

Tracing Atmospheric Deposition of PCDD/Fs in Lake Maggiore (Italy): Preliminary Results on Settling Material and Sediments.

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Introduction

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/ Fs) enter the environment primarily as a result of anthropogenic activities. Many of the congeners bioaccumulate and are considered potent toxicants capable of producing a wide spectrum of adverse health effects in biota and humans such as immunotoxicity, chloracne, carcinogenicity, reproductive and developmental toxicity, disruption of the endocrine system, induction of enzymes, and anti-estrogenic effects¹. As a chemical class, they occur as byproducts of chemical manufacturing and incineration processes¹⁻³. Emissions from incineration of medical, municipal, and chemical wastes and certain facilities in central Europe⁴ provide the major source of PCDD/F to the environment.

PCDD/Fs are delivered to lake systems by atmospheric emission and transport followed by deposition, direct and indirect discharges, and riverine inputs. Polychlorinated dioxins and furans (PCDD/Fs) for example are characterized by low aqueous solubilities and vapor pressures, and resistance to extensive chemical and biological transformation. Their general hydrophobic nature results in high partition coefficients to abiotic and biotic particles. PCDD/Fs exist in the atmosphere as gases and particles although most measurements are dominated by the aerosol concentrations, especially the black carbon (BC) fraction. Once delivered to the water column, the primary removal processes are adsorption to or partitioning into particles and subsequent settling and accumulation in bottom sediments. The sorptive properties are largely controlled by the organic carbon (OC) content of particles, although BC may also play a role. Thus hydrophobic organic contaminants (HOCs) will follow the path of the average clay-size particles and be focused **into** the more quiescent, depositional basins of the lake. Experience from the Laurentian Great Lakes shows that residence times for HOCs are about **2-4** times the fine-particle residence times of ~ 1 year. Once delivered to the bottom sediments, contaminant and particle burial is slowed by the effects of resuspension and mixing of surface sediments by aquatic organisms.

Several studies have focused on the atmospheric transport, reactivity and deposition of these compounds but relatively few on their in-lake behavior. In this short paper, we provide preliminary information on the delivery and accumulation of PCDD/Fs as recorded in sediments from the Lake Maggiore (LM) (Italy). Our strategy was to obtain surface sediment from areas near riverine inputs and in the depositional basins, settling material in sediment traps at one site and preliminary air, aerosol and rain profiles. Similarity in isomer profiles in atmospheric aerosol, rain, water column settling matter and bottom sediment point to an important if not dominant contribution from atmospheric deposition to LM, especially derived from aerosol-bound PCDD/Fs. Later high resolution sediment cores will be analyzed to provide a spatial and temporal view of organic contaminant loading to the lake.

Materials and Methods

Sampling

Sediment (bottom and settling material), air and precipitation samples were taken in the LM area. Sampling locations are depicted in Figure 1.

Ambient air: The air sample was taken at the Joint Research Centre (JRC) EMEP Ispra Site⁵. A weekly sample was collected using a high volume sampler (Echo PUF Hi volume sampler, TCR Tecora, Milano, Italy). A total volume of

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845 Nm³ was obtained. Previously cleaned glass fiber filter (GFF) of 102 mm diameter and polyurethane foam (PUF) of 65 mm diameter and 75 mm length were used for the retention of the studied compounds. Particulate phase (filter) and gas phase (PUF) were analyzed separated. PM10 data were also obtained from the JRC EMEP Ispra Site.

Wet deposition: A device holding three glass funnels of 188 mm diameter each was used for the precipitation collection. A PUF of 18 mm diameter and 100 mm length was placed in each neck funnel. Precipitation was estimated by gravimetric method.

Sediment sampling: Sediment surface grab samples were taken with a Ponar Grab sampler from a boat in the estuary zone of rivers flowing into LM and in the area of the deployed sediment trap. The sampled sediment depth was 5 – 10 cm. Supernatant water was decanted, sediment was frozen and freeze dried (Lio5P, 5 Pascal, Trezzano, Italy). Material > 2 mm was removed by sieving. Sample storage at – 30 °C. An amount of 40 g was processed.

