

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-CDD/Fs. All the homologue groups were routinely detected by HRGC-HRMS, with detection limits for the homologue groups ~1 pg/sample. Cl₂DDs, OCDD, and Cl₂DFs were the most abundant homologues in the water, and the Cl₂DDs were the most abundant in the air (4.3–7.6 pg/m³). The Cl₂DD/Fs and Cl_{7/8}DD/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

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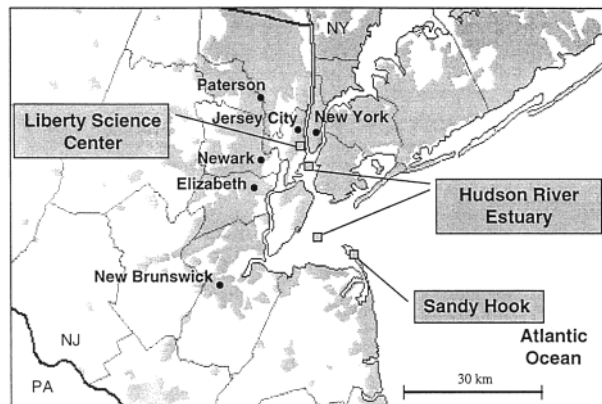


FIGURE 1. Map of the lower Hudson River Estuary. Shaded areas indicate urban areas by population density. Adapted map courtesy of *The National Atlas, USGS*.

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 Cl_{2/3}DD/Fs. The magnitude of Henry's Law constants (1–7 Pa·m³/mol) and octanol–water coefficients (log *K*_{ow} 4.9–6.4) for Cl_{2/3}DD/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

date	July 5	July 6	July 7	July 10
position	40°30.308'N, 74°05.802'W	40°30.396'N, 74°05.771'W	40°30.550'N, 74°05.720'W	40°39.174'N, 74°02.327'W
surface temp (°C)	20.3–22.6	19.9–22.0	21.4–22.9	20.0–20.3
mean SPM (mg/L)	5.59	6.40	4.17	7.87
(f_{oc})	(0.34)	(0.34)	(0.32)	(0.09)
mean DOC (mg/L)	4.04	4.41	3.71	4.90
water vol (L)	39	33	51	60
amount SPM (mg)	218	211	213	472
air temp (°C)	21.7–27.0	20.3–24.9	20.9–24.8	23.6–26.1
air mass origin	Northwest (Canada)	Northeast (Canada)	local (still air)	Northwest (Canada)
air vol (m ³)	384	342	352	370

processes have been quantified (14). Recently, the air–water exchange of nonylphenols has been studied for the lower HRE, depicting net volatilization from the water surface (17). Broman et al. (29) estimated fugacity ratios for PCDD/Fs in waters of the Baltic Sea based on coastal air and water column measurements and derived a net gaseous flux into the Baltic Sea. In this study, measurements in the HRE/RB indicate that outgassing from the Bay can act as a source of some PCDD/Fs to the atmosphere.

Uncertainties remain over the amount of PCDD/Fs in the “truly dissolved phase”, since it is difficult to assess the importance of binding to dissolved organic carbon (DOC) for these compounds. Only the “truly” dissolved phase participates in the approach to air–water equilibrium. However, the observed changes in PCDD/F concentrations of an air mass sampled prior to and after passage over the lower Bay provides strong evidence that volatilization of some PCDD/Fs from the water body occurs.

Materials and Methods

The Hudson River drainage area above the New York metropolitan area covers 34 300 km². The lower Hudson River (Albany to New York City) is 240 km long and consists of a mixed estuary, in part because of marine infusion and tidal influences. The salt front limit can extend up the river 110 km, depending on the freshwater flow (30). The HRE is bordered by the densely urbanized and industrialized areas of New York City, CT, and northern NJ, and in prevailing transport regime downwind of other large atmospheric emission sources: Philadelphia, PA, Wilmington, DE, and the Baltimore–Washington complex. Except for Chesapeake Bay (see 31), there is little information on atmospheric concentrations, deposition, and fate of persistent organic pollutants (POPs) in the Mid-Atlantic States.

Simultaneous air and water sampling on the HRE/RB was performed aboard the RV *Walford* in July 1998. Air and water samples were taken simultaneously, while the boat was anchored at the sampling station, with the bow facing into the wind. The first three samples were taken in the Raritan Bay, and the fourth one was taken in the New York Harbor area (see Figure 1 and Table 1 for details). Samples were processed at Rutgers University immediately following collection and later analyzed at Lancaster University.

