

## SPATIAL DISTRIBUTION OF PCDD/F IN SURFACE SEDIMENTS OF LAKE MAGGIORE (ITALY)

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### Introduction

Lake Maggiore (LM) is the second largest Italian lake in terms of volume, surface and depth, with the northern third residing in Swiss territory. The most important tributaries are River Ticino (Northern inlet) and River Toce (Western inlet). The River Ticino leaves LM at the southern end and connects LM to the River Po.

Extensive monitoring of a series of persistent organic pollutants (POPs) in sediments, plankton, benthic organisms, bivalves and fish was initiated in by the International Commission for the Protection of the Italian –Swiss waters (CIPAIS) in 1996 and is still being continued. Particular concern arose from the contamination with DDT and its metabolites, which exceeded Italian and EU levels for consumption in fish<sup>1</sup>, and was detected in bird eggs from fish feeding species as well<sup>2</sup>. As a consequence the local Health Authorities prohibited commercial fishing of a series of contaminated fish species. The source of DDT contamination was a DDT production site, closed down in 1996. This plant was located on the Marmazza River, a tributary of River Toce entering LM from the westernmost part of LM, close to Baveno. Besides the contamination with DDT, PCBs, including some dioxin like congeners, were found at concentrations exceeding 3-7 times the levels of other sub alpine lakes in Italy. Levels of HCB and HCH in the LM ecosystem instead gave no rise to concern<sup>1</sup>.

The aim of the present study is to supplement the existing data on POPs with sediment levels of PCDD/Fs, where so far only few data<sup>3</sup> are available for LM.

### Materials and Methods

Sediment samples (0-10 cm) were taken with a Ponar Grab Sampler during 2005. The samples were stored at 4°C until wet sieving < 2mm and were subsequently freeze dried and homogenized. 30 g dry weight samples were Soxhlet-extracted for 24h using n-hexane/acetone (220/30). The applied methodology follows USEPA method 1613. Prior the extraction 16 carbon-13 isotope labeled internal standards were added (400 pg each, except OCDD with 800 pg). Extracts were evaporated to nearly dryness, refilled to 10 mL with n-hexane, and purified with an automated clean-up system (Fluid Management Systems, USA) operating with a silica/sulfuric acid-, a basic alumina-, and a carbon-column<sup>4</sup>. The purification principle is described by Smith et al.<sup>5</sup>. Purified extracts were evaporated to nearly dryness using nitrogen (Turbovap, Zymark, USA) and filled up with 30 µL of toluene. Prior the injection, two C<sup>13</sup>-labeled recovery standards were added.

Quantification was done with a high resolution gas chromatograph (HRGC) (Hewlett-Packard/Agilent, Germany) with split/split less injection. Chromatographic column was a 60 m BPX-DXN (SGE, Australia) with 0.25 mm inner diameter and 25µm film thickness. The HRGC was coupled with a high resolution mass spectrometer (HRMS) (Autospec, Micromass/Waters, USA), working in the electron impact mode at 34 eV and with an average resolution of 10 000. For parent congener and corresponding labeled standards two ions each were registered.

Quality assurance and quality control were done by determining laboratory blanks together with each batch of 15 samples, running reference samples in parallel<sup>6</sup> and calibrating the HRGC/HRMS with certified PCDD/F standard mixtures (CS from Wellington Laboratories, USA). All solvents (Sigma Aldrich/ Switzerland) and gas (Alphagaz/Italy) used were ultrapure grade suitable for PCDD/F analysis.

