmospheric sample volumes used at Bermuda and Barbados, it was necessary to test for analyte breakthrough. The collection efficiency of PUF is directly related to the volatility of the compounds being retained by the sample matrix and dependent on temperature (20). Eitzer and Hites found that breakthrough of PCDD/F did not occur when sampling ambient air in Indiana using air volumes as high as 2400 m³ (21). However, PUF at Bermuda and Barbados needed to handle much higher volumes. Therefore, it was necessary to repeat the breakthrough experiment with higher sampling volumes.

Two PUF plugs, through which laboratory air volumes of 3500 and 5500 m³ (at 25°C) had been drawn, were cut in half and analyzed for PCDD/F. The front half of these PUF contained 7 and 10 ng of ΣPCDD/F, respectively. The back half of these PUF contained 0.1 ng of ΣPCDD/F, which was similar to the blank. Thus, we did not find any breakthrough for PCDD/F at these sample volumes, and we can be reasonably confident that breakthrough will not occur until at least 10,000 m³ of air is sampled. Furthermore, breakthrough volumes are lower when sampling air containing a high level of compounds that can be scavenged by PUF.

FIGURE 2. Total PCDD/F concentrations at Bermuda (A) and Barbados (B) versus median sampling date in relative Julian days (day 1 was Jan 1, 1993). The stated errors are standard errors.

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Because our laboratory has higher contamination levels of PCDD/F compared to Bermuda and Barbados, it was necessary to test for breakthrough study using indoor air at 25°C.

For our first sampling period, 21 air samples were taken at Bermuda between September 1993 and November 1994. For our second sampling period, 16 air samples were taken between June 1996 and August 1997. The PCDD/F concentrations in each of these samples were measured and blank-corrected. Total PCDD/F concentrations for these samples are plotted versus sampling date in Figure 2. PCDD/F concentrations for the first sampling period ranged from 220 fg/m³ in October 1994 to 20 fg/m³ in May 1994 with a total average PCDD/F concentration of 105 ± 30 fg/m³. (In all cases, the given errors are standard errors.) These values decreased during the second sampling period to between 10 fg/m³ in July 1996 and 70 fg/m³ in October 1996, with a total average PCDD/F concentration of 35 ± 10 fg/m³.

Knowing the general flow climatology at Bermuda, we decided to compare the concentration data by dividing the data into two sets: (a) data acquired during the months of October through April (winter) when the air parcels arrive from the west and (b) data acquired during the rest of the year when the air parcels arrive from the east. For the first sampling period, an average of 120 ± 15 fg/m³ (N = 13) was found for air arriving from the west, and an average of 90 ± 15 fg/m³ (N = 8) was found for air arriving from the east. For the second sampling period, the average PCDD/F concen-
concentration in air from Germany and England. A concentration for air arriving from the west was 45 ± 7 fg/m³ (N = 8), and an average of 27 ± 7 fg/m³ (N = 8) was found for air arriving from the east. Thus, during these two sampling periods, higher (by about 50%) concentrations of PCDD/F were found when air parcels originated from west of the Bermuda (that is, from North America) during the winter. These results are strong evidence that contamination from local sources is virtually eliminated by our use of sectored air sampling. If contamination were occurring, we would expect higher PCDD/F concentrations from air parcels that originated east of Bermuda, since the air sampler is on the western end of the island.

Previous work on air samples collected in Indiana indicated that total PCDD/F concentrations in the atmosphere are not seasonally dependent or temperature-dependent (21). However, data from Germany and Austria have shown higher concentrations of total PCDD/F during winter months (24, 25). Contributions from home heating and stagnant winter air were the primary explanations for this phenomenon. It is possible that PCDD/F emissions to the North Atlantic atmosphere are higher during the winter months, giving rise to the higher background contamination that we see during this period. However, since we do not see higher PCDD/F in air during the winter months in Barbados, a more likely explanation for our finding stems from the relative proximity of PCDD/F sources to Bermuda during the winter months. During the winter, the air is coming to Bermuda from North America, which is closer than Africa and Europe, where the air is from during the rest of the year. During the winter, contaminants in the air arriving at Bermuda would have had less time to diffuse, deposit, or react than during the rest of the year.