Air samples were collected from the bow, with a modified organics Hi-Vol sampler (Graseby) equipped with quartz fiber filter (20 × 24 cm) and polyurethane foam (10 × 8 cm diameter). Each sample consisted of ca. 350 m³ of air sampled at calibrated flow rates of ~0.8 m³/min. Filters were pre-combusted at 400 °C for 4 h, equilibrated in constant humidity before and after deployment in the field, and weighed. PUFs were cleaned by successive 24 h extraction in acetone and petroleum ether and dried in glass vacuum desiccators.

Water samples were collected using an Infiltrax 100 in situ water sampler operating at ~400 mL/min and equipped with a glass fiber filter followed by a XAD-2 resin column. In

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, acetone, hexane, acetone, 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 material (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 chromatographic (GC) vials, and transported to Lancaster University. They were cleaned-up on a mixed silica-column and fractionated on a basic alumina column. Water GFFs were extracted in acetone–hexane (1:1) followed by toluene, while the XAD resins were extracted in acetone–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 of ~0.1–0.6 pg/sample for the 2,3,7,8-substituted congeners (based on the noise of the baseline), only trace amounts of Cl_{7/8}DDs 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

TABLE 2. Mean Concentrations in the Suspended Particulate Matter (SPM) and Apparent Dissolved Phase for the Raritan Bay ($n = 3$), Hudson River, and Field Blank (F.BI.)

homologue groups	SPM (pg/g SPM)				dissolved phase (fg/L)			
	Raritan Bay		Hudson	F.BI.	Raritan Bay		Hudson	F.BI.
	mean	SD (%)			mean	SD (%)		
Cl ₂ DFs	430	28	800	26	3200	14	5900	270
Cl ₃ DFs	27	23	600	2.9	940	14	2900	84
Cl ₄ DFs	130	17	310	0.9	230	6	560	23
Cl ₅ DFs	80	13	160	1.2	200	24	100	4.1
Cl ₆ DFs	74	14	150	1.5	88	22	38	3.3
Cl ₇ DFs	110	9	240	1.0	27	35	nd ^a	0.2
OCDF	80	23	180	2.3	38	22	16	7.7
Cl ₂ DDs	3600	5	1900	7.6	27000	37	44000	170
Cl ₃ DDs	87	11	140	0.9	400	26	1400	7.8
Cl ₄ DDs	61	12	130	0.7	79	19	360	4.6
Cl ₅ DDs	20	24	47	0.4	42	18	88	4.2
Cl ₆ DDs	150	12	280	0.7	250	36	350	2.5
Cl ₇ DDs	410	12	860	5.2	540	28	830	45
OCDD	1900	12	3600	21.8	1500	39	1400	132
ΣTEQ ^b	23	17	33	1.7	25	37	17	0.4

^a Not detected, nd. ^b I-TEQ, ref 33.

TABLE 3. Measurements of PCDD/Fs in Water Samples

location	particle-fraction		dissolved phase, fg/L		sample volume, L	amount SPM, g
	ΣCl ₄₋₈ DD/Fs	ΣI-TEQ	ΣCl ₄₋₈ DD/Fs	ΣI-TEQ		
River Elbe, Germany ^a	3000–6400 pg/g	41–73 pg/g	210–280	4–17	~390	~29–43
Fraser River, Canada ^b				14–33	100	
Baltic Sea, Sweden ^c	27–61 pg/g DOC	0.1–0.6 pg/g DOC	36–260	0.4–3.6	~2000	~12
Japanese coastal sea ^d	1.2–2.9 pg/L		100		~1000	
Raritan Bay ^e	2970 pg/g	23 pg/g	2940	25	~40	~0.2
Hudson River ^e	5430 pg/g	33 pg/g	2350	17	~60	~0.4

^a Reference 33. ^b Reference 34. ^c Reference 28. ^d Reference 36. ^e This study.

higher for OCDD (13 pg/sample) and Cl_{1/2}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 Cl₅DDs to >3000 pg/g SPM for Cl₂DDs (see Table 2). Expressed in pg/L, concentrations in the solid-phase ranged from 0.08 to 0.15 pg/L for Cl₅DDs up to 15–24 pg/L for Cl₂DDs. Concentrations in the apparent dissolved phase were lower, ranging from 40 fg/L for Cl₅DDs to greater than 40 000 fg/L for Cl₂DDs. 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 Cl₂DDs. Both phases had similar concentrations for the lower chlorinated CDFs, while the higher chlorinated PCDD/Fs were found mostly 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 ~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 ~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 ~2, with concentrations of PCDD/Fs in the apparent dissolved phase being higher in the Raritan Bay by ~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) Cl₁DFs (26) < Cl₂DD/Fs (38/47) < Cl₃DD/Fs (52/62) < Cl₄DD/Fs (80/76) < Cl₅DD/Fs (75/84) < Cl₆DD/Fs (79/86) < Cl₇DD/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 Cl₄DD/Fs.