Sampling of settling material: The sediment trap (JRC central workshop), stainless steel, diameter 50 cm, 150 cm cylinder with funnel end and 250 ml glass sample container, was deployed at 30 m water depth, 3 m above the sediment, using an acoustic release unit 7986 LRT (Sonardyne, Yateley, UK). The trap was deployed on 17 Dec 04 and recovered on 19 April 05. Sample dry weight was 15.75 g. The sample was centrifuged, frozen, freeze dried and stored at – 30 °C until extraction. An amount of 5 g was processed.

Analytical determinations: Samples were extracted with n-hexane/acetone (220/30) by soxhlet for 48 h after spiking with internal standards (16 ¹³C-labelled 2,3,7,8-chlorine-substituted congeners- 400 pg each, except OCDD/OCDF with 800 pg each). Extract purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA) after treatment with conc. H₂SO₄ (the latter was done only for sediments and settling material). Analysis of PCDD/Fs was based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry) for quantification. The GC (HP-6890, Hewlett Packard, Waldbronn, Germany), was coupled with a VG Autospec Ultima mass spectrometer (Micromass, Manchester, UK) operating in EI-mode at 34 eV with a resolution of >10000. The samples were analyzed on a 60 m capillary column with 0.25 mm i.d. and 0.25 µm film (BP-DXN, SGE, Victoria, Australia). The applied methodology follows USEPA method 1613⁶.

For QA/QC a sediment sample of the 9th international intercalibration study (Bert v. Bavel) has been analyzed in parallel.



Code	Date	Type	Location	Depth (m)
UMMS003	02 Feb 2005	bottom sediment	hika, river San Bernardino	17
UMMS004	02 Feb 2005	bottom sediment	Verbania, river Toce	8
UMMS005	02 Feb 2005	bottom sediment	Ispra, river Aquanera	2
UMMS021	11 Mar 2005	bottom sediment	Ticino outlet	13.5-18
UMMS022	11 Mar 2005	bottom sediment	Ticino outlet, close to bridge	8.3
UMMS023	14 Apr 2005	bottom sediment	Ispra bay, 10 m distance from sediment trap	30
Sediment trap	17 Dec 2004 - 19 Apr 2005	settling material	Ispra bay	27
BNEP Station	22-30 May 2005	air	JRC-Ispra BNEP site	
BNEP Station	22-30 May 2005	wet deposition	JRC-Ispra BNEP site	

Figure 1. Sampling locations at Lake Maggiore area

Results and Discussion

Gas and particle phase

PCDD/F concentrations in air of 24 WHO-TEQ fg/m^3 (gas + particle phase, Table 1) as well as the congener patterns (Figure 3) obtained were in agreement with those typically reported for rural areas⁷⁻⁸.

Table 1: Levels of PCDD/Fs in air, rain, settling material and bottom sediment in the Ispra area, Lake Maggiore.

PCDD/F-congener	Air	Air	Wet	Settling	Bottom Sediment
	Gas Phase	Particle Phase	Deposition	Material	
	Ispra JRC	Ispra JRC	Ispra JRC	Ispra bay	Ispra bay
	22-30 Mar 05	22-30 Mar 05	22-30 Mar 05	17 Dec 04 - 19 Apr 05	02 Feb 05
	fg/m^3	fg/m^3	pg/m^2	conc. pg/g dry weight	conc. pg/g dry weight
2,3,7,8-TCDD:	<0.55	<0.25	4.8	0.35	0.60
1,2,3,7,8-PeCDD:	1.0	1.1	13	1.0	1.7
1,2,3,4,7,8-HxCDD:	<0.82	3.8	21	1.8	2.1
1,2,3,6,7,8-HxCDD:	<0.60	7.1	47	2.9	5.4
1,2,3,7,8,9-HxCDD:	1.7	6.0	33	3.3	4.2
1,2,3,4,6,7,8-HpCDD:	4.5	76	699	47	76
OCDD:	13	197	2887	229	538
2,3,7,8-TCDF:	15	4.8	86	12	15
1,2,3,7,8-PeCDF:	7.9	3.6	72	5.5	10
2,3,4,7,8-PeCDF:	11	7.9	95	9.6	12
1,2,3,4,7,8-HxCDF:	4.2	13	112	6.6	14
1,2,3,6,7,8-HxCDF:	5.3	11	72	4.9	9.3
2,3,4,6,7,8-HxCDF:	4.3	19	141	6.2	12
1,2,3,7,8,9-HxCDF:	<1.4	4.0	36	1.5	4.2
1,2,3,4,6,7,8-HpCDF:	3.6	52	504	44	52
1,2,3,4,7,8,9-HpCDF:	<0.57	8.0	53	3.0	7.7
OCDF:	6.0	37	421	103	84
PCDD/F-WHO-TEQ	11	14	137	11	17