Comparing the 1993–1994 Bermuda samples to the 1996–1997 samples taken in Bermuda, we see that the average PCDD/F concentrations for these two periods decreased from 105 ± 30 to 35 ± 10 fg/m³, a decrease of about 70%. Using these two concentrations, we calculate a half-life for PCDD/F in air at Bermuda of about 2 years.

The literature provides only two studies of PCDD/F concentrations in air sampled at the same location over an extended time. In the first such study, PCDD/F was measured at four locations in Germany in 1987–1988 and again in 1993–1994 (see Table 1). These data suggest a half-life of about 3–6 years (25). In the second such study, Coleman et al. (26) reported PCDD/F concentrations in London and Manchester for each of the years from 1991 to 1994. They found decreasing trends at both of these locations. These data suggest half-lives of PCDD/F in air of about 1–2 years in England. Clearly, both studies show that PCDD/F concentrations in air have been decreasing relatively quickly over the past several years, and our observations at Bermuda indicate that North Atlantic concentrations are decreasing at about the same rate.

We know that PCDD/F are formed through various combustion processes and that the ubiquitous environmental contamination by these compounds is a result of atmospheric transport from these sources (16). Thus, a decrease in atmospheric PCDD/F concentrations should be mirrored by decreases in other environmental sinks. Indeed, this is the case. Sediment samples have shown that PCDD/F concentrations have decreased by at least 50% since the mid-1970s (16, 27). In addition, PCDD/F studies in cow’s milk, vegetation, and various biota have all shown substantial decreases of PCDD/F concentrations over the last 20 years (28, 29).

Barbados Air Concentrations. To examine the possibility that atmospheric PCDD/F contamination near Bermuda was biased high compared to even more remote oceanic locations, we selected the island of Barbados as another sampling location. Like Bermuda, Barbados has few temperature variations; however, the air arriving at Barbados almost always originates east of Barbados, making the closest PCDD/F sources nearly 5000 km away.

We collected and analyzed 22 air samples from Barbados between March 1996 and August 1997. Total PCDD/F concentrations in these samples ranged from 1 to 47 fg/m³ (see Figure 2). The average total PCDD/F concentration during this sampling period was 15 ± 7 fg/m³. This value is not statistically different from the PCDD/F concentrations found during the summer in Bermuda when wind was arriving from the east (27 ± 7 fg/m³), indicating that the nominal background concentrations for these compounds over the North Atlantic is on the order of 20 fg/m³.

At this point we should note some of the difficulties that occur when working with such low concentration levels. To decrease our detection limits for individual PCDD/F congeners, air volumes of at least 5000 m³ for each PUF/GFF pair were taken in Bermuda and Barbados during the 1996–1997 period. Many of the samples analyzed during this time period represented the composite of two or three PUF/GFF pairs so that they represented volumes as high as 20 000 m³ and a sampling period of about 1 month. This process brought our detection limits down to as low as 0.1 fg/m³ for certain congeners depending on the actual sample volume, and it allowed us to obtain concentration information that would have otherwise been impossible. However, even after applying this method of analysis, the concentrations of individual congeners that were at or below detection limits and/or blank levels varied from sample to sample. This meant that it was rare for an individual sample to contain all or even most of the PCDD/F homologues. It was only when we looked at the entire sampling period as a whole or seasonally that we were able to obtain meaningful information that could be considered representative of the particular site. Unfortunately, extended sampling durations prevented data interpretation based on the use of trajectory analysis or other meteorological trends that occur on a time scale that is faster than seasonal. For these reasons, we did not try to overinterpret individual data points, but we looked at these data as representative of the background concentrations over the seasons and years they represent.

