

Occurrence of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in Lake Maggiore (Italy and Switzerland)†

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Received 23rd January 2007, Accepted 12th March 2007

First published as an Advance Article on the web 11th April 2007

DOI: 10.1039/b700919d

Samples of air (gas and particulate phases), bulk deposition, aquatic settling material and sediments were collected in Lake Maggiore (LM) in order to determine their content of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Air (gas and particulate phases) concentrations were 0.5 pg m⁻³, 80 pg m⁻³, 13 pg m⁻³ and 106 pg m⁻³ for ΣPCDD/Fs, ΣPCBs, Σ dioxin-like PCBs (DL-PCBs) and ΣPBDEs, respectively. Deposition fluxes ranged from 0.7 ng m⁻² d⁻¹ for ΣPCDD/Fs to 32 ng m⁻² d⁻¹ for ΣPCBs. Aquatic settling material presented concentrations of 0.4 ng g⁻¹ dry weight (dw) for ΣPCDD/Fs, 13 ng g⁻¹ dw for ΣPCB, 3.4 ng g⁻¹ dw for ΣDL-PCBs and 5.7 ng g⁻¹ dw for ΣPBDEs. Mean sediment concentrations were 0.4 ng g⁻¹ dw for ΣPCDD/Fs, 11 ng g⁻¹ dw for ΣPCB, 3 ng g⁻¹ dw for ΣDL-PCBs and 5.1 ng g⁻¹ dw for ΣPBDEs. Similar PCDD/F and DL-PCB congener patterns in all the environmental compartments of LM point to an important, if not dominant, contribution of atmospheric deposition as source of these pollutants into LM. In contrast, PBDE congener distribution was not similar in the different environmental compartments. BDE 47 dominated air and settling material, while BDE 209 was the predominant congener in the bulk atmospheric deposition. Moreover, sediments showed two distinct PBDE congener profiles. Lower PBDE concentrated sediments were dominated by congeners 47 and 99, while BDE 209 dominated in higher PBDE concentrated samples. This suggests the influence of local sources as well as atmospheric input of PBDEs into LM.

Introduction

Anthropogenic contaminants are loaded into aquatic systems through point and diffuse sources. Depending on their physico-chemical properties, their use and transport processes, chemical distribution may be widespread or local. Aquatic sediments are a sink for hydrophobic organic contaminants and may pose an unacceptable risk to aquatic organisms.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants which enter the environment as a result of anthropogenic activities. These compounds, emitted into the atmosphere, can be transported over long distances.¹ After deposition they are distributed into various environmental

compartments. Many congeners bioaccumulate and are considered potent toxicants, capable of producing a wide spectrum of adverse health effects in biota and humans, such as cognitive disorders, immunosuppression, skin disease, carcinogenicity, reproductive and developmental toxicity, disruption of the endocrine system, induction of enzymes, estrogenic and anti-estrogenic effects.²⁻⁵ These group of chemicals are present in complex mixtures in the environment.

PCDD/Fs are formed as unintentional byproducts of chemical manufacturing and incineration processes.^{6,7} Emissions from incineration of industrial wastes such as metal reclamation and domestic heating (especially in central Europe) are considered as current sources of PCDD/Fs to the environment.^{8,9} Among the 210 different PCDD/F congeners, only those isomers presenting chlorine substitution in the 2,3,7,8 positions have been reported to present toxic properties.¹⁰

PCBs were mainly used by the power industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants. These compounds were also added to many consumer products, like adhesives, waxes and inks. Since the mid 1970s PCBs have been banned from active use in most countries due to their toxicity and extreme persistence. However, sediments of rivers, lakes, and oceans, and soils of temperate areas, as well as marine waters are primary locations for PCB

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† Presented at Sources, Fate, Behaviour and Effects of Organic Chemicals at the Regional and Global Scale, 24th–26th October 2006, Lancaster, UK.

accumulation in the environment and, therefore, themselves can act as emission sources if environmental conditions change.^{11–13}

Twelve out of the 209 existing PCB congeners have been identified as dioxin-like PCBs (DL-PCBs) by the World Health Organization (WHO).¹⁰ Their molecular characteristics make them similar to the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD), since they can adopt a co-planar configuration, and they exhibit toxicity in a manner similar to dioxins.¹⁴

PBDEs constitute an important group of brominated flame retardants and, unlike PCBs, are still being used as additives in commercial products (especially in electrical equipment and textiles) to meet fire safety regulations. Three major PBDE commercial mixtures are commonly used worldwide: Deca-BDE, Octa-BDE and Penta-BDE. Their usage in Europe during 2001 was 7600, 610, and 150 tons, respectively.¹⁵ According to the EU Risk Assessment,^{16,17} the Penta- and Octa-BDE formulations are banned since August 2004,¹⁸ while the Deca commercial product received an exemption to the ban, and this exemption is presently under evaluation. Temporal trends have shown recent PBDE concentrations to increase in sediment and biota tissues.^{19–22} The occurrence of these compounds in the environment has also been reported in remote sites, where the atmosphere is the only pollutant input pathway.^{15,20,22–25} The widespread environmental presence and global distribution of PBDEs deserve growing concern because of their stability, lipophilicity and potential bioaccumulation and toxicity.^{22,26,27}