Air Samples. Atmospheric concentrations of PCDD/Fs varied strongly over the course of the sampling campaign,

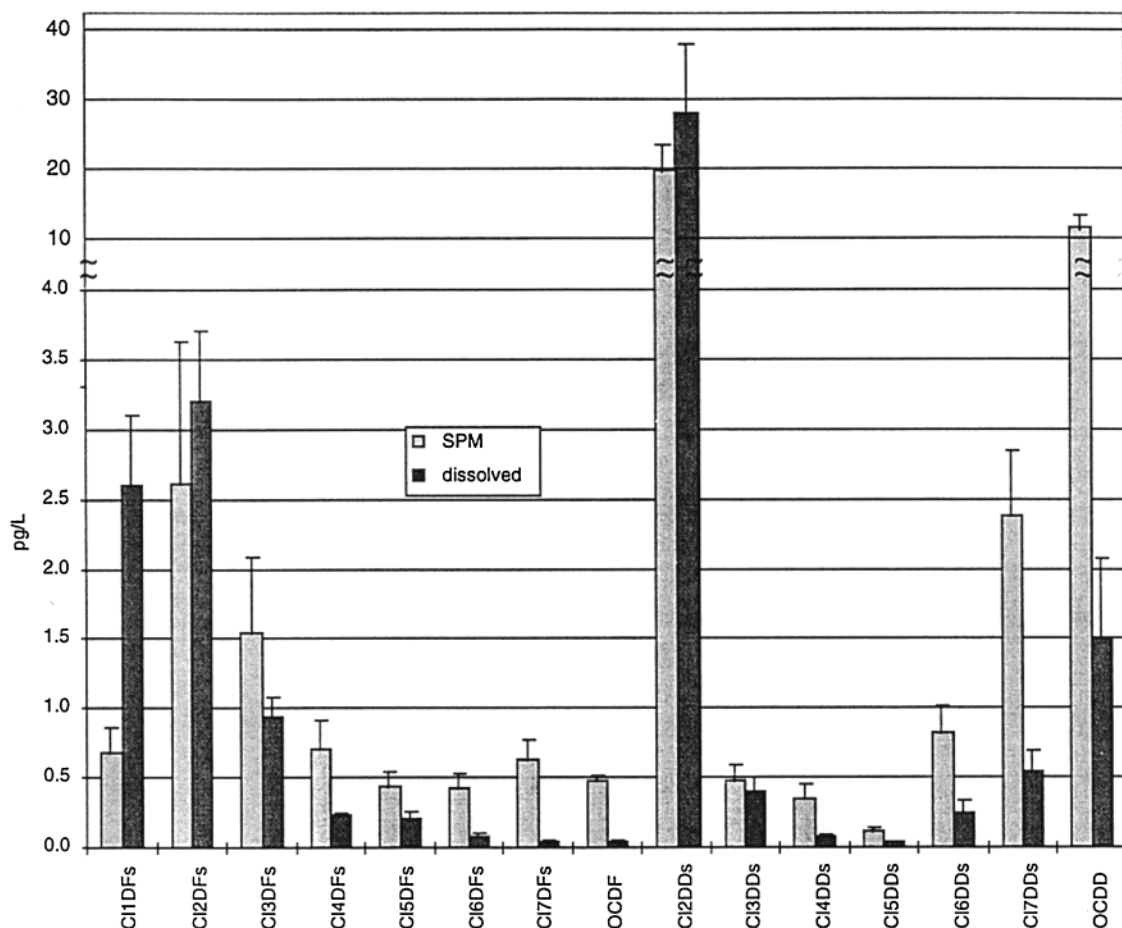


FIGURE 2. Mean PCDD/F homologue group concentrations in the particle and apparent dissolved phase in the Raritan Bay (in pg/L; note: broken y-axis).

