

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P293

Air - water exchange of PCDD/Fs in the Raritan Bay / Hudson River Estuary

Rainer Lohmann, Eric Nelson*, Steven J. Eisenreich* and Kevin C. Jones

Department of Environmental Science, IENS, Lancaster University, Lancaster, LA1 4YQ, UK

*Department of Environmental Science, Rutgers University, New Brunswick, NJ 08901, USA

Introduction

PCDD/Fs are ubiquitous contaminants which are released as by-products of incomplete combustion or as chemical impurities. Atmospheric transport is believed to be the major pathway for their distribution away from sources (1,2). We are the first to report simultaneously measured air and water concentrations of PCDD/Fs. Air-water exchange processes of PCBs and PAHs have been studied for the Great Lakes and Chesapeake Bay, with a resulting net volatilisation of the contaminants from the water surface (3,4). Measurements in the Raritan Bay / Hudson River Estuary indicate that outgassing from the Bay can act as a source of PCDD/Fs to the environment. Fugacity calculations based on Henry's law constants for the Hudson River Estuary / Raritan Bay show a gradient favouring volatilisation of PCDD/Fs from the aqueous phase. Uncertainties remain over the concentrations in the 'truly dissolved phase'.

Materials and Methods

Air and water sampling on the Raritan Bay / Hudson River Estuary was performed aboard the RV Walford in July 1998. Air samples were taken from the bow with a high-volume sampler (GPS1 Graseby) equipped with glass fibre filter and polyurethane foam. Each sample consisted of ca. 350m³ of air sampled at ~ 0.8 m³/min. Water samples were collected with a sampling train of a quartz fibre filter followed by a XAD-2 resin column at ~13L/hr. Air and water samples were taken simultaneously once the boat anchored at the sampling station. Additional water samples were taken for TSP, DOC and f_{oc} determination. Air and water temperature, wind speed and direction were recorded throughout the sampling interval (see table 1).

Table 1: Summary of 4 sampling events in the Raritan Bay / Hudson River Estuary

Date	07/05/98	07/06/98	07/07/98	07/10/98
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.	20.3 - 22.6°C	19.9 - 22.0°C	21.4 - 22.9°C	20.0 - 20.3°C
mean SPM (f _{oc})	5.36 mg/L (0.33)	5.67 mg/L (0.35)	4.25 mg/L (0.32)	5.45 mg/L (0.12)
water vol / amount SPM	39 L / 218 mg	33 L / 211 mg	51 L / 213 mg	60 L / 472 mg
air temp.	21.7 - 27.0°C	20.3 - 24.9°C	20.9 - 24.8°C	23.6 - 26.1°C
air mass origin	North-West (Can.)	North-East (Can.)	local (still air)	North-West (Can.)
air vol	384 m ³	342 m ³	352 m ³	370 m ³

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P293

For the air samples the GFFs were extracted in toluene, the PUFs in DCM; both fractions were cleaned-up by passage through a mixed silica-column and fractionation on basic alumina and analysed by HRGC/MS on a Micromass Autospec Ultima (for details see 5). Water GFFs were extracted in acetone:hexane (1:1), followed by toluene, XAD resins were extracted in acetone:hexane (1:1) and partitioned against water. Both fractions were cleaned-up and analysed as described above. ¹³C₁₂-labelled PCDD/Fs standards were added to the XAD-resin before employment in the water, GFFs and PUFs were spiked prior to extraction in the lab. Recoveries were good for most samples, with the first three XAD-samples having lower recoveries (50-65%). Detection limits for the 2,3,7,8-substituted congeners, based on the noise of the baseline, were ~ 0.1-0.5 pg/sample.

Results and discussion

Water samples: in the particulate fraction virtually all PCDD/F homologue groups and 2,3,7,8-substituted congeners were measured with an excellent reproducibility. Average standard deviations were 15% for the homologue groups and 17% for the individual congeners. Concentrations ranged from 20pg/g SPM for PeCDDs to >3000pg/g SPM for di-CDDs (see table 2). Concentrations in the dissolved phase were lower, with concentrations ranging from 40 fg/L for PeCDDs to over 40,000 fg/L for di-CDDs.