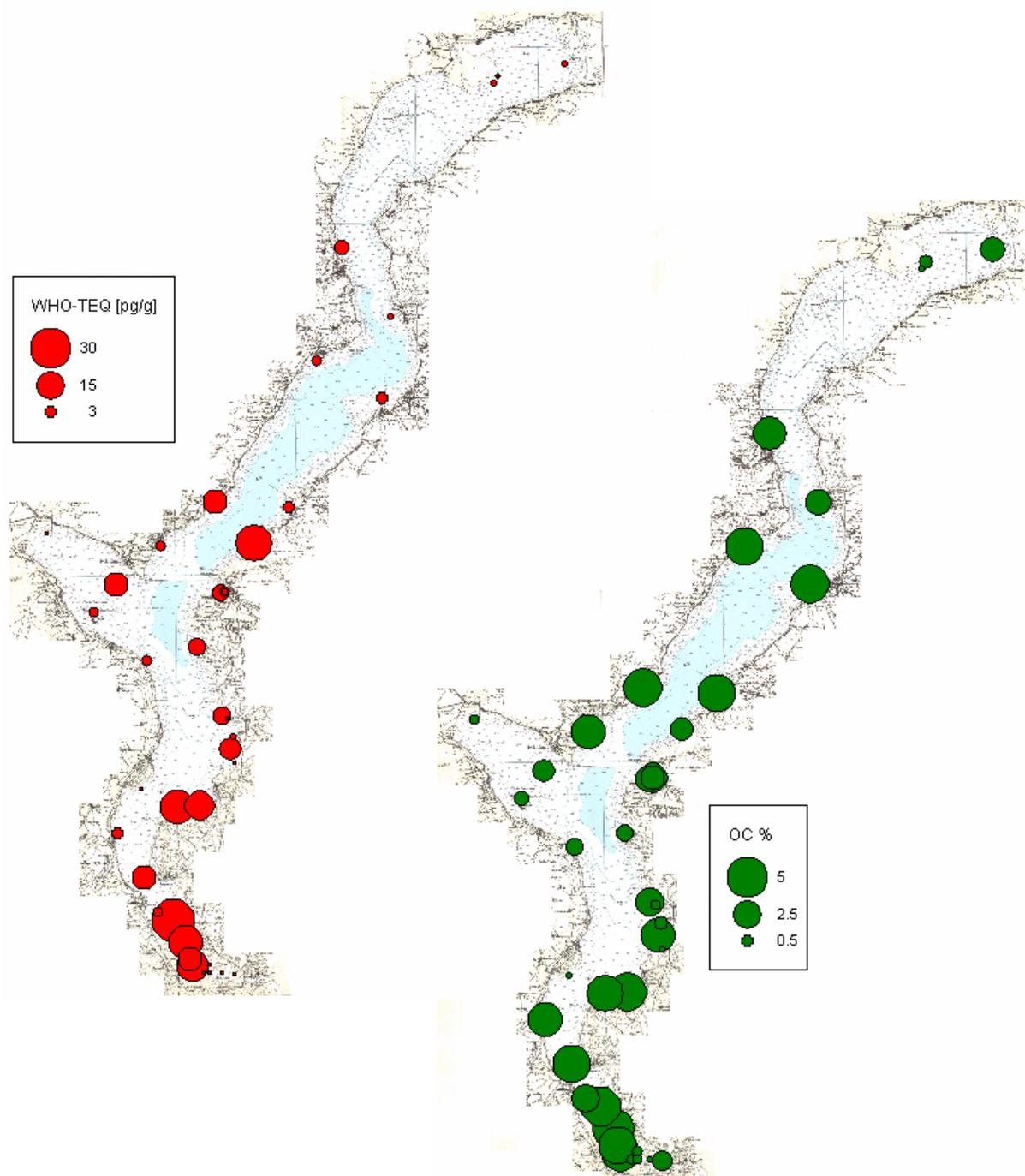


Figure 1: PCDD/Fs in LM sediments in pg WHO TEQ g<sup>-1</sup>d.w. and Organic Carbon (OC) content in %

**Results and Discussion**

The PCDD/F concentration in the 50 surficial sediment samples taken at water depths between 5 and 60 m in LM display a broad range of concentrations, from 0.13 to 32 pg WHO TEQ g<sup>-1</sup> d.w. (see Figure 1). The PCDD/Fs show a consistent congener pattern (see Figure 2). In the sample taken at the inlet of River Bardello the congener distribution was dominated by Octachloro- followed by Heptachloro-dioxins; the Heptachloro- and Octachloro – furans occurred at a level of only 0.80 pg WHO TEQ g<sup>-1</sup> d.w..

