

PCDDS/PCDFS IN THE ATMOSPHERE-MEASUREMENT, TRENDS, SOURCES, FATE AND TRANSPORT

PCDD/Fs in the New Jersey coastal atmosphere: Evidence for secondary sources and OH-radical initiated depletion reactions

Rainer Lohmann^{1,3}, Paul L. Brunciak², Cari L. Gigliotti², Eric Nelson², Daryl Van Ry², Thomas Glenn², Steven J. Eisenreich², Joanne L. Jones¹ and Kevin C. Jones¹

¹Department of Environmental Science, Institute of Environmental and Natural Sciences, Lancaster University, Lancaster, LA1 4YQ, UK; ²Department of Environmental Sciences, Rutgers - The State University of New Jersey, 14 College Farm Road, New Brunswick, NJ 08901, USA;

³present address: Ralph M. Parsons Laboratory, 48-336, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA.

Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) are ubiquitous contaminants that are released into the environment 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). Air-water diffusive exchange of PCDD/Fs, investigated in the Lower Hudson River Estuary (LHRE), is a source to the atmosphere: Fugacity ratios of PCDD/Fs in the aquatic and gaseous phase indicated net volatilisation of PCDD/Fs from the water surface (3). Tracking air masses prior to and after transport over the lower HRE demonstrated significant enrichment of ambient PCDD/F concentrations, with volatilisation of the Cl₂₋₆DDs and Cl₂₋₇DFs being the likely cause (3).

Materials and Methods

Air samples (consecutive 12-hour day-night) were taken at three land-based sites during a week-long sampling campaign, whilst additional over water samples were being collected (3). The sampling sites were chosen to reflect contrasting environments in New Jersey: the urban/industrial signal from the NJ-NY agglomeration (Liberty Science Centre, LSC), the coastal Atlantic environment (Sandy Hook, SH) and the suburban background (New Brunswick, NB; see Figure 1). More details on the air sampling procedure and the analytical method used is given in 3.

Results and discussion

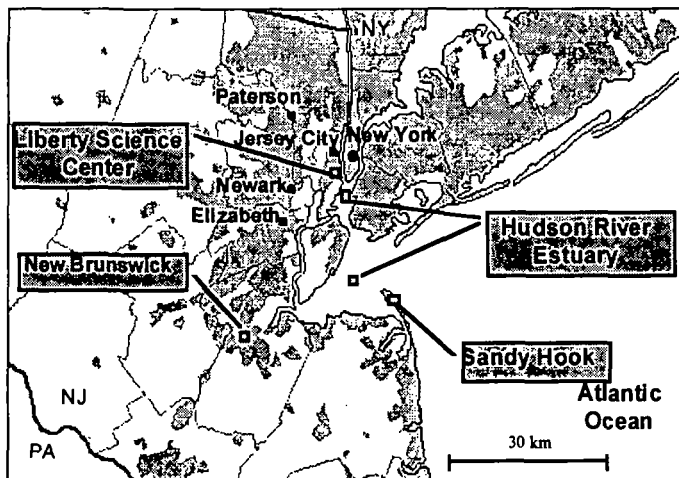
Ambient Air Concentrations: Table 1 summarises the mean and the range of ambient PCDD/F concentrations (in fg/m³) for the different sampling sites.

Ambient PCDD/F concentrations were dominated by either Cl₂DFs (NB, LSC) or Cl₂DDs (SH, HRE). The marked spatial divergence in the atmospheric PCDD/F concentrations was surprising given the proximity of the sites.

Surprisingly, ΣCl₄₋₈DD/Fs and ΣTEQ concentrations in the ambient air in New Jersey, despite the vicinity to the NJ-NY conurbation and being densely populated, occurred at concentrations only 2 to 3 times higher than measured at a remote Irish site (4). While the mean relative homologue profiles from the Irish and English samples matched closely, the NJ profiles did not (4).

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Figure 1: Sampling sites around the lower Hudson River Estuary
LOWER HUDSON RIVER ESTUARY



Shaded areas indicate urban areas by population density.
 Adapted map courtesy of The National Atlas, USGS

Table 1: Ambient PCDD/F Concentrations (fg/m³) in Coastal New Jersey

	New Brunswick		Sandy Hook		Liberty Science		HRE
	Mean	Range	Mean	Range	Mean	Range	
Cl ₂ DFs	3,200	440-21,000	1,000	320-2,900	1,600	720-3,700	1,800
Cl ₃ DFs	1,000	150-4,500	340	100-1200	430	230-990	940
Cl ₂ DDs	230	79-470	2,000	940-3,900	930	170-2,500	6,500
Cl ₃ DDs	39	11-150	28	15-46	36	20-59	130
ΣCl ₄₋₈ DD/Fs	1,400	450-3,800	830	72-6,300	880	290-1,800	1,000
ΣTEQ *	16	3.2-55	6.6	0.6-38	8.5	1.2-19	9.5

