Evidence for Dynamic Air—Water Exchange of PCDD/Fs: A Study in the Raritan Bay/Hudson River Estuary

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The first detailed evidence for dynamic air—water exchange of polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) is presented. Samples of air (340–380 m³) and water (33–60 L) were taken simultaneously during July 1998 at two sites in the lower Hudson River Estuary, NY. The atmospheric gas and particulate phases and the aqueous dissolved and particulate phases were analyzed for di- to octa-PCDD/Fs. All the homologue groups were routinely detected by HRGC-HRMS, with detection limits for the homologue groups ~1 pg/sample. Cl₂DDs, OCDD, and Cl₃DFs were the most abundant homologues in the water, and the Cl₄DDs were the most abundant in the air (4.3–7.6 pg/m³). The Cl₂DD/Fs and Cl₃DD/Fs were 25–53% and 78–99% associated with the water particulate phase, respectively. The likelihood of sampling artifacts influencing the apparent dissolved/particulate partitioning of the higher chlorinated congeners is discussed. Water concentrations were constant over the sampling period, while atmospheric concentrations varied with air mass origin. The fugacity ratios between the dissolved phase in water and the gas phase in air were usually >1, implying a net volatilization flux. Evidence for outgassing of the lower chlorinated homologues, obtained by the simultaneous measurement of air over adjacent land and water, provided further support for the outgassing of the lower chlorinated homologues from the water body.

Introduction

Polychlorinated dibenzo-p-dioxins and furans (PCDD/Fs) are ubiquitous contaminants that are released into the environment as byproducts of incomplete combustion or as chemical impurities. Atmospheric transport is believed to be the major pathway for their distribution away from sources (1, 2). Municipal, medical, and chemical waste incinerators were identified as the major sources of PCDD/Fs to the contemporary environment and have since been regulated with regard to their emissions or shut down in many industrialized countries, such as Germany, the U.K., and the U.S.A. (3–5). As these major sources have been reduced, diffuse sources of PCDD/Fs, such as domestic burning and vehicular traffic, have become proportionally more important to the current emissions to the atmosphere (6). Unclear as yet is the extent to which previously deposited PCDD/Fs present in the key environmental compartments of soils and sediments are now subject to recycling into the atmosphere. Discussions have also centered around possible natural sources of PCDD/Fs (e.g. refs 7–10). The role of air—water diffusive exchange in large aquatic systems as a source or sink for PCDD/Fs has not been investigated to our knowledge, although this process is important for other semivolatile compounds, such as polychlorinated biphenyls (PCBs) (11–15), polynuclear aromatic hydrocarbons (PAHs) (15, 16), and nonylphenols (17). Hence the extent to which current ambient air levels are maintained by air-surface exchange is clearly of considerable significance.

The lower Hudson River Estuary and Raritan Bay (HRE/RB) near the New York—New Jersey area in the U.S. (NY—NJ) receives freshwater input mainly from the Hudson, Hackensack, and Passaic rivers; it remains a brackish water body (see Figure 1). The concentrations of many contaminants in samples from within the HRE have consistently been among the highest measured at U.S. sites (18). Dioxin contamination of the Newark Bay, associated with discharges from the Lister Avenue Superfund site, occurred in the 1960/1970s and stimulated measurements of 2,3,7,8-TCDD in animals and sediments of the area (e.g. refs 19 and 20). The importance of wastewater treatment discharges, combined sewer overflows, and atmospheric deposition to the overall contamination of the HRE/RB have been discussed (21–24). Recent studies comparing concentrations of OCDD and 2,3,7,8-TCDD in sediments found a strong decrease over time with levels of 2,3,7,8-TCDD in the mid-1980s lower by a factor of 3–15 compared to the mid-1960s (25).