TABLE 4: Atmospheric PCDD/F Concentrations and Field Blank (F.BI.) Data in the Gaseous and the Particle-Bound Phase over Water on the Raritan Bay and the Hudson River (fg/m³)

homologue groups	gaseous phase				F.BI.	particle-bound phase				F.BI.
	Raritan Bay			Hudson		Raritan Bay			Hudson	
	July 5	July 6	July 7	July 10		July 5	July 6	July 7	July 10	
Cl ₁ DFs	1100	2000	750	890	9.1	21	18	16	19	13
Cl ₂ DFs	2000	2800	620	1400	10	36	26	20	23	19
Cl ₃ DFs	540	2100	190	820	0.9	20	29	9.2	19	1.7
Cl ₄ DFs	120	1400	57	170	0.6	21	53	7.4	19	1.0
Cl ₅ DFs	42	370	25	65	0.2	18	57	6.5	24	0.2
Cl ₆ DFs	13	50	7.8	24	0.5	18	58	10	39	0.6
Cl ₇ DFs	0.5	1.8	0.5	2.7	0.1	13	21	6.1	40	0.9
OCDF	1.2	1.4	1.3	2.5	0.4	7.4	5.1	2.2	40	0.9
Cl ₂ DDs	7300	6500	4200	7500	1.8	110	80	74	34	9.3
Cl ₃ DDs	90	230	33	160	0.6	9.0	4.4	5.7	3.6	0.4
Cl ₄ DDs	27	300	12	46	0.4	10	14	2.6	5.7	0.5
Cl ₅ DDs	5.4	140	2.7	4.2	1.0	5.4	23	1.8	4.2	0.1
Cl ₆ DDs	2.0	23	1.0	8.6	0.0	17	62	5.2	14	0.0
Cl ₇ DDs	2.1	2.0	2.3	2.1	0.9	34	36	9.0	41	1.2
OCDD	8.5	10	9.3	8.8	5.2	99	72	19	130	6.1
ΣTEQ	1.0	13	0.4	3.0	~0.1	2.5	7.2	1.1	3.4	~0.1

with ΣCl₁₋₈DD/Fs occurring at 12, 17, 6.1, and 12 pg/m³ (ΣTEQ 4.0, 21, 2.1, and 6.1 fg/m³), 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 Cl₂DDs (4.2–7.6

pg/m³) and Cl₁₋₃DFs (0.2–2.8 pg/m³). Concentrations of Cl₂-DDs were consistently high, regardless of the wind direction, whereas Cl₁₋₃DFs 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 Cl₃DD/Fs, but Cl₂DDs were higher by a factor of ~50 (32). Cl₄₋₈DD/Fs were low for samples taken close to a major urban/industrial conglomeration; similar concentrations have been reported for rural areas in the

United States (see ref 38 and references therein) at the end of the 1980s. The contribution to ΣTEQ was similar to that found in the apparent dissolved phase: Two congeners, namely 2,3,4,7,8-PeCDF and 2,3,7,8-TCDF, each contributed > 10% to the ΣTEQ for all samples; 2,3,7,8-TCDF contributed > 10% for the first and third sampling event.

Ambient Gas-Particle Distribution. $\text{Cl}_{1-4}\text{DD}/\text{Fs}$ were < 30% particle-associated, with $\text{Cl}_{6-8}\text{DD}/\text{Fs}$ > 50% in the apparent particle phase, consistent with other distribution studies reported for such warm periods (38) (%PCDDs/%PCDFs): Cl_1DFs (2) ~ $\text{Cl}_2\text{DD}/\text{Fs}$ (2/2) < $\text{Cl}_3\text{DD}/\text{Fs}$ (7/3) < $\text{Cl}_4\text{DD}/\text{Fs}$ (15/10) < $\text{Cl}_5\text{DD}/\text{Fs}$ (39/23) < $\text{Cl}_6\text{DD}/\text{Fs}$ (77/58) < $\text{Cl}_7\text{DD}/\text{Fs}$ (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 extent to which the “dissolved” phase in the water is affected by partitioning to DOC is uncertain. The few studies on the aquatic fate of PCDD/Fs do not report detection of OCDD in the truly dissolved fraction, only associated with DOC (39). PCDD/Fs bound to DOC were not bioavailable (40) and would not be readily available for air–water exchange processes.

