

PCDD/F, DL-PCB AND PBDE IN LAKE MAGGIORE (ITALY)

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Introduction

Halogenated organic contaminants (HOC) are found in various environmental compartments, even at remote sites where they have never been used. This indicates that they are sufficiently persistent and mobile to undergo atmospheric (long range) transport.

Aquatic systems are a sink for persistent pollutants and the input of HOC could occur through atmospheric emission and transport followed by deposition, by local sources, and by direct discharges or indirect transport by tributaries. In this study we take in consideration three different families of persistent organic pollutants (POPs) coming from different anthropogenic source history.

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are unintentional byproducts of human activities, are released into the environment by controlled/uncontrolled combustion sources (municipal and industrial incineration, accident fire, metallurgic industry, etc.) or as impurities in chlorinated chemicals (pesticides, plastics, etc.)¹.

Polychlorinated biphenyls (PCBs) were mainly used by the power industry in electrical transformers, capacitors, hydraulic equipment, and as lubricants. These compounds were also added to many products used directly by the public or the small industry like adhesives, waxes and inks. Since the mid 1970s PCBs use has been banned but they are still present in most environmental compartments. They are released into the environment by different combustion sources; from landfills and mobilization from contaminated compartments².

In the last years a new class of emerging compounds, brominated flame retardants, has shown increasing concentration in different environmental compartments. Polybrominated diphenyl ethers (PBDEs) constitute an important group within this family and have been used in resins, polymers, textiles and in circuit boards, electrical components, panels, coatings, etc.³. Three major PBDE commercial mixtures are commonly used: Deca-BDE, Octa-BDE and Penta-BDE. The European Union (EU) has decided to ban the Penta and Octa-BDE products since August 2004 (Directive 2003/11/EC)⁴ while the Deca-BDE is still used.

Here we present the results on the concentrations in the different compartments around river mouths of Lake Maggiore that reflect the atmosphere (air, bulk deposition) and riverine sources, aquatic settling matter and the bottom lake sediments from zones in order to evaluate the input of these chemicals.

Material and Methods

Sampling:

During the week March, 22nd-30th, 2005 a weekly air high volume and bulk deposition sample was collected simultaneously at the JRC EMEP in order to characterize the situation in the atmospheric and the related deposition. Aquatic settling matter was collected with a sediment trap placed at 400m from the coast at a depth of 27m covering a period of 4 months, from December, 17th, 2004 to April, 19th, 2006 (in order to evaluate the vertical transport through the water column, the link from atmosphere and sediments). In the same place sediment sample (LMMS023) was collected for provide a direct comparison. Others 5 surface sediments were collected in proximity of the mouths

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of different tributaries (LMMS002, LMMS003, LMMS004, LMMS008 and LMMS009) and 2 were collected close to the outflow of River Ticino (Fig.1, Tab.1).

Sampling device and method details were described previously^{5,6,7}.

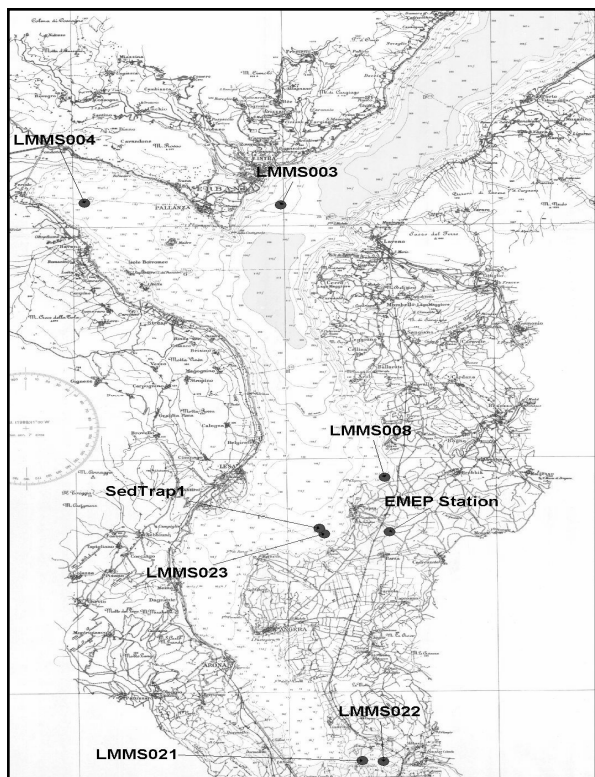


Fig.1: Sampling locations of ambient air, bulk deposition (EMEP), settling matter (SedTrap) and sediments on Lake Maggiore.