This study of air—water exchange in the HRE/RB establishes fugacity ratios for PCDD/Fs across a water surface. The sampling site was chosen because of its contamination history, proximity to major urban and industrial centers, and the support offered by an in-place air toxics network (26). Simultaneous air and water samples were analyzed for a full range of PCDD/Fs, including Cl₂₃DD/Fs. The magnitude of Henry’s Law constants (1–7 Pa·m³/mol) and octanol—water coefficients (log Kow 4.9–6.4) for Cl₂₃DD/Fs makes them susceptible to water—air exchange (27, 28), similar to the 1–4 Cl-substituted PCBs for which air—water exchange
TABLE 1. Summary of Four Sampling Events in the Raritan Bay/Hudson River Estuary

<table>
<thead>
<tr>
<th>Date</th>
<th>Position</th>
<th>Surface Temp (°C)</th>
<th>Mean SPM (mg/L)</th>
<th>Mean DOC (mg/L)</th>
<th>Mean Temp (°C)</th>
<th>Amount SPM (mg)</th>
<th>Air Temp (°C)</th>
<th>Air Mass Origin</th>
<th>Air Vol (m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>July 5</td>
<td>40°36.308N, 74°05.802W</td>
<td>20.3–22.6</td>
<td>5.59</td>
<td>4.04</td>
<td>39.3</td>
<td>218</td>
<td>21.7–27.0</td>
<td>Northwest (Canada)</td>
<td>384</td>
</tr>
<tr>
<td>July 6</td>
<td>40°30.396N, 74°05.771W</td>
<td>19.9–22.0</td>
<td>6.40</td>
<td>4.41</td>
<td>33</td>
<td>211</td>
<td>20.3–24.9</td>
<td>Northeast (Canada)</td>
<td>342</td>
</tr>
<tr>
<td>July 7</td>
<td>40°30.550N, 74°05.720W</td>
<td>21.4–22.9</td>
<td>4.17</td>
<td>3.71</td>
<td>51</td>
<td>213</td>
<td>20.9–24.8</td>
<td>local (still air)</td>
<td>352</td>
</tr>
<tr>
<td>July 10</td>
<td>40°39.174N, 74°02.327W</td>
<td>20.0–20.3</td>
<td>7.87</td>
<td>4.90</td>
<td>60</td>
<td>472</td>
<td>23.6–26.1</td>
<td>Northwest (Canada)</td>
<td>370</td>
</tr>
</tbody>
</table>

Total, 40–60 L water were sampled, yielding between 200 and 400 mg of suspended particulate matter. GFFs were precombusted at 400 °C for 4 h, and XAD was cleaned by successive 24 h extractions with methanol, acetonite, hexane, acetonite, and methanol in a Soxhlet and rinsed several times with deionized water. Additional details can be found in Zhang et al. (14).

Additional water samples were taken for total suspended particulate matter (SPM), dissolved organic carbon (DOC), and particulate organic carbon (POC) determination. SPM samples were analyzed for inorganic and organic carbon and nitrogen (CHN). Analysis of DOC and CHN were performed by Analytical Services of the Chesapeake Biological Laboratory, University of Maryland. Air and water temperature, wind speed, and direction were recorded throughout the sampling interval (see Table 1). Further meteorological information was obtained from Newark airport, ca. 20 km from the coast.

Additional air samples (consecutive 12-h day–night) were taken at two land-based sites during the sampling campaign, while the over-water samples were being collected. The sites were chosen to represent the coastal environment and the urban NJ–NY area. Sandy Hook is located on a barrier spit separating Raritan Bay from the Atlantic Ocean, and the “Liberty Science Center” (LSC) is in the heart of the metropolitan NY and NJ industrial region (see Figure 1).

**Analytical Procedure** For the air samples the GFFs were extracted with toluene and the PUFs in DCM in a Soxhlet apparatus. The extracts were reduced to ~1 mL, transferred into gas chromatography (GC) vials, and transported to the Lancaster University. They were cleaned-up on a mixed silica-column and fractionated on a basic alumina column. Water GFFs were extracted in acetonite–hexane (1:1) followed by toluene, while the XAD resins were extracted in acetonite–hexane (1:1) and partitioned against water. The extracts were cleaned-up as described above. 13C12-labeled PCDD/Fs standards (Promochem, Welwyn Garden City, AL7 1EP, U.K.) were added to the XAD-resin before deployment in the water; GFFs and PUFs were spiked prior to extraction in the laboratory. Field and laboratory blanks were routinely included (one in 10 each) and treated as the other samples.