PCDD/Fs, PCBs and PBDEs are delivered to lake systems by atmospheric deposition, air–water interchange, direct discharges and riverine inputs. These compounds are characterized by low aqueous solubilities, medium vapour pressures, and resistance to extensive physical, chemical and biological transformation. Their general hydrophobic nature results in high partition coefficients to organic matter, to biotic tissues and to black carbon delivered into the lake system.

PCDD/Fs, PCBs and PBDEs exist in the atmosphere as gases and bound to particles. Most measurements are dominated by the aerosol concentrations for PCDD/Fs, whereas total airborne PCBs are normally dominated by the gas-phase burden.^{28,29} Most of the PBDEs are evenly distributed between gas and particle phases.^{30,31}

Once delivered to the water column, the primary removal processes are sedimentation of atmospheric particles and partitioning of the gaseous/dissolved phase contaminants into organic carbon (OC)-rich particles with subsequent settling, and finally accumulation in surface sediments. The final contaminant and particle burial is slowed by the effects of resuspension of sediments and bioaccumulation in aquatic organisms.

The present study was conducted in Lake Maggiore (LM) situated at the south of the Alps, northwest of the industrialized area of Milan, Italy (Fig. 1). The lake is located at 194 m above sea level and is the second largest (212.5 km²) and the deepest (370 m) of the Italian lakes. Input from the catchment area (6600 km²) into the lake occurs directly and through three major rivers and numerous smaller creeks. The Ticino River is the only outflow from LM. Besides a recreational use of its

waters (swimming, diving and yachting), the lake is used as source of water for the population in the area, fisheries and navigation.

Several studies carried out in LM have provided insight into the pollution levels of the lake: mercury contamination from mining and other industrial activities, eutrophication, and more recently a large DDT discharge into the lake. DDTs, hexachlorocyclohexanes, hexachlorobenzene and PCB concentrations have been determined in water, sediments and biota from the lake.^{32–35} Concentrations of polycyclic aromatic hydrocarbons in surface water and precipitation input to the lake have been recently reported.³⁶ However, only few data on environmental concentrations and fate of PCDD/Fs, DL-PCBs and PBDEs in this aquatic system are available to date.^{37–40}

The aim of the present study is to expand the existing database on persistent organic pollutants in the different environmental compartments of LM and to elucidate the role of the atmosphere as an important source of pollutants into the lake. To achieve our goals, air (gas and particulate phases), bulk deposition, aquatic settling material, and sediment samples were collected and analysed for 17 toxic PCDD/F, 18 PCB and 8 PBDE congeners.

Methods

Sampling

Sample location details are depicted in Fig. 1.

Air and bulk deposition. A high volume air sample and bulk deposition sample were collected simultaneously from March 22nd to March 30th 2005 at the Joint Research Centre (JRC) EMEP site (Cooperative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) at Ispra, Italy. Meteorological conditions of this period were characterised by minimum and maximum temperature ranges of 6–10 °C and 12–25 °C, respectively, an average wind speed of 7 m s⁻¹ and a bulk precipitation of 108 mm. Meteorological data were obtained from the European Solar Test Installation site at JRC.

Air samples were collected with a high volume sampling device (Echo PUF Hi Volume Sampler, TCR Tecora, Milan, Italy) equipped with a pre-cleaned glass fiber filter (GFF) (102 mm diameter) and a pre-cleaned polyurethane foam (PUF) (65 mm diameter) for sampling particulate and gas phases, respectively. A sample of 845 m³ was collected and both phases were separately analysed.

A validated rain collector holding three glass funnels of 188 mm diameter each was used for the precipitation collection. A PUF plug of 18 mm diameter and 100 mm length was placed in each neck funnel.⁴¹ Precipitation intensity was estimated by gravimetry. During the sampling period \approx 3 L of bulk precipitation were collected.

Aquatic settling material. Aquatic settling matter was collected with a sediment trap at a depth of 27 m and 3 m above the lake sediment, covering a period of 4 months, from December 2004 to April 2005. The sediment trap was deployed at Quassa Bay (southern part of LM) at a distance of 400 m