It was observed that TEQ concentrations in both particle and gas phase were similar but the lower chlorinated compounds were more abundant in gas phase while the high chlorinated ones were dominant in particle phase (Table 1, Figure 3).

The distribution of the tetra- and penta-chlorinated dibenzodioxins/-furans in particular are operationally defined by the applied sample collection technique and hence concentrations measured and TEQ values calculated for particle and gas phases in actual samples are an approximation.

Precipitation

The rainfall registered during the sampling period was 108 mm (2990 ml of precipitation collected), following a dry period of several months. A deposition of 137 WHO-TEQ pg/m^2 resulted during this week (Table 1). This value and the congener pattern distribution (Figure 3) were in agreement with levels previously reported^{7, 9}.

Settling material

The total amount of collected settling material was 15 g and the concentration obtained was 11 WHO-TEQ pg/g (Table 1). The pattern distribution (Figure 3) was similar than the one reported for sediments⁸.

Bottom sediments

Low PCDD/Fs concentrations were found in bottom sediments samples. Values varied from 0.13 to 17 WHO-TEQ pg/g. Congener patterns obtained are depicted in Figure 2. All sediment analysed showed similar fingerprints pointing out the homogeneity of this pattern in the processed samples from different parts of LM (Figure 1). The patterns are in agreement with findings reported in available literature⁸.

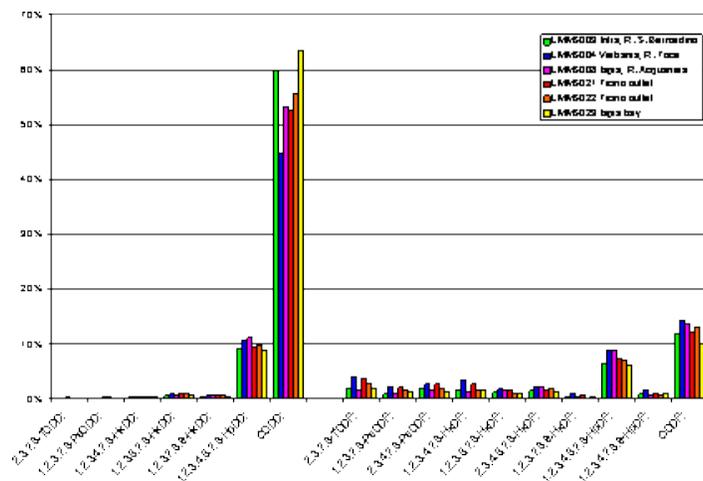


Figure 2: PCDD/F congener patterns from bottom sediments of Lake Maggiore.

Consistency of PCDD/F fingerprints

Except for the PCDD/F pattern found in the gas phase (Figure 3), the fingerprints of the other compartments were very similar. This suggests that the atmospheric particulate matter is the prominent driver of PCDD/F deposition into and through the water column. Wet and dry particulate depositions seemed to determine the PCDD/Fs flux along with the settling material into the sediments.