All samples were analyzed by HRGC/HRMS on a Micro Mass Autospec Ultima, operated at a resolving power of ~10 000 (for details see ref 32). Homologue groups were quantified relative to a full suite of 13C12-labeled congeners on a 30m, DB-5 column; the 2,3,7,8-substituted congeners were separated and quantified on a 60 m SP-2331 column. Mean recoveries of the various 13C12-labeled congeners were generally 50–100% but were 50–65% in the first three XAD-samples. At detection limits (~0.1–0.6 pg/sample), only trace amounts of Cl7/8DDs were detected in the blanks. Method detection limits for the homologue groups, expressed as the mean blank level plus three times its standard deviation, were generally 1–2 pg/sample but...
higher for OCDD (13 pg/sample) and Cl$_2$DFs (6 and 60 pg/sample).

### Results and Discussion

#### Water Samples
In the SPM of the Raritan Bay water samples (ca. 210–470 mg/sample), virtually all PCDD/F homologue groups and 2,3,7,8-substituted congeners were measured at above detection limits with good reproducibility \((n = 3)\). Average standard deviations were \(\pm 15\%\) for the homologue groups and \(\pm 17\%\) for the individual 2,3,7,8-substituted congeners. Concentrations ranged from 20 pg/g SPM for Cl$_5$DDs to \(> 3000\) pg/g SPM for Cl$_4$DDs (see Table 2). Expressed in pg/L, concentrations in the solid-phase ranged from 0.08 to 0.15 pg/L for Cl$_5$DDs up to 15–24 pg/L for Cl$_2$DDs. Concentrations in the apparent dissolved phase were lower, ranging from 40 fg/L for Cl$_5$DDs to greater than 40 000 fg/L for Cl$_2$DDs. Figure 2 shows the mean concentrations (in pg/L) for the Raritan Bay samples, with error bars representing single standard deviations. The apparent dissolved and particulate phases were dominated by Cl$_2$DDs. Both phases had similar concentrations for the lower chlorinated CDFs, while the higher chlorinated PCDD/Fs were found mainly in the particulate phase.

#### Toxic Equivalents (ΣTEQ) in the Water Samples
The concept of ΣTEQ was derived for the biological/biochemical responses to 2,3,7,8-TCDD and similar pollutants. It is now common practice to calculate the ΣTEQ in abiotic matrices to compare the contamination of samples. Concentrations of ΣTEQ (I-TEQ, ref 33) associated with the SPM ranged from 20 to 33 pg/g SPM (85–160 fg ΣTEQ/L). Contributions to the ΣTEQ in the SPM were dominated by 2,3,7,8-TCDD and 2,3,4,7,8-PeCDF, both accounting for \(\sim 20\%\). Interestingly, similar concentrations were reported for a sediment sample (in pg/g dry weight) from the main stem of the Hudson River taken in 1996 (site 8 in ref 25, courtesy of R. Bopp). 2,3,4,7,8-PeCDF was more abundant in the sediment (43 pg/g compared to 12 pg/g SPM in the water), while all the other 2,3,7,8-substituted congeners agreed well, with an average 24% difference between the two samples (34). Concentrations in the apparent dissolved phase were lower with 17–25 fg ΣTEQ/L. 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, and, when detected, 2,3,7,8-TCDD were the major contributors to the ΣTEQ in the apparent dissolved phase.

There are limited data with which to compare PCDD/F concentrations in water (see Table 3). Homologue and ΣTEQ concentrations (per g SPM) were similar to those found in the River Elbe and the Fraser River. Concentrations of homologue groups in the dissolved phase exceeded those for the Elbe by factors of \(\sim 2–10\) for the homologue groups, while the ΣTEQ was similar (35, 36). Concentration per g SPM were higher in the Hudson River by a factor of \(\sim 2\), with concentrations of PCDD/Fs in the apparent dissolved phase being higher in the Raritan Bay by \(\sim 2\) times (see Table 2). Enhanced analytical sensitivity enabled us to work with substantially smaller sample volumes and mass of particulate matter than many others (see Table 3).