Table 2: Mean concentrations in the suspended particulate matter and dissolved phase for the Raritan Bay, Hudson River and Field Blank (FB)

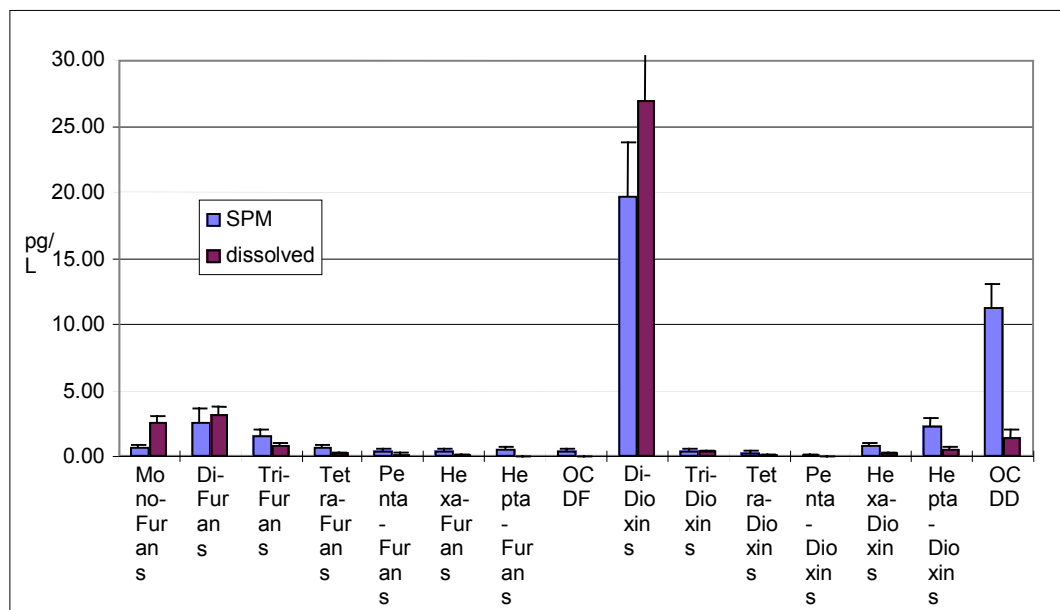
	suspended particulate matter (pg/g SPM)				dissolved phase (fg/L)			
	Raritan Bay		Hudson	FB	Raritan Bay		Hudson	FB
homologue groups	mean	std			mean	std		
Mono-Furans	99	18%	110	27	2,600	19%	1,200	88
Di-Furans	430	28%	800	26	3,200	14%	5,900	270
Tri-Furans	27	23%	600	2.9	940	14%	2,900	84
Tetra-Furans	130	17%	310	0.9	230	6%	560	23
Penta-Furans	80	13%	160	1.2	200	24%	100	4.1
Hexa-Furans	74	14%	150	1.5	88	22%	38	3.3
Hepta-Furans	110	9%	240	1.0	27	35%	nd	0.2
OCDF	80	23%	180	2.3	38	22%	16	7.7
Di-Dioxins	3,600	5%	1,900	7.6	27,000	37%	44,000	170
Tri-Dioxins	87	11%	140	0.9	400	26%	1,400	7.8
Tetra-Dioxins	61	12%	130	0.7	79	19%	360	4.6
Penta-Dioxins	20	24%	47	0.4	42	18%	88	4.2
Hexa-Dioxins	150	12%	280	0.7	250	36%	350	2.5
Hepta-Dioxins	410	12%	860	5.2	540	28%	830	45
OCDD	1900	12%	3,600	21.8	1,500	39%	1,400	132
ΣTEQ (I-TEQ)	23	17%	33	1.7	25	37%	17	0.4

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P293

There is limited data to compare our concentrations with - concentrations per g SPM are similar to those found in the river Elbe, while the concentrations in the dissolved phase exceed the Elbe ones by a factor of ~2-10 (6).

Mono- to tri-CDD/Fs were 20-60% particle-bound, whereas tetra- to octa-CD/Fs were to 50-100% associated with the particulate matter. Figure 1 shows the mean concentrations in the particulate and dissolved phase, with error bars representing single standard deviations.

Figure 1: Mean concentrations in the particle and dissolved phase in the Raritan Bay



Air samples: Atmospheric concentrations of PCDD/Fs varied strongly over the course of the sampling campaign, with $\Sigma P_{4-8}CDD/Fs$ of 460, 2,700, 190 and 700 fg/m^3 (ΣTEQ 4.0, 21, 2.1 and 6.1) respectively on the different sampling events. The first and last samples were characterised by north-westerly winds; the highest concentrations came with the air from the NY metropolitan region (NE) and the lowest concentrations during a very calm day. Di-CDDs dominated the homologue groups with concentrations between 4,300 and 7,600 fg/m^3 , regardless of the wind direction. The other lower chlorinated homologues had factors of 3-10 between their lowest and highest concentration. Mono- to tetra-CDD/Fs were <30% particle-associated, with hexa- to octa-CDD/Fs >50%.