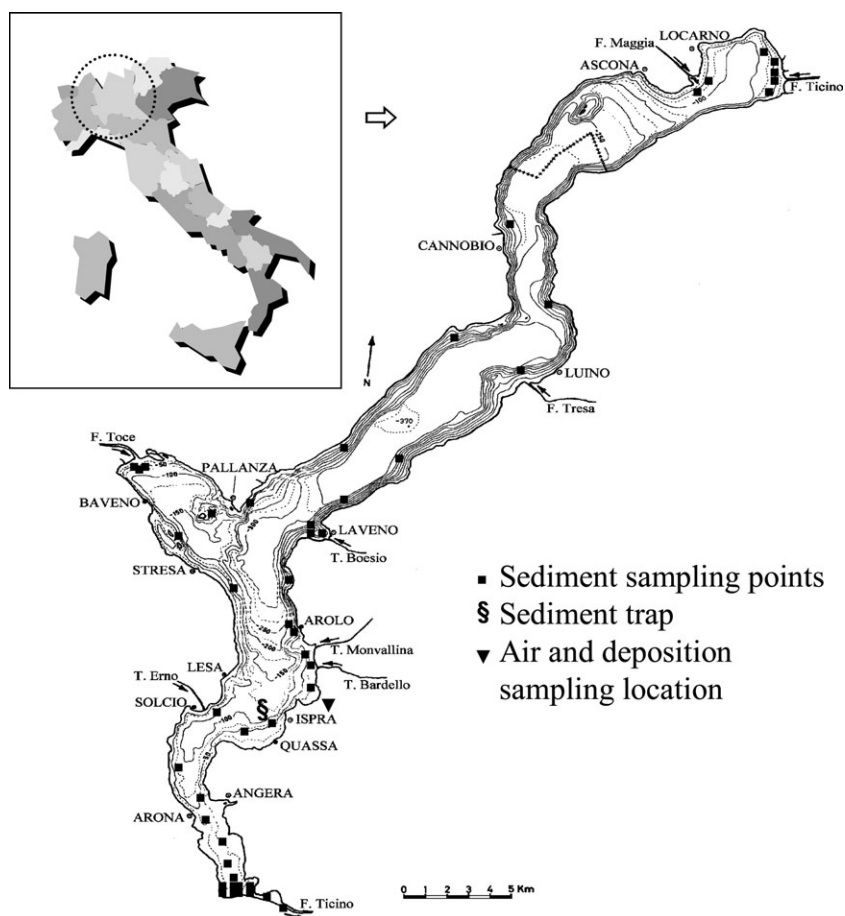


Fig. 1 Location of Lake Maggiore and sampling sites.

from the coast and about 2.5 km from the atmospheric sampling site. This location is a sedimentation zone with no direct inputs from local tributaries.

The sediment trap was a stainless steel cylinder (50 cm diameter and 150 cm length with funnel end) that leads into a 250 mL glass vessel equipped with an acoustic release unit 7986 LRT (Sonardyne, Yateley, UK). The collected sample (16 g) was centrifuged, decanted, frozen, freeze dried and stored in dark bottles in a cool place until analysis. An amount of 5 g was processed.

Sediment. Forty-eight superficial sediment samples were collected at depths between 5 and 60 m in LM during 2005. The sediment sampling sites were homogeneously distributed along the extension of the lake, including sites near river inlets/outlets and sites located in settling basins (Fig. 1).

Sediment samples were collected using a Ponar Grab Sampler from a boat. The sampled sediment depth was around 10 cm. Supernatant was decanted and sediments were frozen and freeze dried (Lio5P, 5 Pascal, Trezzano, Italy). Material > 2 mm was removed by sieving. Sediment samples were then stored in dark bottles in a cool place until analysis. Each processed sample consisted of about 30 g dry weight (dw).

Chemicals

All organic solvents were dioxin analysis grade from Sigma–Aldrich (Buchs SG, Switzerland). All the gases (Alpha-

gaz, Italy) used were ultrapure grade suitable for PCDD/F analysis. Sulfuric acid 98% extra pure was obtained from VWR International s.r.l. (Milan, Italy). Pre-packed multi-layer silica, basic alumina and carbon columns were purchased from Fluid Management Systems Inc. (Watertown, MA, USA).

Glass fiber extraction thimbles (MN649) were purchased from Macherey-Nagel (Düren, Germany) and copper powder (–200 mesh, 99%) was from Sigma–Aldrich (Steinheim, Germany).

EPA-1613-CVS, EPA-1613LCS and EPA-1613-ISS (Wellington Laboratories, Guelph, Ontario, Canada) were native, ^{13}C -labelled internal and injection standards, respectively, for 17 PCDD/F congeners.

^{13}C -labelled PCB standards (EC 4058) were obtained from CIL (Andover, MA, USA). Standard mixtures 68-CVS and 68-LCS (Wellington Laboratories, Guelph, Ontario, Canada) were native and ^{13}C -labelled internal standards for 12 DL-PCB congeners, respectively.

Penta/octa/deca-bromo standard solutions were obtained from Dr Ehrenstorfer GmbH (Augsburg, Germany). ^{13}C -labelled standards (according to IUPAC nomenclature: BDE-28, BDE-47, BDE-99, BDE-100, BDE-118, BDE-153, BDE-183) were obtained from CIL (Andover, MA, USA).