Analytical determination:

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) by Soxhlet for 48 h after spiking with internal standards ¹³C-labelled (16 isomers of 2,3,7,8-PCDD/F, 12 isomers of dioxin-like PCBs and 7 isomers of PBDEs). After treatment of the raw extract with conc. H₂SO₄ (for sediments and settling material), the extract purification was executed with an automated clean-up system (Power-Prep P6, from Fluid Management Systems (FMS) Inc., Watertown, MA, USA). Two fractions were collected, one containing PCBs and PBDEs and one for PCDD/Fs. Instrumental analysis were based on isotope dilution using HRGC-HRMS (high resolution gas chromatography – high resolution mass spectrometry) for quantification on the basis of EPA1613, EPA1614 and EPA1668 methods. The detail method was described previously⁷.

Table 1: Location and sampling details.

Code	Co-ordinate	Date	Type	Depth (m)
LMMS003	45° 56' N, 8° 34' E	02 Feb 2005	sediment	17
LMMS004	45° 56' N, 8° 30' E	02 Feb 2005	sediment	8
LMMS008	45° 50' N, 8° 37' E	02 Feb 2005	sediment	2
LMMS021	45° 43' N, 8° 37' E	11 Mar 2005	sediment	13.5-18
LMMS022	45° 43' N, 8° 37' E	11 Mar 2005	sediment	8.3
LMMS023	45° 48' N, 8° 36' E	14 Apr 2005	sediment	30
Sediment trap	45° 48' N, 8° 36' E	17 Dec 2004 -19 Apr 2005	settling matter	27
EMEP Station	45° 48' N, 8° 38' E	22-30 Mar 2005	air	
EMEP Station	45° 48' N, 8° 38' E	22-30 Mar 2005	bulk deposition	

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. Non-ortho PCBs and PCDD/Fs were analyzed on BP-DXN and mono-ortho PCBs on HT-8 capillary columns, both columns types were 60 m long with 0.25 mm i.d. (inner diameter) and 0.25 μm film. PBDEs were analyzed on a Sol-Gel-1ms

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capillary column, 15 m with 0.25 mm i.d. and 0.1 µm film. All capillary columns were obtained from SGE, Victoria, Australia.

Discussion

Figure 2 gives an overview on the concentration and patterns of the investigated compounds in the atmosphere and the compartments related to their pathway into sediments.

PCDD/F patterns present in atmospheric particulate phase and DL-PCB patterns in both atmospheric gas and particulate are similar in all compartments that reflect the atmospheric input into sediments. The sediments sampled in the other locations of the lake showed similar congener distributions both for PCDD/F and DL-PCB suggesting that the atmospheric transport is the main source of input in the lake^{5,6} for these chemicals.