It is appropriate to first consider the potential importance of sampling artifacts. As expected, the fraction of particle-bound PCDD/Fs increased with increasing degree of chlorination (with the exception of Cl_4DDs , see above), pointing toward a good separation of the phases. Apparent (organic C normalized) partition coefficients (K_{oc}^{app} , in L/g) were calculated for the water samples using eq 1

$$K_{oc}^{app} = C_{SPM}/C_{diss}^{app}/f_{oc} \quad (1)$$

where C_{SPM} is the PCDD/F particulate concentration (fg/g SPM), C_{diss}^{app} is the apparent dissolved concentration of PCDD/Fs (fg/L), and f_{oc} is the fractional organic carbon content in the SPM.

Investigations of the sorption of hydrophobic organic compounds onto natural sediments as summarized by Schwarzenbach et al. (41 and references therein) demonstrate a linear relationship between K_{oc} and K_{ow} in the water column:

$$\log K_{oc} = \log K_{ow} - 0.21 \quad (2)$$

Calculated K_{oc}^{app} values agreed within a factor of 2–5 with K_{oc} values predicted from eq 2 for the $\text{Cl}_{1-4}\text{DD}/\text{Fs}$. However, the K_{oc}^{app} values for the $\text{Cl}_{5-8}\text{DD}/\text{Fs}$ were lower by an order of magnitude than the predicted values. We interpret this observation as suggestive of a sampling artifact for the $\text{Cl}_{5-8}\text{DD}/\text{Fs}$ in the operational separation of dissolved and particulate phases.

A partitioning coefficient for PCDD/Fs onto DOC (K_{DOC}) is defined as

$$K_{DOC} = C_{DOC}/C_{diss} \quad (3)$$

with C_{DOC} the concentration of PCDD/Fs bound to DOC (fg/g DOC) and C_{diss} the PCDD/F concentration in the truly dissolved phase (fg/L). Correcting for the amount of PCDD/

Fs bound to DOC is problematic since there are no literature data available for PCDD/F- K_{DOC} values. However, K_{DOC} is about 5–10 times lower than K_{oc} values (42, 43). Freidig et al. reports a linear relationship between $\log K_{ow}$ and $\log K_{DOC}$ (42), with

$$\log K_{DOC} = 0.67 \cdot \log K_{ow} + 1.46 \quad (4)$$

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_{diss} and c_{DOC} were calculated and compared to c^{app}_{diss} . There was good agreement between the predicted and measured apparent dissolved phase for the higher chlorinated PCDFs, while c^{app}_{diss} were lower than predicted for $\text{Cl}_{1-2}\text{DFs}$ by a factor of ~2–3 (see Figure 3). $\text{Cl}_{2-4}\text{DDs}$ showed good agreement with the predicted concentrations, while $\text{Cl}_{5-8}\text{DDs}$ had a ~50% higher concentration than predicted in c^{app}_{diss} . Clearly, the linear relationship between K_{DOC} and K_{ow} derived in eq 4 does not satisfactorily explain the partitioning of PCDD/Fs in the water column, as the calculated partitioning to DOC accounted for only ~50% of the $\text{Cl}_{5-8}\text{DDs}$ detected in the c^{app}_{diss} . In particular, the high concentrations of OCDD in c^{app}_{diss} 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

$$f_w/f_a = \alpha = C_{diss} \cdot H/C_{gas} \cdot R \cdot T \quad (5)$$

where α is the fugacity ratio, f_w and f_a are the fugacities in water and air, respectively, H is Henry's law constant (HLC), T the temperature (K), 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, when $\times a_6w/\times a_6a$ ratios were < 1 for the $\text{Cl}_{3-6}\text{DFs}$ and $\text{Cl}_{4-5}\text{DDs}$. Fugacity ratios were highest for $\text{Cl}_{6-8}\text{DDs}$ and OCDF with $\alpha > 5$ –10, while $\text{Cl}_{2-5}\text{DD}/\text{Fs}$ had α of up to 5–7.