Sample extraction and cleanup

A sample preparation method for determination of PCDD/Fs and PCBs was adopted to include PBDEs in the analysis of the

extract of different matrices. Samples were extracted with a mixture of *n*-hexane–acetone (220 : 30; v/v) by Soxhlet for 24 h after being spiked with ¹³C-labelled internal standards (16 congeners of 2,3,7,8-PCDD/F, 7 congeners of PCBs, 12 congeners of dioxin-like PCBs and 7 congeners of PBDEs). For sediments and settling material, copper powder was added to the solvent during the extraction to remove sulfur. Extracts were evaporated to nearly dryness and refilled to 10 mL with *n*-hexane.

Sediment and settling material extracts were treated with concentrated H₂SO₄ prior the following purification step. This oxidative process provides a good procedure to eliminate many organic components that could interfere in the analyses by GC.

Cleanup of the extracts was executed with an automated system (Power Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA). This system, previously described by Abad *et al.*,⁴² uses a multi-layer silica column, a basic alumina column and a carbon column combination. Two fractions were collected, one containing indicator PCBs and PBDEs and one for PCDD/Fs and DL-PCBs.

Purified extracts were evaporated to nearly dryness under a gently nitrogen flow (Turbovap, Zymark, USA) and filled up with 30 μL of toluene.

Prior to injection, ¹³C-labelled standards were added to determine the recoveries of the internal standards.

Instrumental analysis

Instrumental analysis of PCDD/Fs, PCBs and PBDEs was carried out using a high resolution gas chromatograph (HP-6890, Hewlett Packard/Agilent, Waldbronn, Germany) coupled with a VG Autospec Ultima high resolution mass spectrometer (Micromass, Manchester, UK) (HRGC/HRMS). The operating mode was electron impact at 34 eV with a resolution of > 10 000. Split/splitless injector was set at 300 °C.

Non-*ortho* PCBs and PCDD/Fs were analyzed on a BP-DXN capillary column, whereas for the mono-*ortho* PCBs an HT-8 capillary column was used. Both columns were 60 m long, 0.25 mm i.d. (inner diameter) and 0.25 μm film thickness. PBDEs were analyzed on a Sol-Gel-1 MS capillary column, 15 m long with 0.25 mm i.d. and 0.1 μm film thickness. All capillary columns were obtained from SGE, Victoria, Australia.

For PCDD/F and PCB congeners and the corresponding labelled standards two ions each were registered. For tri- to octa-brominated congeners, two ions of the isotopic molecular cluster were recorded both for native and labelled congeners. For nona- and deca-brominated congeners two isotopic ions of the cluster M⁺-2Br were recorded for native compounds. The identification was done by retention time comparison of the corresponding internal standard and isotopic ratio between two ions recorded. When standards were not available, identification was optimised following literature indications.^{43–46}

Quantification was done by the isotope dilution method following the EPA1613, EPA1614 and EPA1668 protocols, except for deca-BDE where the internal standard ¹³C-BDE-183 was used.

Levels are reported as ΣPCDD/Fs, ΣPCBs, ΣDL-PCBs and ΣPBDEs. The PCDD/Fs analysed were all the 2,3,7,8-chlorine substituted congeners. ΣPCB includes the indicator PCB congeners with IUPAC numbers 52, 101, 118, 138, 153, and 180. ΣDL-PCBs included four non-*ortho* PCBs (congeners 81, 77, 126, and 169) and eight mono-*ortho* PCBs (congeners 105, 114, 118, 123, 156, 157, 167, and 189). These congeners comprise the so-called dioxin-like PCBs as described by the WHO. PBDEs analysed included congeners 28, 47, 100, 99, 154, 153, 183, and 209.

Total organic carbon analysis

The content of total organic carbon (TOC) of sediments was analyzed using a TOC-5000A instrument (Shimadzu, Europe GmbH) according to the ISO10694 method.

QA/QC

Quality assurance and quality control were done by carrying out simultaneously laboratory blanks together with each batch of 15 samples. Only concentration values at least 10 times higher than the blank values were considered in the present work.

The detection limits were calculated directly on the samples taking into consideration a signal/noise ratio of 3/1. Recoveries of the ¹³C-labelled compounds in all cases ranged from 50 to 100%, which falls within the limits established by the EPA standard methods.

In addition, the analytical methodologies employed were tested by the parallel analysis of a sediment sample from the 9th International Intercalibration Study⁴⁷ for PCDD/Fs and PCBs. No environmental matrix was available as reference material for PBDE analysis.

Results and discussion

The pollutant levels in air (gas and particulate phases), deposition, settling material and sediments of LM are summarised in Table 1 and the chemical groups are separately discussed below.