#### Apparent Distribution in the Water Column
The average percent particulate phase followed the sequence (\(\%\)PCDDs/\(\%\)PCDFs) Cl$_2$DFs (26) < Cl$_4$DD/Fs (38/47) < Cl$_2$DD/Fs (52/62) < Cl$_3$DD/Fs (80/76) < Cl$_4$DD/Fs (75/84) < Cl$_5$DD/Fs (79/86) < Cl$_2$DD/Fs (83/96) < OCDD/F (90/96). For the same number of chlorines per group, PCDDs were generally less associated with the particulate fraction, with the exception of Cl$_2$DD/Fs.

#### Air Samples
Atmospheric concentrations of PCDD/Fs varied strongly over the course of the sampling campaign,
with $\Sigma Cl_1 - 3DFs$ occurring at 12, 17, 6.1, and 12 pg/m$^3$ ($\Sigma TEQ$ 4.0, 21, 2.1, and 6.1 fg/m$^3$), for the samples taken on July 5, 6, 7, and 10, respectively (see Table 4). The first and last sample were characterized by northwesterly winds from the heart of the urban-industrial area. The highest atmospheric concentrations derived from the NY metropolitan region (NE) on July 6, and the lowest concentration occurred under calm atmospheric conditions. Over-water ambient PCDD/F concentrations were dominated by the gaseous $Cl_2DDs$ (4.2–7.6 pg/m$^3$) and $Cl_1-3DFs$ (0.2–2.8 pg/m$^3$). Concentrations of $Cl_2DDs$ were consistently high, regardless of the wind direction, whereas $Cl_1-3DFs$ varied strongly with wind direction (see Table 4). Compared to measurements in the U.K. and Ireland, the over-water samples in this study showed slightly higher concentrations of $Cl_3DFs$, but $Cl_2DDs$ were higher by a factor of $\approx 50$ (32). $Cl_2DD/Fs$ were low for samples taken close to a major urban/industrial conglomerate; similar concentrations have been reported for rural areas in the

![FIGURE 2. Mean PCDD/F homologue group concentrations in the particle and apparent dissolved phase in the Raritan Bay (in pg/L; note: broken y-axis).](image)

### TABLE 4: Atmospheric PCDD/F Concentrations and Field Blank (F.Bl.) Data in the Gaseous and the Particle-Bound Phase over Water on the Raritan Bay and the Hudson River (fg/m$^3$)

<table>
<thead>
<tr>
<th>homologue groups</th>
<th>Raritan Bay</th>
<th>Hudson</th>
<th>F.Bl.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>July 5</td>
<td>July 6</td>
<td>July 7</td>
</tr>
<tr>
<td>$Cl_1DFs$</td>
<td>1100</td>
<td>2000</td>
<td>750</td>
</tr>
<tr>
<td>$Cl_2DFs$</td>
<td>2000</td>
<td>2800</td>
<td>620</td>
</tr>
<tr>
<td>$Cl_3DFs$</td>
<td>120</td>
<td>1400</td>
<td>57</td>
</tr>
<tr>
<td>$Cl_4DFs$</td>
<td>42</td>
<td>370</td>
<td>25</td>
</tr>
<tr>
<td>$Cl_5DFs$</td>
<td>13</td>
<td>50</td>
<td>7.8</td>
</tr>
<tr>
<td>$Cl_6DFs$</td>
<td>0.5</td>
<td>1.8</td>
<td>0.5</td>
</tr>
<tr>
<td>OCDF</td>
<td>1.2</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>$Cl_2DDs$</td>
<td>7300</td>
<td>6500</td>
<td>4200</td>
</tr>
<tr>
<td>$Cl_3DDs$</td>
<td>90</td>
<td>230</td>
<td>33</td>
</tr>
<tr>
<td>$Cl_4DDs$</td>
<td>27</td>
<td>300</td>
<td>12</td>
</tr>
<tr>
<td>$Cl_5DDs$</td>
<td>5.4</td>
<td>140</td>
<td>2.7</td>
</tr>
<tr>
<td>$Cl_6DDs$</td>
<td>2.0</td>
<td>23</td>
<td>1.0</td>
</tr>
<tr>
<td>$Cl_7DDs$</td>
<td>2.1</td>
<td>2.0</td>
<td>2.3</td>
</tr>
<tr>
<td>OCDD</td>
<td>8.5</td>
<td>10</td>
<td>9.3</td>
</tr>
<tr>
<td>$\Sigma TEQ$</td>
<td>1.0</td>
<td>13</td>
<td>0.4</td>
</tr>
</tbody>
</table>