Uncertainties in the calculation of the fugacity ratios stem from (i) the analytical precision in determining C_{diss} and C_{gas} ; (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 m³ 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 α stems from the HLCs. Hence, the uncertainty in the fugacity ratios will be on the order of ~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_2DDs 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,

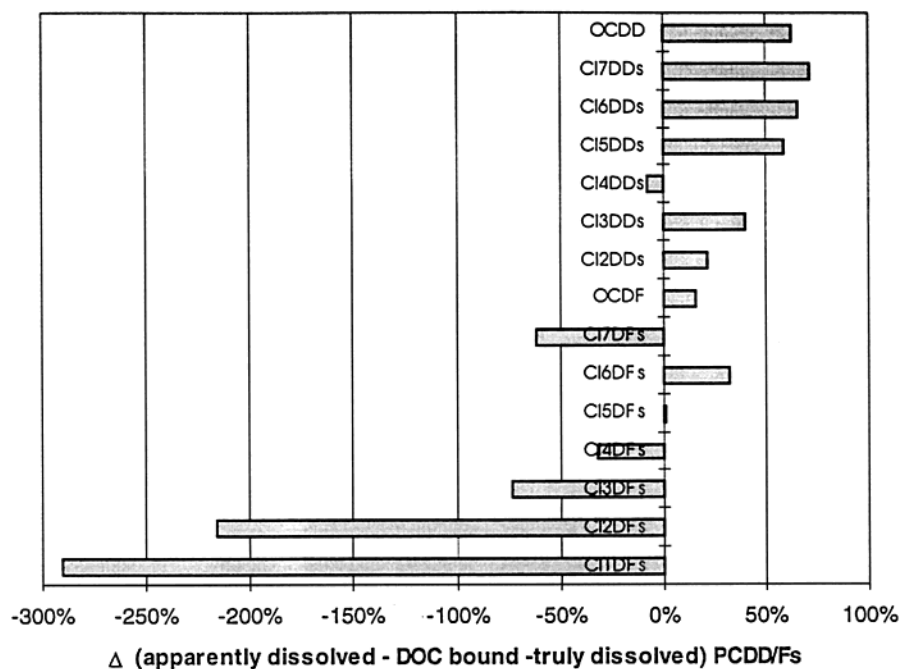


FIGURE 3. Difference between apparent dissolved PCDD/Fs and calculated truly dissolved and [DOC]-bound PCDD/Fs. A negative Δ value means that the calculated distribution accounted for more PCDD/Fs in the truly dissolved phase and [DOC]-bound than was detected in the apparent dissolved phase. A positive 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.

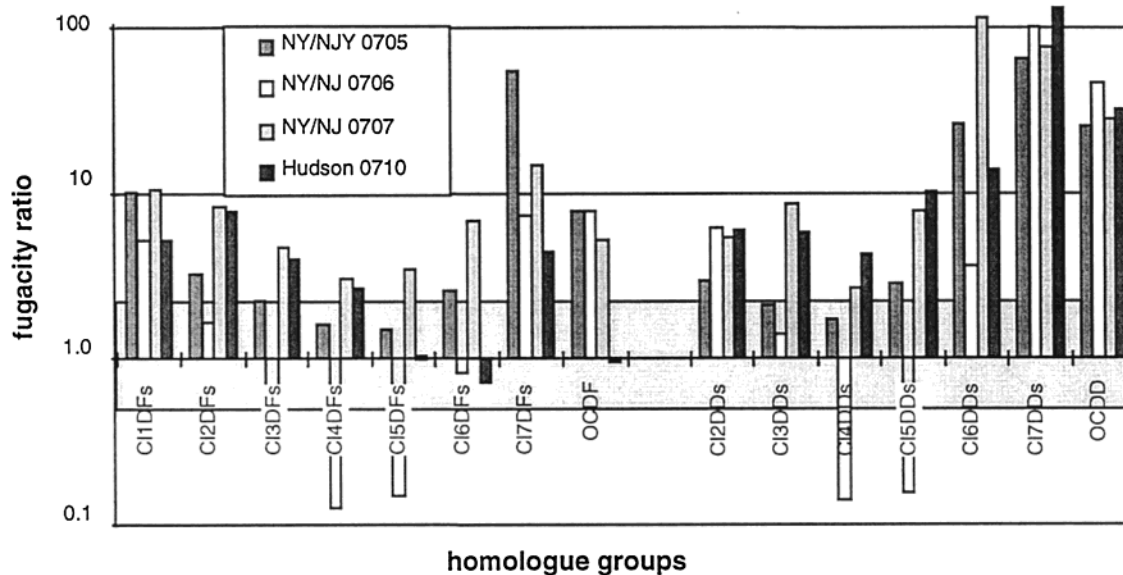


FIGURE 4. Water-air fugacity ratios for PCDD/F homologue groups for the Raritan Bay/Hudson River Estuary (gray shaded background indicates estimated uncertainty range for equilibrium, i.e., $\pm 100\%$).

one-dimensional flux into the water by means of wet and dry deposition.