PCDD/Fs

The ΣPCDD/F (gas and particulate phases) concentrations in air and bulk deposition near LM were 532 fg m⁻³ and 760 pg m⁻² d⁻¹, respectively (Table 1). These values are in agreement with levels reported for rural sites.^{48–52} ΣPCDD/F concentrations in the particulate phase were one order of magnitude higher than in the gas phase. Bulk deposition flux is approximately one order of magnitude less than what has been found in polluted sites in Japan.⁵³

PCDD/Fs were found in all sediment samples (*n* = 48), including those under direct influence of riverine inputs. ΣPCDD/F sediment concentrations ranged from 3.5 pg g⁻¹ dw to 2211 pg g⁻¹ dw (0.1–32 pg WHO TEQ g⁻¹ dw), with a mean value of 435 pg g⁻¹ dw (Table 1). Settling material presented a similar PCDD/F concentration value (490 pg g⁻¹ dw).

ΣPCDD/F sediment concentrations in the present study are in the range of those considered to be background levels due to atmospheric deposition.^{54–56} Suspended particulate matter

Table 1 Levels of PCDD/Fs, PCBs and PBDEs in air, bulk deposition, settling material and sediments in Lake Maggiore

Compound	Air gas phase	Air particle phase	Bulk deposition	Settling material	Surface sediment
	Ispra JRC 22–30 Mar 05 /pg m ⁻³	Ispra JRC 22–30 Mar 05 /pg m ⁻³	Ispra JRC 22–30 Mar 05 /ng m ⁻² d ⁻¹	Ispra bay 17 Dec 04–19 Apr 05 /ng g ⁻¹ dry weight	2005–2006 /ng g ⁻¹ dry weight
ΣPCDDs ^a	0.023	0.29	0.53	0.29	0.34 (<i>n</i> = 48)
ΣPCDFs ^a	0.059	0.16	0.23	0.20	0.095 (<i>n</i> = 48)
ΣPCBs ^b	73	6.6	32	13	11 (<i>n</i> = 22)
ΣDL-PCBs ^c	11	1.5	7.0	3.4	3.0 (<i>n</i> = 22)
ΣPBDEs ^d	77	29	17	5.7	5.1 (<i>n</i> = 8)

^a All 2,3,7,8 substituted congeners. ^b 52,101,118,138,153 and 180 congeners. ^c Non-ortho (81, 77, 126, 169) and mono-ortho (105, 114, 118, 123, 156, 157, 167, 189) congeners. ^d 28, 47, 100, 99, 154, 153, 183 and 209 congeners.

from up-stream of Trenton Chanel in Detroit River (non-impacted zone) presented similar values.⁵⁷

The spatial distribution of ΣPCDD/Fs in LM shows that sediments located in the northern basin(s) exhibit significantly lower concentrations than the ones from the central and southern basins (*p* < 0.001). Mean ΣPCDD/F values from the north (*n* = 11), central (*n* = 23) and south (*n* = 14) sediments are 64 pg g⁻¹ dw, 489 pg g⁻¹ dw and 648 pg g⁻¹ dw, respectively. The north–south gradient could be caused from the flushing of the sediment from the north to the south due to intermittent re-suspension in the shallower north basin and the natural north–south direction of lake water flow, as well as input locally only to the southern basin.

When PCDD/F concentrations are normalized to TOC content, the spatial variation between samples decreases from a factor of 246 (dw basis) to a factor of 85 (OC weight basis). This observation is supported by the plot of ΣPCDD/F concentrations versus sedimentary TOC (Fig. 2). Sediments from flushing regions (near riverine inlets and outlets) of the lake show a linear relationship between concentration and TOC, while the settling basin sediments show a logarithmic relationship. Moreover, settling basin sediments present significantly higher TOC normalized PCDD/F concentrations than the ones found in flushing sediment regions (*p* < 0.001). These findings suggest that in the settling basins, where

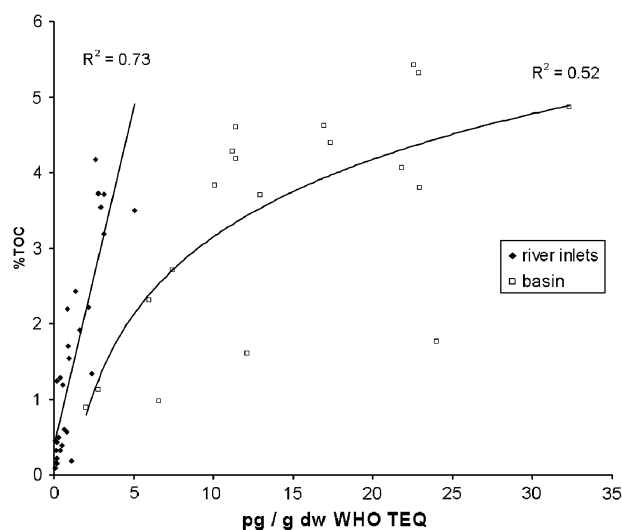


Fig. 2 PCDD/F concentration (expressed in pg g⁻¹ WHO-total toxic equivalent) vs. total organic carbon of the sediment.

organic matter is continuously settling, decomposition of organic matter leads to a reduction of OC, and therefore a higher PCDD/F load per unit of TOC.