*WHO-TEF, ref. 5

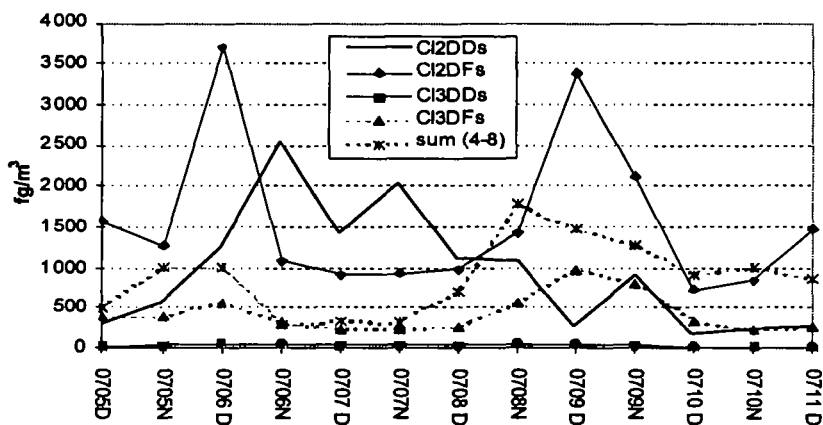
Spatial and Temporal Variation The different sites did not follow the same trends. PCDD/F concentrations at the NB site peaked on the days of July 6 and 7, with ΣCl₄₋₈DD/Fs of ~ 4,000 fg/m³, but none of the other sites had higher concentrations for those day-time samples. Similarly, at the marine coastal site at SH, ΣCl₄₋₈DD/Fs increased to 6,300 fg/m³ on the night of July 9, which was not observed at the other sites. The LSC site showed the least variation over the course of the sampling campaign with ΣCl₄₋₈DD/F concentrations not exceeding 2,000 fg/m³.

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Sandy Hook Ambient PCDD/F concentrations at the coastal site exhibited the biggest variation of any site; An exception to the strong fluctuation of ambient PCDD/F concentrations at marine coastal SH site was exhibited by the Cl_{2,3}DDs. Both homologue groups displayed stable concentrations with max/min ratios of 3 to 4. This again is indicative of local source(s) of these PCDD/Fs to the atmosphere, most likely volatilization from the HRE surrounding the SH site (3).

Liberty Science Center Ambient PCDD/F concentrations at LSC displayed the least variation of all land-based sites: Cl_{2,6}DFs and Cl_{3,5}DDs varied only by factors of ~ 5 over the entire sampling campaign; Cl₂DDs concentrations were highest for the night-samples of July 06 and 07 (see Figure 2).

Figure 2 Ambient concentrations of Cl₂DDs, Cl₂DFs, Cl₃DDs, Cl₃DFs and ΣCl_{4,8}DD/Fs at LSC



OH radical depletion of Cl₂DDs: The atmospheric depletion of a gaseous compound due to reaction with OH-radicals should be measurable in the field, if certain conditions apply, namely: i) samples need to be taken close to a continuous atmospheric source of the compounds; ii) the source must be strong compared to advective ('background') transport and / or calm ambient conditions must dominate; iii) separate day and night samples should be taken reflecting the pronounced day-night differences in atmospheric OH-radical concentrations (6); iv) the compound of interest must be sufficiently labile to display analytically-detectable changes. Our day-night sampling program in July at the LSC, next to the NY Harbor, a known source of atmospheric Cl₂DDs, fulfilled all the criteria mentioned above.

Estimation of the ambient Cl₂DD half-life: Average atmospheric OH-radical concentrations for a site at 40°N in July were estimated to be ~ 4 x 10⁶ molecules/cm³ for the day and approximately zero during the night (6). The pseudo first-order rate constant ($k'_{OH^{obs}}$) of a compound X with OH-radicals is defined as: $k'_{OH^{obs}} = \ln(C_{day}/C_{night})/t$ with C_{night} the concentration of the compound at reaction time $t=0$ (prior to reaction with OH-radicals) and C_{day} the concentration of the compound at reaction time t . For the night samples of July 06 to 09, Cl₂DD night-time concentrations were compared to their day-time concentrations: the mean $k'_{OH^{obs}}$ was ~1.5 day⁻¹ (0.9-2.8 day⁻¹). Comparing the laboratory-derived half-lives with our field results (normalized to 1x10⁶ OH-

ORGANOHALOGEN COMPOUNDS

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radicals/cm³) gives the following: Cl₂DD - t_{1/2} (this study) 1.8 days (1.0-3.0 days); Cl₂DD - t_{1/2} 1.4-1.7 days (Kwok *et al.*; 7).

To our knowledge, this is the first time that field evidence has been presented for the atmospheric reaction of PCDD/Fs with OH-radicals. The excellent agreement of laboratory and field half-lives for Cl₂DDs also supports our contention that the lower HRE supplies the surrounding atmosphere with a range of PCDD/Fs, notably Cl₂DDs. Taken together, there is little evidence of major local primary PCDD/F emission sources for the coastal sites during this sampling period in summer 1998.

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