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 $\sim 340^\circ$. 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

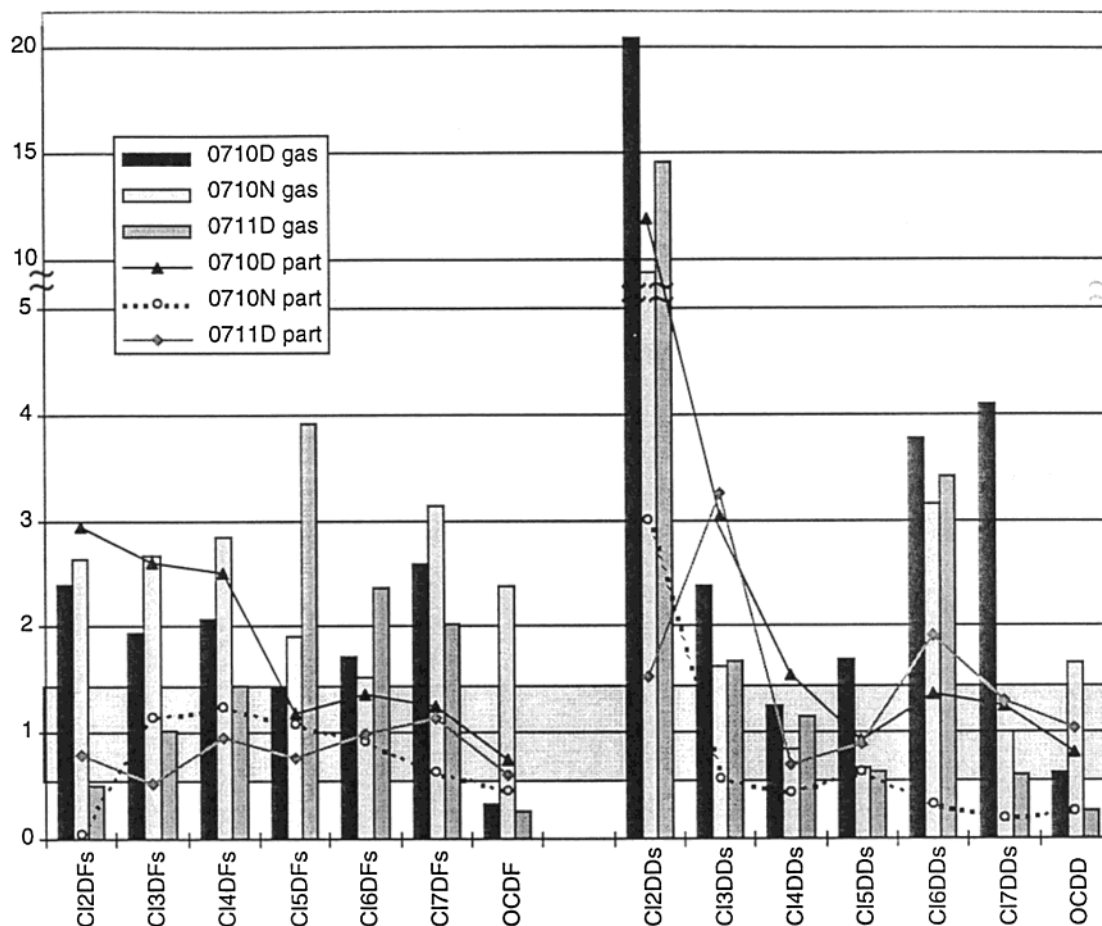


FIGURE 5. Ratios of observed changes in the gas phase and PCDD/Fs on particles at the coastal site over concentrations at the urban/industrial site (shaded gray area indicates estimated analytical uncertainty range, i.e., $\pm 40\%$; note: broken y-axis).

(34). (iii) 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. (iv) 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 ($\pm 40\%$) 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 Cl_2DD 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 $\text{Cl}_{2-7}\text{DFs}$ and $\text{Cl}_{2-6}\text{DDs}$ increased from the industrial to the coastal site. The $\text{Cl}_{4-5}\text{DDs}$ on the night of

July 10, and Cl_5DDs and Cl_2DFs 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 $\text{Cl}_{2-4}\text{DD/Fs}$ 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 Cl_2DDs 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 Cl_2DDs 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_{6/7}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 Cl₂DDs in the water and the atmosphere is unknown.

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