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Ambient Gas-Particle Distribution. Cl$_1$-DD/Fs were <30% particle-associated, with Cl$_6$-DD/Fs >50% in the particle phase, consistent with other distribution studies reported for such warm periods (38) (%PCDDs/PCDFs): Cl$_1$DD/Fs (2) ~ Cl$_2$DD/Fs (2/2) < Cl$_3$DD/Fs (7/3) < Cl$_5$DD/Fs (15/10) < Cl$_4$DD/Fs (39/23) < Cl$_6$DD/Fs (77/58) < Cl$_7$DD/Fs (91/94) < OCDD/F (85/80). In contrast to their distribution in the water column, atmospheric PCDD/Fs were predominantly in the gaseous phase, and PCDDs had a higher particulate-bound fraction than PCDFs. The ambient ΣTEQ was evenly distributed between the two phases, with 35–61% occurring in the particle-bound fraction.

Partitioning in the Water Column. The calculation of net air–water exchange ratios for PCDD/Fs requires water concentrations in the truly dissolved phase. Differences between truly and “apparent” dissolved phase may be due to the passage of colloids dissolved organic carbon through the GFF onto the XAD-column. Measurements of PCDD/Fs in the dissolved phase are also complicated because of the low levels of PCDD/Fs in water, in general, and low water solubilities, especially of the higher chlorinated PCDD/Fs. The ambient ΣTEQ was evenly distributed between the two phases, with 35–61% occurring in the particle-bound fraction.

Based on reported log K$_{ow}$ values and our measured concentrations of [POC], [DOC], and apparent dissolved PCDD/F concentrations, the theoretical partitioning onto DOC, POC, and truly dissolved phase may be calculated. Thus c$_{gw}$ and c$_{doc}$ were calculated and compared to c$_{appdiss}$. There was good agreement between the predicted and measured apparent dissolved phase for the higher chlorinated PCDD/Fs, while c$_{appdiss}$ were lower than predicted for Cl$_1$-DFs by a factor of ~2–3 (see Figure 3). Cl$_2$-DDs showed good agreement with the predicted concentrations, while Cl$_3$-DDs had a ~50% higher concentration than predicted in c$_{appdiss}$. Clearly, the linear relationship between K$_{doc}$ and K$_{ow}$ derived in eq 4 does not satisfactorily explain the partitioning of PCDD/Fs into the water column, as the calculated partitioning to DOC accounted for only ~50% of the Cl$_1$-DDs detected in the c$_{appdiss}$. In particular, the high concentrations of OCDD in c$_{appdiss}$ point toward a sampling artifact.

Air–Water Exchange. The direction of net air–water exchange may be determined by calculating dissolved/gas-phase fugacity ratios

$$\text{fw/ta} = \alpha = \frac{C_{\text{diss}}}{C_{\text{gas}}^*} + R_T$$

where $\alpha$ is the fugacity ratio, $\text{fw}$ and $\text{ta}$ are the fugacities in water and air, respectively, $H$ is Henry's law constant (HLC), $T$ the temperature (°C), and $R$ the universal gas constant. Equilibrium between the atmospheric and dissolved phase yields $\alpha = 1$. Net volatilization occurs when $\alpha > 1$ and deposition (i.e., absorption) when $\alpha < 1$. HLCs at 298 K were used since air and water temperatures during the sampling campaign ranged only from 20 to 27 °C.