Fig. 3 shows the PCDD/F congener profile distribution in the LM basin. Throughout the basin, congener profiles are remarkably similar, dominated by octachloro- and heptachloro-dioxins, followed by octachloro- and heptachloro-furans. This sedimentary pattern is attributed to long range atmospheric transport.^{48,55,56} At all but two sites, a single congener (OCDD) accounted for more than 40% of the total PCDD/Fs. The sediment sample taken at the inlet of River Bardello (Fig. 1) differed from the general pattern, and the distribution was dominated by octachlorodibenzofuran followed by octachlorodibenzodioxin. The predominance of the cited PCDD/F congeners has been related to industrial processes, such as oxychlorination or ethylene dichloride production^{56,58} and metal industry.⁵⁹ However, in the present study, the PCDD/F source for the Bardello sediment signal could not be identified.

The spatial homogeneity of the PCDD/F sediment pattern along the whole lake underlines the absence of important local sources and riverine inputs into LM. Moreover, the sediment pattern is similar to that of PCDD/Fs in atmospheric particulate matter and bulk deposition (Table 2), which, as stated before, represents a typical profile for long range atmospheric transport. Mass balance fluxes of PCDD/Fs into LM as well as congener patterns in the different compartments of the lake presented elsewhere⁶⁰ suggest that atmospheric deposition is

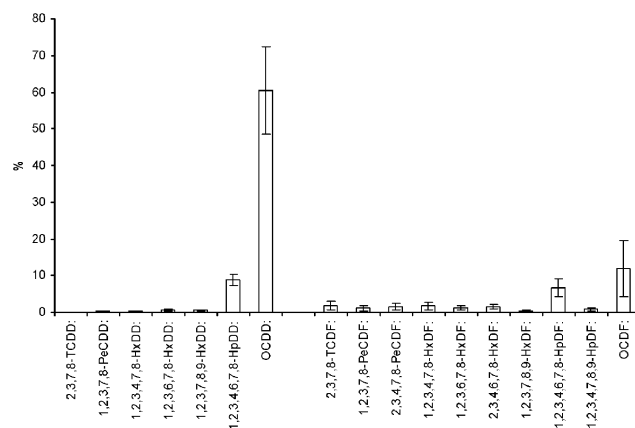


Fig. 3 PCDD/F congener pattern in the Lake Maggiore sediments (average % ± SD) (*n* = 48).

Table 2 PCDD/Fs, PCBs, DL-PCBs and PBDEs congener patterns (%) in air, bulk deposition, settling material and sediments of Lake Maggiore

Compound		Gas phase ^a	Particulate phase	Bulk deposition	Settling material	Sediments	
2,3,7,8- isomers PCDD/Fs	TCDD	0.6	0	0.1	0.1	0.1	
	PeCDD	1	0.2	0.2	0.2	0.2	
	HxCDD	4	4	2	2	2	
	HpCDD	6	17	13	10	9	
	OCDD	16	44	55	47	60	
	TCDF	18	1	2	2	2	
	PeCDF	23	3	3	3	3	
	HxCDF	18	10	7	4	5	
	HpCDF	6	13	11	10	8	
	OCDF	7	8	8	21	12	
	PCBs	TeCB-52	28	19	33	8	13
		PeCB-101	19	15	17	13	17
		PeCB-118	8	9	9	13	14
HxCB-138		15	19	15	22	20	
HxCB-153		22	20	18	26	23	
HpCB-180		7	17	9	18	14	
DL-PCBs	TeCB-81	0.4	0.6	0.9	0.2	0.2	
	TeCB-77	8	15	20	5	4	
	PeCB-126	0.4	0.5	0.4	0.5	0.6	
	HxCB-169	0.04	0.1	0.1	0.1	0.1	
	PeCB-105	20	22	24	21	18	
	PeCB-114	2	2	2	1	1	
	PeCB-118	56	39	40	50	53	
	PeCB-123	1	0.8	0.8	0.8	0.8	
	HxCB-156	8	12	7	12	13	
	HxCB-157	1	2	1	2	2	
	HxCB-167	4	5	3	5	6	
	HpCB-189	0.2	1	0.9	2	2	
	PBDE ^b	BDE-28	3	0	0.5	2	1
BDE-47		93	59	14	34	28	
BDE-100		1.2	6	3	6	7	
BDE-99		1.7	14	11	29	28	
BDE-154		n.d.	1	2	8	5	
BDE-153		n.d.	1	4	4	5	
BDE-183		n.d.	2	17	8	8	
BDE-209		n.d.	16	48	9	17	

^a n.d. not detected. ^b Two distinct sediment patterns were found. Mean relative distribution is presented for each group.

the dominant input mode for the introduction of PCDD/Fs into LM sediments.