Homologue Profiles. The PCDD/F homologue profiles for each of the sampling periods are shown in Figure 3. These profiles are all very similar, showing the relatively high amounts of the lower chlorinated furans and the higher chlorinated dioxins that are typically seen in air. It is also interesting to note that, although urban air samples give homologue profiles that are dominated by particle-phase PCDD/F, a significant portion of the total PCDD/F in these samples can be found in the gas phase (21). Even octachlorodioxin, which is found almost entirely associated with particles in urban air, is found to a great extent in the gas phase for these samples. There are three reasons for this observation: First, the temperature at each of these locations is typically 25–30 °C, and these compounds partition to a greater extent into the vapor phase at higher temperatures (21). Second, the particles that are collected on the GFF at

<table>
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<tr>
<th>ref</th>
<th>C0</th>
<th>C</th>
<th>Δt (years)</th>
<th>t1/2 (years)</th>
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<tr>
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<td>25</td>
<td>200</td>
<td>76</td>
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<tr>
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<td>25</td>
<td>330</td>
<td>120</td>
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<td>470</td>
<td>86</td>
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<tr>
<td>London, England</td>
<td>26</td>
<td>200</td>
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*C0 is the average initial concentration, and C is the average concentration Δt years later.*
these sites are primarily sea salt and Saharan dust (19); consequently, the organic carbon content of these samples is low compared to urban samples. Third, air parcels typically arrive in Bermuda and Barbados after travelling over the North Atlantic for several days. This time may allow many of the larger particles that might contain PCDD/F to settle out of the atmosphere before they arrive at our sites.

The air-sampling system used in this study operationally defines PCDD/F collected on the GFF as particle phase and PCDD/F collected on the PUF as vapor phase. Thus, PCDD/F defined as vapor phase in this study may partially represent compounds bound to particles smaller than 0.1 \( \mu \text{m} \). In addition, adsorption and desorption of PCDD/F from the GFF may occur with this type of sampling system, which would further tend to confuse the exact definition of particle and vapor phases. Luckily, these artifacts are negligible for PCBs and PAHs (30), and we will assume these artifacts are negligible for PCDD/F as well.

We plotted the vapor/particle ratio (log \( \frac{V}{P} \)), for each of the average homologue profiles, versus the subcooled liquid vapor pressure (log \( p_{Lo} \)) in Figure 4. We have segregated the data by site and by time. Since the tetra- and penta-chlorodioxins were only detected in a few samples, they were not plotted. The correlation coefficients for both of the Bermuda data sets are significant at the 95% confidence level, and both plots show increasing vapor-to-particle partitioning with higher vapor pressures, as expected. It is interesting that these two plots show slopes that are much less than unity, which is predicted by theory (32). This difference could be due to the large sample volumes that we employ, combined with the averaging that was necessary with these data. Additionally, theory may not apply in the same manner to the types of particles that exist over the ocean. It is also interesting to note that research conducted over the Great Lakes showed less than predicted slopes for PCBs and PAHs when cleaner air was sampled (30). The Barbados regression line (see Figure 4, bottom) is also significant, but only at the 90% confidence level. This lower level of correlation is likely due to the low levels of PCDD/F found in Barbados. Individual samples were often at or below our detection limits, thus introducing a higher relative standard deviation for these data.

Deposition to the World’s Oceans. If we assume that the concentrations that we found in Barbados, and during the summer in Bermuda, are representative of global background levels, it is possible to determine a dry particle flux to the world’s oceans by using the following:

\[
F_{\text{(dry)}} = C_p V_d
\]

where \( F_{\text{(dry)}} \) is the dry particle flux of PCDD/F to the oceans in fg/cm\(^2\)-year, \( C_p \) is the average PCDD/F concentration in the atmospheric particle phase (5 ± 2 fg/m\(^3\) in this case), and \( V_d \) is the dry particle deposition velocity (0.3 cm/s; 33). Total PCDD/F dry deposition to the world’s oceans per year was calculated by multiplying \( F_{\text{(dry)}} \) by the total surface area of the oceans and converting to kilograms/year. In this calculation, the flux was found to be 50 ± 20 fg/cm\(^2\)-year. Using the total ocean surface area of 3.6 \( \times 10^8 \) m\(^2\), we estimate that 200 ± 80 kg of PCDD/F are deposited to the world’s oceans each year by dry deposition.