Air-water exchange: The water-air fugacity ratio is defined as:

$$(1) f_w/f_a = \alpha = C_w \cdot H / C_a \cdot R \cdot T$$

where α is the fugacity quotient, f_w and f_a the fugacities in water and air, respectively, H Henry's law constant (HLC), T the temperature and R the universal gas constant. At equilibrium between the gas and dissolved phase $\alpha=1$, volatilisation occurs when $\alpha>1$ and net gaseous deposition when

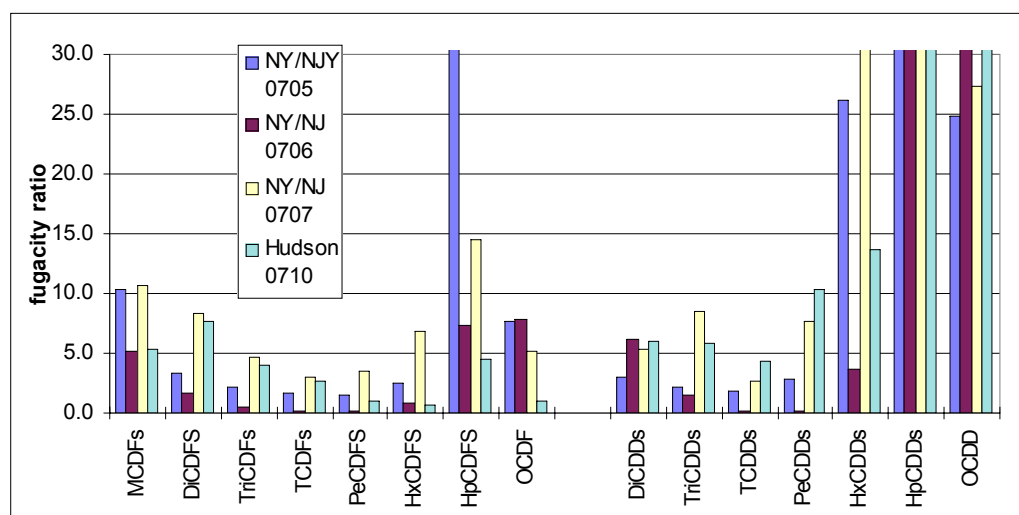
Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P293

$\alpha < 1$. Only HLC at the sampling temperature is needed to calculate the fugacity quotient. We used published HLCs at 298K, reasonably close to air and water temperatures during the sampling campaign (20 - 27°C) (7,8).

Figure 2 shows the calculated fugacity quotients. With very few exceptions they are all > 1 , indicating a net volatilisation from the Raritan Bay/ Hudson River Estuary. The exception is the second sampling event with high ambient air concentrations, where fugacities are < 1 for the tri- to hexa-CDFs and tetra/penta-CDDs. Fugacity quotients are highest for hexa- to octa-CDDs and OCDF with $\alpha > 5-10$, while di- to penta-CDD/Fs have α of up to 5-7.

As is apparent from equation 1, the water-air fugacity depends on the analyte concentrations in the dissolved and gas phase. There is uncertainty to what degree the operationally defined 'dissolved' phase in the water is affected by colloids or small particles. The homologue group pattern for the two phases is different, pointing towards a good separation between the two phases (see Figure 2). Concentrations in the dissolved phase of ~ 2 pg/L for OCDD and ~ 40 pg/L for di-CDDs are well below their solubilities of 74 pg/L (OCDD) and ~ 4 μ g/L (2,7-di-CDD) (7). We calculated apparent partition constants (K_p) for the water samples ($K_p = C_{SPM}/C_{diss}/f_{oc}$). Our K_p values agree well with published K_{ow} values (7,8): mono- to tetra within a factor of 2-5, whereas penta- to octa- K_p s are lower by an order of magnitude. Further studies are required to assess the role of water bodies as sources/sinks of atmospheric PCDD/Fs.

Figure 2: Water-air fugacity quotients for the Raritan Bay / Hudson River Estuary



Acknowledgements

We thank Paul Brunciak, Jordi Dachs and Cari Lavorgna for their help and support during the entire sampling campaign.

Environmental Levels (Air and Soil) of Other Organohalogenes and Dioxins P293

References

1. Ballschmiter K, Bacher R; Dioxine. VCH, Weinheim, 1996: ISBN 3-527-28768-X
2. Rappe, C.; Chemosphere, 1992, 25, 41
3. Hornbuckle, K.C., Jeremiason, J.D., Sweet, C.W., Eisenreich, S.J; Environ Sci Technol., 1994, 28, 1491
4. Nelson, E.D., McConnell, L.L., Baker, J.E; Environ Sci Technol., 1998, 32, 912
5. Lohmann, R., Green, N.J.L., Jones K.C; Organohal. Compounds, 1998, 36, 413
6. Götz, R., Enge, P., Friesel, P., Roch, K., Kjeller, L.-O., Kulp, S.E., Rappe, C; Chemosphere, 1994, 28, 63
7. Mackay D, Shiu WY, Ma KC; Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals Vol.II polynuclear aromatic hydrocarbons, polychlorinated dioxins and dibenzofurans. Lewis Publishers, 1991: ISBN 0-87371-513-6.
8. Govers, H.A.J., Krop, H.B; Chemosphere, 1998, 37, 2139

**Environmental Levels (Air and Soil) of Other Organohalogen
and Dioxins P293**