Indicator PCBs. Air (gas and particulate phases) shows a Σ PCB concentration of 80 $\mu\text{g m}^{-3}$ (Table 1). This value is similar to those reported for rural and remote sites from around the world.^{28,61–68} More than 90% of all PCBs analysed in air were found in the gas phase, in agreement with previous studies.^{28,29,61,65}

Bulk deposition showed a Σ PCB flux of 32 $\text{ng m}^{-2} \text{d}^{-1}$ (Table 1). This value is in the range of what has been found in European and North American rural and urban sites (3.8–20 $\text{ng m}^{-2} \text{d}^{-1}$).^{69–71} However, remote sites and the open oceans present Σ PCB deposition concentrations at least one order of magnitude less than in LM.^{72,73}

Σ PCB settling material concentration was of 13 $\text{ng g}^{-1} \text{dw}$ (Table 1). This value is within the range found in a study on the River Guadiana in Portugal that reported concentrations between 0.4 $\text{ng g}^{-1} \text{dw}$ and 30 $\text{ng g}^{-1} \text{dw}$ for suspended particulate matter.⁷⁴

Sediments exhibit Σ PCB concentrations between 0.3 $\text{ng g}^{-1} \text{dw}$ and 38 $\text{ng g}^{-1} \text{dw}$, with a mean value of 11 $\text{ng g}^{-1} \text{dw}$ ($n = 22$) (Table 1). These values are in agreement with values reported in another study on LM.⁷⁵ Sediments from River Guadiana (Portugal) and Niagara River (USA) show Σ PCB

concentrations of 0.1–1.8 $\text{ng g}^{-1} \text{dw}$ and 1.7–124 $\text{ng g}^{-1} \text{dw}$,^{74,76} respectively. Rural and remote lake sediments present lower range of Σ PCB concentrations (0.05–2.5 $\text{ng g}^{-1} \text{dw}$ in Finland and 2.3–15 $\text{ng g}^{-1} \text{dw}$ in European high mountain lakes).^{55,77}

PCB congener pattern varied among the different environmental compartments of LM (Table 2 and Fig. 4). PCB 52 dominated the atmospheric gas phase and deposition profiles (around 30% of the total PCBs). This is in agreement with results presented for other rural areas.⁶⁵

Higher chlorinated PCBs (congeners 138 and 153) were predominant in the settling material and sediments (each around 20% of Σ PCB) (Table 2 and Fig. 4). The predominance of congeners 138 and 153 in sediments has been widely found in other freshwater ecosystems.^{76,77} Congener 153 was also the most abundant in the LM sediments published elsewhere.⁷⁵

Dioxin-like PCBs

Σ DL-PCB concentration in air (gas and particulate phases) was 13 $\mu\text{g m}^{-3}$ (Table 1). This value is nominally higher than the levels reported for rural area in Germany.⁷⁸ Gas-phase DL-PCB concentrations were higher than in the aerosol, as observed with the other PCB congeners reported.

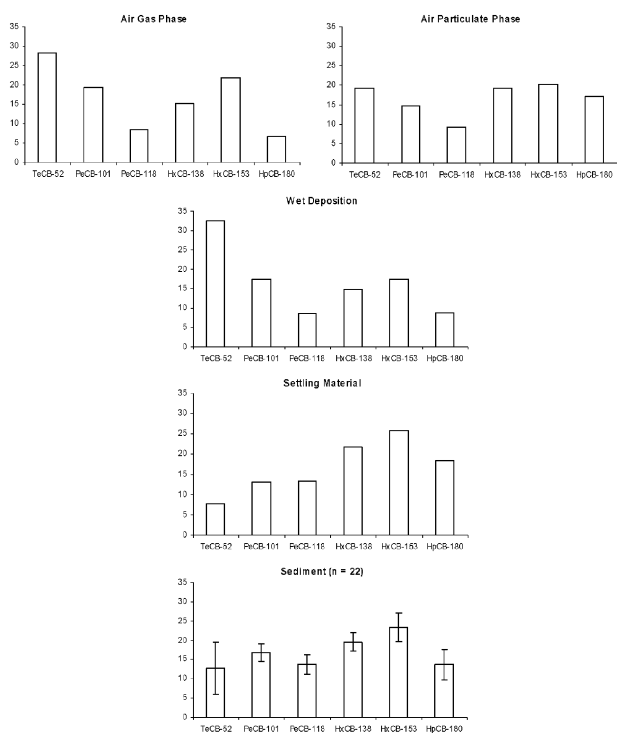


Fig. 4 PCB congener pattern of the deposition chain into the Lake Maggiore.

