

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

www.jrc.ec.eu.int

G. Mariani, E. Canuti, J. Castro-Jiménez, E.H. Christoph, S.J. Eisenreich, G. Hanke, H. Skejo, G. Umlauf and J. Wollgast.

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 transport. Aquatic systems are one of the 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 HOCs with a different anthropogenic source history. Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are unintentional by-products of human activities¹. 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. Currently they are released into environment by combustion sources; landfills and mobilization from more or less contaminated compartments that have become sources under determined conditions². Polybrominated diphenyl ethers (PBDEs) constitute an important group of brominated flame retardants and have been used in different kind of 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 that govern the atmospheric transport (air, bulk deposition), aquatic settling matter and the bottom lake sediments from zones around river mouths of Lake Maggiore in order to evaluate the input of these chemicals.



Code	Co-ordinate	Date	Type	Depth (m)
LMM003	45° 56' N, 8° 34' E	02 Feb 2005	sediment	17
LMM004	45° 56' N, 8° 30' E	02 Feb 2005	sediment	8
LMM008	45° 50' N, 8° 37' E	02 Feb 2005	sediment	2
LMM021	45° 43' N, 8° 37' E	11 Mar 2005	sediment	13.5-18
LMM022	45° 43' N, 8° 37' E	11 Mar 2005	sediment	8.3
LMM023	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	setting 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	

Figure 1 and Table 1: Location and sampling details.

Results and 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 in both atmospheric gas and particulate were found in all compartments that guide the atmospheric input into sediments. The sediments sampled in the other location of the lake showed similar congeners distributions both for PCDD/F and DL-PCB suggesting that the atmospheric transport is the main source of input in the lake^{5,6}.

The situation for PBDE is completely different, the atmospheric pattern, dominated by congener BDE-47, was different from the sediment signal, dominated by Deca-BDE congener. Nevertheless the pattern of bulk deposition and sediment were more similar in contrast, the settling matter that is the main link between these two compartments, didn't correspond to both.

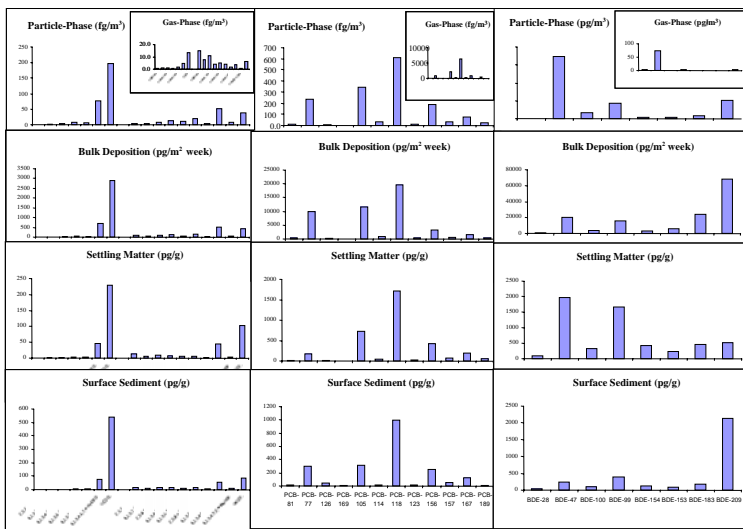


Figure 2: Pattern of PCDD/F, DL-PCB and PBDE found in air, bulk deposition, settling matter and sediment (LMM023).

References

- ECH-88, 1989. Polychlorinated dibenzo-*para*-dioxins and dibenzo furans. International Programme on Chemical Safety, World Health Organization, Geneva, Switzerland.
- Breivik, K., Sweetman, A., Pacyna, J.M., and Jones, K.C., 2002. *The Science of the Total Environment* 290, 199-224.
- EHC-162, 1994. Brominated diphenyl ethers. International Programme on Chemical Safety, World Health Organization, Geneva, Switzerland.
- Directive 2003/11/EC of the European parliament and of the council of February 2003 amending for 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether). Official Journal of the European Union.
- Castro-Jiménez J, Canuti E, Christoph E H, Eisenreich S J, Hanke G, Mariani G, Skejo H, and Umlauf G. *Organohalogen Compounds* 2005; 67: 1209.
- Castro-Jiménez J, Mariani G, Eisenreich S J, Christoph E H, Hanke G, Canuti E, Skejo H, and Umlauf G. *Chemosphere* 2006; Submitted.
- Mariani G, Canuti E, Castro-Jiménez J, Christoph E H, Eisenreich S J, Hanke G, Skejo H, and Umlauf G. *Chemosphere* 2006; Submitted.

Samplings and Analytical Methods

Sampling:

During March, 22nd-30th, 2005 a weekly air high volume and bulk deposition sample was collected simultaneously at the JRC EMEP station in order to characterize the situation in the atmosphere 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 between atmosphere and sediments). In the same place sediment sample (LMM023) was collected for provide a direct comparison. Others 5 surface sediments were collected in proximity of the mouths of different tributaries (LMM002, LMM003, LMM004, LMM008 and LMM009) 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}.

Analytical methods:

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 sediments sampled in the other location of the lake presented two well different patterns, one was dominated by BDE-47 (27-30%) and BDE-99 (26-34%); BDE-209 occurred at 15-19% abundance (figure 3A). The second one was dominated by BDE-209 ranging from 58-65% of the total, whereas the BDE-47 and BDE-99 represented only 7-14% and 12-17%, respectively⁷ (figure 3B). 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 on the PBDE input into the Lake Maggiore.

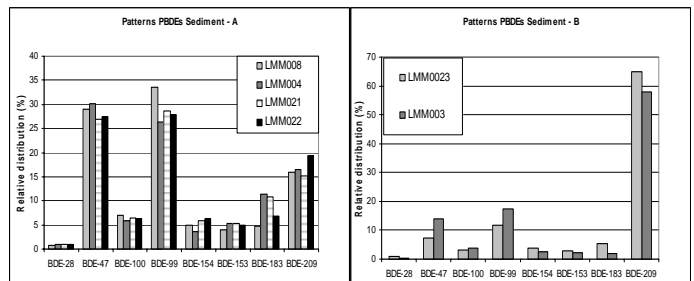


Figure 3: PBDE patterns in sediments

In support of this hypothesis (figure 4A) a good correlation ($R^2:0.995$) 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 ($R^2: 0.973$).

In contrast the same approach applied on total-PBDE and PCDD/F WHO-TEQ results (figure 4B) 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 ($R^2: 0.591$).

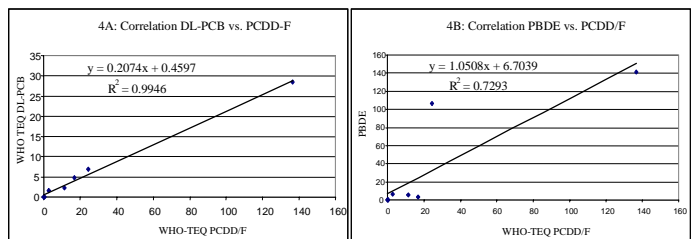


Figure 4: A- Correlation of PCDD/F WHO-TEQ versus DL-PCB WHO-TEQ. B- Correlation of PBDE versus PCDD/F WHO-TEQ.

Contact:

Giulio Mariani

European Commission – DG Joint Research Centre
Institute for Environment and Sustainability
Tel +39 0332 786781 – Fax +39 0332 786351
E-mail: giulio.mariani@jrc.it