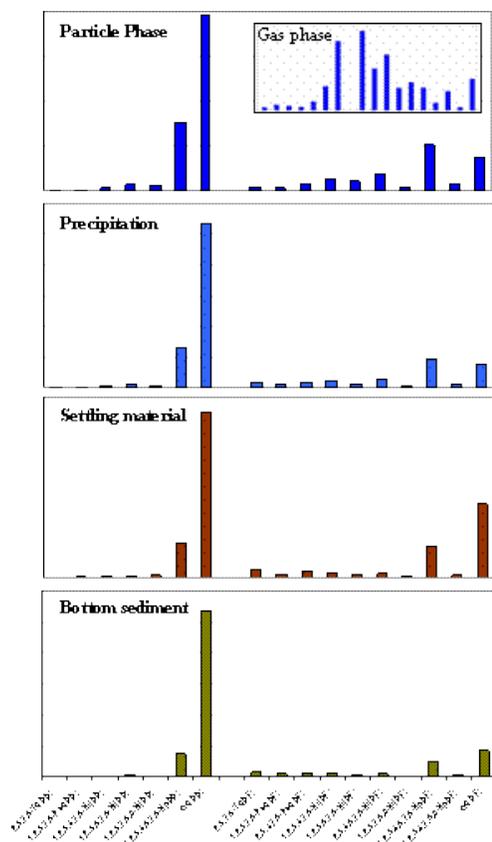


Figure 3: PCDD/F congener patterns of the deposition chain into Lake Maggiore.

The fact that the PCDD/F patterns of particulate matter and sediments in LM showed a typical atmospheric long range transport signal⁸, demonstrated a minor impact from local sources.

PCDD/F fluxes into LM during 22-30 March 2005 at Ispra bay

In order to check the hypothesis that the sedimentation of PCDD/Fs into LM is mainly driven by the atmosphere, we present a comparison of the related fluxes into and through the water column, estimated on the basis of the concentration data presented in Table 1. Dry particulate matter flux into the water column was estimated on the basis of atmospheric particulate matter concentration (TSP) in Ispra air (average of $65 \mu\text{g}/\text{m}^3$ during 22-30 March 2005)⁵ and the related PCDD/Fs data, assuming a deposition velocity of $0.2 \text{ cm}/\text{s}$ ¹⁰⁻¹¹. Wet deposition was calculated from the amount of PCDD/Fs measured in the rain sampler. The flux of settling material (SM) and the related PCDD/F flux through the water column were estimated from the sediment trap data during that time.

Finally, the flux into the bottom sediment was approximated from the grab sample representing an area of 0.015 m^2 and a depth of 10 cm. Assuming a sedimentation rate at the Ispra bay ranging between $0.25 - 0.5 \text{ cm per year}$ ¹²⁻¹³, the sediment sample would represent a sedimentation record of 20 to 40 years. Resulting fluxes are summarized in Table 2.

Table 2: Estimate of weekly fluxes into Lake Maggiore.

Type of flux	Particle deposition	Wet deposition	Settling material	Bottom sediment
	22-30 Mar 05	22-30 Mar 05	17 Dec 04-19 Apr 05	2 Feb 05
TSP/SM/Sediment	77 mg/m ²	n.d.	4.5 g/m ²	7.5-15 g/m ²
PCDD/Fs (WHO-TEQ)	17 pg/m ²	136 pg/m ²	50 pg/m ²	125-250pg/m ²

The PCDD/F data for dry particulate fluxes and wet deposition into LM match fairly well the PCDD/F flux of settling material taking into account, that we are comparing the weekly averages of atmospheric deposition fluxes of the last week of March 2005 with a settling material flux measured between December 04 and April 05.

The flux estimate into the bottom sediment of Ispra bay is higher compared to the flux of settling material. This may be explained by the fact that the bottom sediment sample represents the whole annual cycle of sedimentation, including the atmospheric inputs during the rainy winter season, where PCDD/F and particulate matter concentrations and the related fluxes are higher than during the period in March 2005 where the data on ambient air and settling material were acquired.

Despite the preliminary character of the data presented, the PCDD/Fs fingerprints and the related flux estimates suggested a prominent role of atmospheric deposition in the accumulation of PCDD/Fs in LM sediments.

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