With few exceptions the calculated fugacity ratio values were $> 1$, indicating net volatilization of PCDD/Fs from the HRE/RB (Figure 4). The exception was the second sampling event, characterized by high ambient air concentrations, with $\text{fw}/\text{ta}$ ratios of $< 1$ for the Cl$_1$-DDs and Cl$_4$-DDs. Fugacity ratios were highest for Cl$_6$-DDs and OCDF with $\alpha > 5$–10, while Cl$_2$-DD/Fs had $\alpha$ of up to 5–7.

Uncertainties in the calculation of the fugacity ratios stem from (i) the analytical precision in determining $C_{\text{gas}}$ and $C_{\text{sm}}$; (ii) the operational separation of the dissolved phase; and (iii) the uncertainty in HLC values and their temperature dependency. Our analytical precision was ~15% SD for the three water samples taken in Raritan Bay and comparable to what we presented earlier for five air samples taken concurrently (SD of ~10% for 700 m$^3$ each, ref 32). We employed the appropriate HLC-values reported by Govers and Krop (28). However, there is on average a factor of 2 difference between values by Govers and Krop (28) and those recommended by Mackay et al. (27); the dominating quantifiable uncertainty for $\alpha$ stems from the HLCs. Hence, the uncertainty in the fugacity ratios will be on the order of $\sim 2$, as indicated by a gray shaded background in Figure 4. However, most fugacity ratios exceeded that uncertainty range, indicating net water-to-air exchange.

Evidence of the real importance of air-to-water exchange was the dominance of Cl$_1$DDs in both the apparent dissolved and gas phases and the high concentrations of lower chlorinated furans (and by direct evidence discussed in the next section). This is consistent with the types of chemical profiles observed for PCBs (10, 14) and PAHs (15). We note, however, that PCDD/Fs bound to particles undergo a net,
Evidence for Net Outgassing from Measured Changes in the Gas Phase over the Raritan Bay. The fugacity ratios presented are strong evidence that lower chlorinated PCDD/Fs undergo a net gas-phase flux out of the water column during the study period. Further direct evidence comes from the air measurement program. Three sampling events are of interest in this discussion, taken on the day (0800–2000 h), night (2000–0800 h), and day (0800–2000 h) of July 10 and 11, 1999. With winds from the NW the air mass passed consecutively over the urban site, the lower Bay and the coastal site. We were therefore able to measure the changes in PCDD/F concentrations prior to (at LSC) and after crossing over the Bay (Sandy Hook). Back-trajectories showed the air mass moving to New York from the northwest and local wind readings were consistent at ~340°. The distance between the two land sites is ca. 30 km, which combined with wind speeds of 7.5, 5.0, and 7.6 m/s on the different events gave an average travel time of 1.1–1.6 h for the air masses between the sites. Comparing the PCDD/F profiles at the two sites relative to air–water exchange is valid if the following assumptions hold: (i) A well mixed air mass arrived at the urban sampling site. PCDD/F concentrations at the LSC site depended on the wind direction, suggestive that the site was not surrounded by major sources. (ii) PCDD/F air emissions were dominated locally by air–water exchange. Ambient air concentrations were generally low for the vicinity to the urban/industrial NY–NJ area, suggesting that even though additional sources cannot be ruled out they were minimal.

FIGURE 3. Difference between apparent dissolved PCDD/Fs and calculated truly dissolved and [DOC]-bound PCDD/Fs. A negative Δ value means that the calculated distribution accounted for more PCDD/Fs in the truly dissolved phase and [DOC]-bound than was detected in the apparent dissolved phase. A positive balance, e.g., for OCDD, means that the calculated distribution of PCDD/Fs in the truly dissolved phase and [DOC]-bound accounted for roughly half the amount of OCDD detected in the apparent dissolved phase.