The calculation of a wet depositional flux is straightforward when rain concentration data are available. This flux is simply:

\[
F_{\text{(wet)}} = C_{\text{rain}} P
\]

where \( C_{\text{rain}} \) is the concentration of PCDD/F in rain and \( P \) is the rainfall rate. We know that the average rainfall rate to the oceans is about 1 m/year (34). However, because we do not know the concentration of PCDD/F in rain, we will need to calculate it.
A parameter that is commonly used to describe the wet depositional process is known as the washout ratio (W), which is defined by the following:

\[ W = C_{\text{rain}} / C_{\text{air}} = W_p \phi + W_g (1 - \phi) \] (3)

where \( C_{\text{rain}} \) and \( C_{\text{air}} \) are the concentrations of the compound in rain and air on a mass/volume basis, \( W_p \) and \( W_g \) are the washout ratios for the particle and gas phases, respectively, and \( \phi \) is the fractional PCDD/F bound to particles in the atmosphere. \( W_p \) and \( W_g \) values for each of the PCDD/F homologues were obtained using data from rain samples taken in Indianapolis, Indiana (35). Using the concentration data from Barbados to obtain \( \phi \), we calculated \( W \) for each homologue. Finally, by rearranging eq 3, we calculated the concentration of PCDD/F in rain over the oceans. Using this concentration in eq 2 and the area of the oceans, we found a wet depositional rate to the oceans of 900 ± 300 kg/yr. Thus, according to this calculation, wet deposition dominates dry deposition as the major depositional pathway of PCDD/F from the air to the oceans.

We recognize that these wet depositional calculations may be biased high because washout ratios from an urban setting were used. Ideally, washout ratios should be calculated using rain and air data from the same time and place, since both of these values are dependent on temperature and on the types of particles being scavenged. We would have needed to sample approximately 100 L of ocean rain in order to obtain a detectable amount of PCDD/F. Unfortunately, a sampling system capable of collecting these large volumes of rain was unavailable.

If we combine these wet and dry deposition calculations, we obtain a total PCDD/F flow of 1 ± 0.4 t/year to the world’s oceans. Brzusy et al. (17) estimated PCDD/F deposition to land to be on the order of 12 t/year. Thus, our calculation indicates that less than 10% of the yearly deposition of PCDD/F to the surface of the earth is to the oceans. This may seem surprising since the world’s oceans constitute 70% of the earth’s surface and we consider that the sources of PCDD/F to the atmosphere and the depositional processes involved with these compounds. Major sources of PCDD/F, such as municipal waste incineration, form compounds that are primarily associated with large particles that have short atmospheric lifetimes (36). Consequently, PCDD/F from these sources will deposit relatively close to their point of emission, and it is unlikely that PCDD/F from these sources will travel to remote areas such as the oceans. Additionally, the filtering effect of forests and vegetation is an important removal pathway for PCDD/F (37); obviously this is a pathway that can only occur over land. These two processes could combine to remove a major portion of the yearly inputs of PCDD/F before they can reach remote ocean atmospheres.

We recognize that air-water exchange (deposition or vaporization) with the oceans may be an important process; however, there are no reliable remote ocean–water concentration measurements. Therefore, these types of calculations are not yet feasible. For now, we must assume that the air over the oceans and the underlying water are in equilibrium until further research in this area is conducted.

Acknowledgments

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Supporting Information Available

Table of concentrations (4 pages). Ordering information can be found on any current masthead page.

Literature Cited


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