Total deposition flux of Σ DL-PCB was $7 \text{ ng m}^{-2} \text{ d}^{-1}$ (Table 1). Similar values have been reported for an urban area in Japan.⁵³ The settling material presented Σ DL-PCB concentrations of $3.4 \text{ ng g}^{-1} \text{ dw}$ (Table 1). This is in the range of values considered as background level in other studies.⁵⁷

Σ DL-PCB concentrations in surface sediments ($n = 22$) ranged between $0.08 \text{ ng g}^{-1} \text{ dw}$ and $11 \text{ ng g}^{-1} \text{ dw}$. Mean DL-PCB concentration in sediment was $3 \text{ ng g}^{-1} \text{ dw}$ (Table 1). DL-PCB concentrations found in sediments from a lake in China are in the lower range of those reported in the present study,⁷⁹ while similar values to our results are found in coastal sediments in Spain.⁵⁶

The congener patterns were similar in all studied compartments (Table 2). Among the non-ortho congeners, PCB-77 was found at a highest concentration, whereas PCB-118 followed by PCB-105 and PCB-156 were predominant among the mono-ortho congeners. Similar results were reported from a rural area in Germany,⁷⁸ from coastal sediments in Spain⁵⁶ and from Chinese lake sediments.⁷⁹

The homogeneity in DL-PCB congener pattern in all the environmental compartments (Table 2) indicates that the atmosphere is the dominant source of these pollutants into LM. An estimation of DL-PCB mass balance fluxes in LM supports these findings.⁶⁰

PBDEs

Σ PBDE air (gas and particulate phases) concentration was 106 pg m^{-3} , and 72% was in the gas phase (Table 1). Similar PBDE concentrations values were found in air of urban sites in Europe,^{80,81} North America,^{31,82} and Asia.⁸³

Air PBDE congener pattern was dominated in both phases by BDE 47 (Table 2). The higher contribution of congener 47 in air samples has also been found by Shen *et al.*⁶⁷ and Stranberg *et al.*³¹ in the North America atmosphere. BDE 154, 153, 183 and 209 were only detected in the particulate phase of the air. PBDEs have been described to be distributed between the gas and the particle phases, with lighter congeners found in the gas phase and heavier ones in particle phase.^{30,31}

Deposition of Σ PBDE was $17 \text{ ng m}^{-2} \text{ d}^{-1}$ (Table 1). Similar values of PBDE deposition have been reported for rural sites in other studies.^{41,84} BDE 209 was the predominant congener in the bulk deposition as it has for other studies.^{41,84}

Settling material exhibited a Σ PBDE concentration of $5.7 \text{ ng g}^{-1} \text{ dw}$ (Table 1). Only a few studies report PBDEs in settling material in lakes. Moche and Stephan⁸⁵ reported $0.38 \text{ ng g}^{-1} \text{ dw}$ and $1.1 \text{ ng g}^{-1} \text{ dw}$ for two samples of suspended particulate matter in the River Danube in Austria (17 BDE congeners considered). Congeners 47 and 99 accounted for nearly 65% of the total PBDE concentration found in settling material (Table 2). BDE 47 and 99 concentrations in the present work were similar to a study carried out in surface waters in the Netherlands.⁸⁶ However, the mentioned study reports higher concentrations for BDE 209 (mean of $71 \text{ ng g}^{-1} \text{ dw}$) than found in LM ($0.52 \text{ ng g}^{-1} \text{ dw}$).

Minimum and maximum Σ PBDE concentrations in sediments ($n = 8$) were $0.06 \text{ ng g}^{-1} \text{ dw}$ to $27 \text{ ng g}^{-1} \text{ dw}$, respectively. A mean concentration of Σ PBDE in sediments was $5.1 \text{ ng g}^{-1} \text{ dw}$ (Table 1). The range of BDE concentrations is similar to what has been reported for other freshwaters.^{76,85–89}

Two different congener profiles were found in the set of sediment samples (Table 2). BDE 209 was the predominant congener in sediment samples with high concentrations of PBDEs. However, BDE 47 and 99 were predominant in samples with low concentrations. Congener BDE 209 constituted between 50–99% of the total PBDE concentrations in Spanish coastal sediments, with a higher range of concentration ($2.7 \text{ ng g}^{-1} \text{ dw}$ to $134 \text{ ng g}^{-1} \text{ dw}$) in comparison with our results.⁵⁶

Conclusions

PCDD/F, PCB and PBDE content in air, bulk deposition, settling material and sediments from Lake Maggiore was analysed. Concentrations of these pollutants were in the range of those reported for rural areas and other freshwater systems with background environmental levels.

The atmospheric particulate phase PCDD/F pattern was similar to the ones found in all the environmental compartments studied in the lake. In contrast, lighter PCBs dominated the air gas phase whereas heavier PCBs were predominant in settling material and sediments.

Two distinct congener distribution profiles were found for PBDEs in sediments, which may respond to the existence of local input sources for these pollutants into LM.

Ongoing research on LM will evaluate, in more depth, the spatial and temporal variances of these pollutants in order to identify the existence of local sources and the annual contribution of atmospheric loads.

Acknowledgements

We thank Wolfgang Mehl and Friedrich Lagler for the help with the recovery of the sediment trap and Alessandro Dell'Acqua for the collaboration regarding the EMEP Station.

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