FIGURE 4. Water–air fugacity ratios for PCDD/F homologue groups for the Raritan Bay/Hudson River Estuary (gray shaded background indicates estimated uncertainty range for equilibrium, i.e., ±100%).
The signal received at the coastal site reflects the air mass derived from the urban/industrial site following transport across the water. The coastal site was affected by a diurnal sea-breeze as a function of the relative temperature changes of land and ocean during the course of a day. This may have the effect of diluting the signal coming from the NY/NJ area with air from the ocean. Degradation/depletion reactions in the gas phase were negligible compared to the air-water exchange.

What would we expect to observe if our assumptions were true? It is hypothesized that (i) PCDD/Fs in the gas phase of the air mass would reflect the air-water exchange with the lower Bay, with increasing concentrations for the lower chlorinated congeners; (ii) total suspended particle (TSP) concentrations in the air would decrease due to deposition over the Bay; and (iii) particle-bound PCDD/F concentrations per g TSP would not be likely to vary significantly, depending on the kinetics of exchange from a modified gas phase.

The observed changes, expressed as the ratio of the concentrations measured at the coastal site over the urban/industrial site, are shown in Figure 5. Whereas most gas-phase PCDD/Fs ratios are > 1, the predominantly particle-bound PCDD/Fs did not change much (ratios of ~1). The uncertainty in the ratios (±40%) is included as a gray shaded background which arises from the analytical uncertainty in determining ambient PCDD/Fs (estimated as a SD = 25%).

The key observations are as follows: (i) Highest Cl2DD concentrations were found over water. This, together with the fugacity ratios, indicates net volatilization from the water surface. (ii) On the three events on July 10/11, gas-phase concentrations of Cl2-DFs and Cl2-DDs increased from the industrial to the coastal site. The Cl2-DDs on the night of July 10, and Cl3-DDs and Cl3-DFs on the day of July 11, were exceptions to this (see Figure 5). (iii) TSP concentrations decreased from the urban to the coastal site, probably due to deposition of particles during transport across the Bay (data not shown). (iv) Concentrations of PCDD/ Fs per g TSP increased for Cl2-2DD/Fs for the day time sample on July 10; for the other homologue groups and the other samples concentrations per g TSP remained roughly constant (see Figure 5). A priori the change in PCDD/F concentrations on particles in equilibrium with the gas depended on kinetic constraints. Based on our observations, wind speeds of 5–7.5 m/s were not sufficient to create significant marine aerosol, so that only deposition should have affected the TSP (see also ref 44). If, however, there was sufficient enrichment of PCDD/Fs in the gas phase during the passage over the water, there would be a tendency for PCDD/Fs to partition onto particles to reach gas-particle equilibrium. (v) The Cl2-DDs were the homologue group with the greatest increases in the gas phase and the only homologue group with increasing concentrations in the particulate phase per g TSP for the three samples.

Together this provides support for the hypothesis that Raritan Bay acted as a net source of lower chlorinated PCDD/Fs to the local atmosphere during this sampling period. Particularly strong evidence stems from (i) the Cl2-DDs being most abundant over the water itself; (ii) the calculated fugacity ratios; (iii) the observed changes in the gas phase; and (iv) increasing concentrations on particles. Fugacities and observed changes point toward evaporation of a full range of PCDFs and many PCDDs as well, similar to the story for PCBs (13–15). However, uncertainties remain over the effective partitioning of PCDD/Fs in the water column and...
therefore about the “real” fugacities for mainly the higher chlorinated PCDD/Fs. If our observed changes in the gas phase reflect a true picture, then evaporation is a key process influencing PCDD/Fs up to Cl\textsubscript{12}DD/F homologues. This is of course only part of the story, as dry and wet particle deposition of PCDD/Fs into the Bay also occurs. What is unknown at present is the origin of the PCDD/Fs in the water. Key possibilities are remobilization of PCDD/Fs from sediments or discharges into the Hudson–Raritan Bay area. Similarly the cause of the elevated concentrations of Cl\textsubscript{2}DDs in the water and the atmosphere is unknown.

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