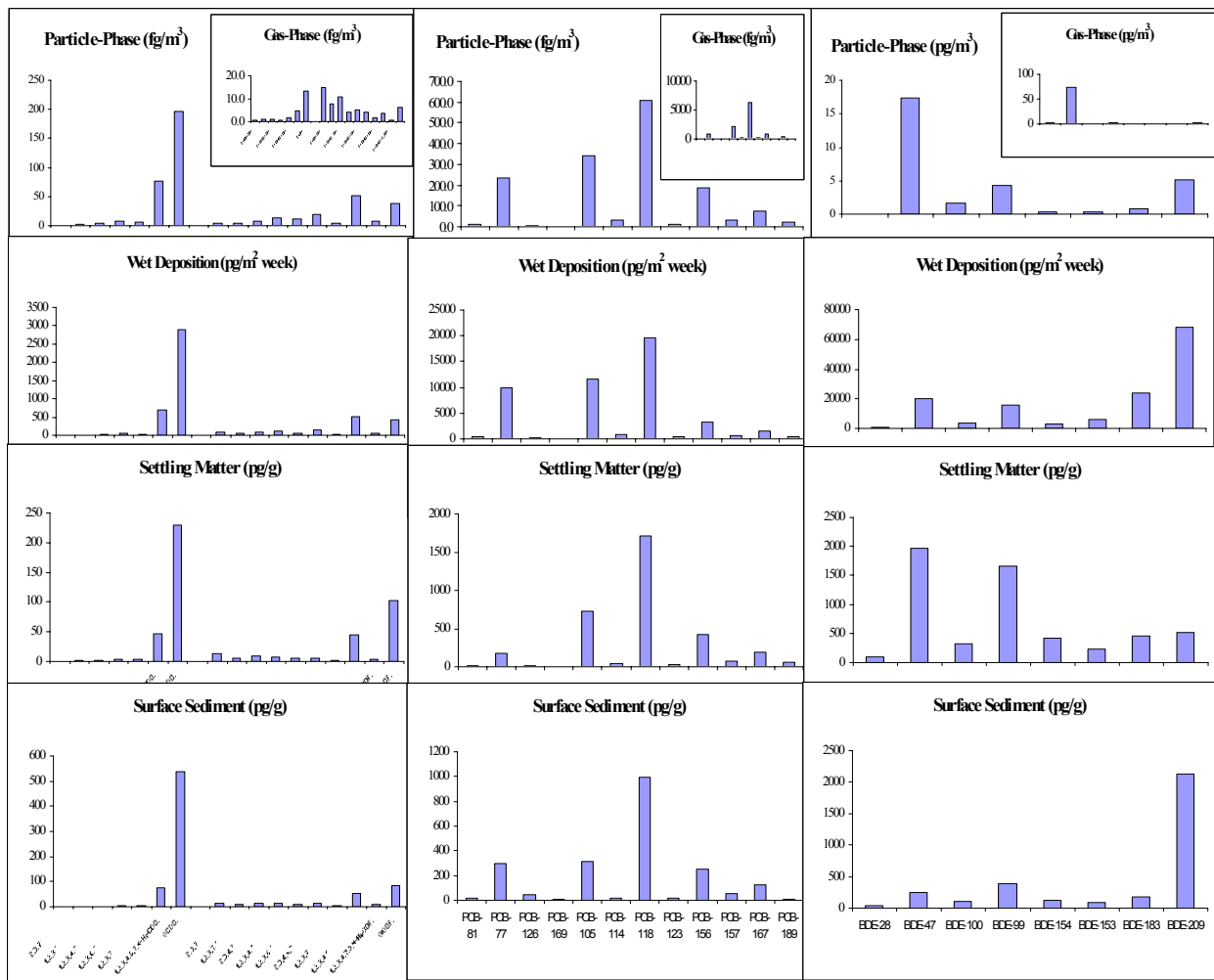


Figure 2: Pattern of PCDD/F, DL-PCB and PBDE founded in air, bulk deposition, settling matter and sediment (LMM023).

The situation for PBDE is different. The atmospheric pattern, dominated by congener BDE-47, was different from the sediment signal, which was dominated by the Deca-BDE congener. Nevertheless the pattern of bulk atmospheric deposition and sediment were similar; however, the settling matter is unlike either of these patterns even though it connects the two compartments.

Besides the sediments sampled in the other locations of the lake presented two different patterns. One was dominated by BDE-47 (27-30%) and BDE-99 (26-34%); BDE-209 occurred at 15-19% abundance. The second one was dominated by BDE-209 ranging from 58-90% of the total, whereas the BDE-47 and BDE-99 represented only 2.4-14% and 5-17%, respectively⁷.

The clear match of the patterns, as observed for PCDD/F and DL-PCB, along the whole deposition chain is missing for the PBDE. These results suggest an important contribution of diffuse local sources and different processes contributing to the pattern of PBDE input into the Lake Maggiore.

In support of this hypothesis (figure 3A) a good correlation ($R^2:0.995$; fig. 3) of PCDD/F WHO-TEQ versus DL-PCB WHO-TEQ concentrations recorded among all samples analyzed ($n=9$: air, wet deposition, settling matter and 6 sediments). Also without the extreme value, corresponding at the wet deposition, the good correlation is obtained ($R^2: 0.973$).

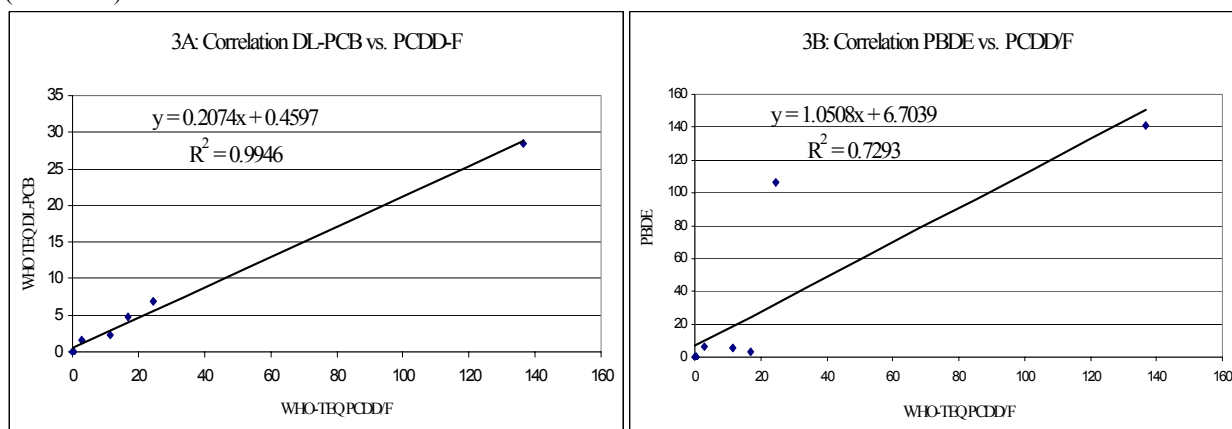


Figure 3: A- Correlation of PCDD/F WHO-TEQ versus DL-PCB WHO-TEQ. B- Correlation of PBDE versus PCDD/F WHO-TEQ.

In contrast the same approach applied to PBDE and PCDD/F WHO-TEQ results in a lower correlation coefficient ($R^2: 0.729$), mainly affected by the extreme value. In fact, without the extreme value, (corresponding at the wet deposition) a significant decrease of the correlation coefficient occurs ($R^2: 0.591$).

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