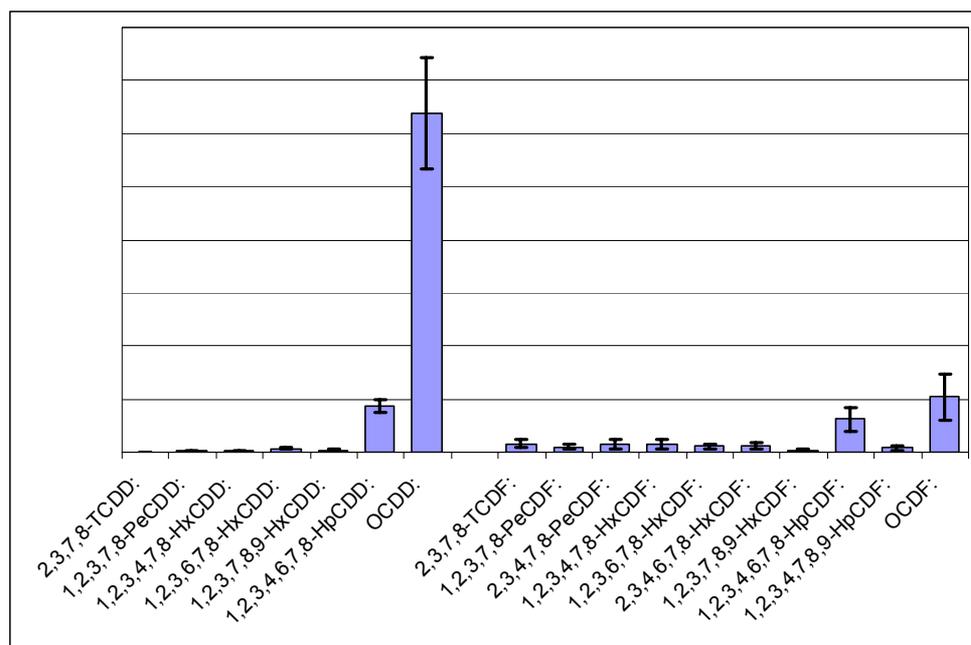


Figure 2: PCDD/F congener pattern in the LM sediments (average % ±SD)

The spatial homogeneity of the pattern along the whole lake (Figure 2) underlines the absence of local sources and important riverine inputs into LM. Moreover, the pattern is similar to that of PCDD/Fs in atmospheric particulate matter and bulk deposition collected locally from LM<sup>3</sup>, and is typical for long range transport. This suggests that atmospheric deposition is the dominant vector for the introduction of PCDD/Fs into LM sediments.

The spatial distribution of the PCDD/Fs (Figure 1) shows two principal tendencies. First, a north/south gradient of the PCDD/F concentrations probably deriving from the flushing of sediment from the north to the south due to intermittent resuspension in the shallower north basin. Second, sediments close to incoming rivers show lower concentrations than sediments in settling basins where no direct riverine discharges occur. A similar observation can be made at the southern outlet (River Ticino) of LM where the PCDD/F concentrations decrease considerably compared to the southern section of the lake. This indicates that the settling conditions for particulate organic carbon (OC), the dominant transport vehicle for lipophilic compounds like PCDD/Fs in aquatic systems, are an important parameter for the PCDD/F burden in sediments. Consequently, lower concentrations of PCDD/Fs occur in the sediments close to river in and outlets, where turbulences inhibit the settling of OC.

The spatial distribution of the total OC content in the sediments (Figure 1) reflects the concentration distribution of the PCDD/Fs to some extent, however, not as pronounced as seen for PCDD/Fs. Only part of the spatial variations of PCDD/Fs in LM sediments can be explained by variations in total OC content of the sediments: The normalization of

the PCDD/F concentration on the OC content of the sediments reduces the spatial variations from a factor of 246 (d.w. basis) to a factor of 85 (OC weight basis).

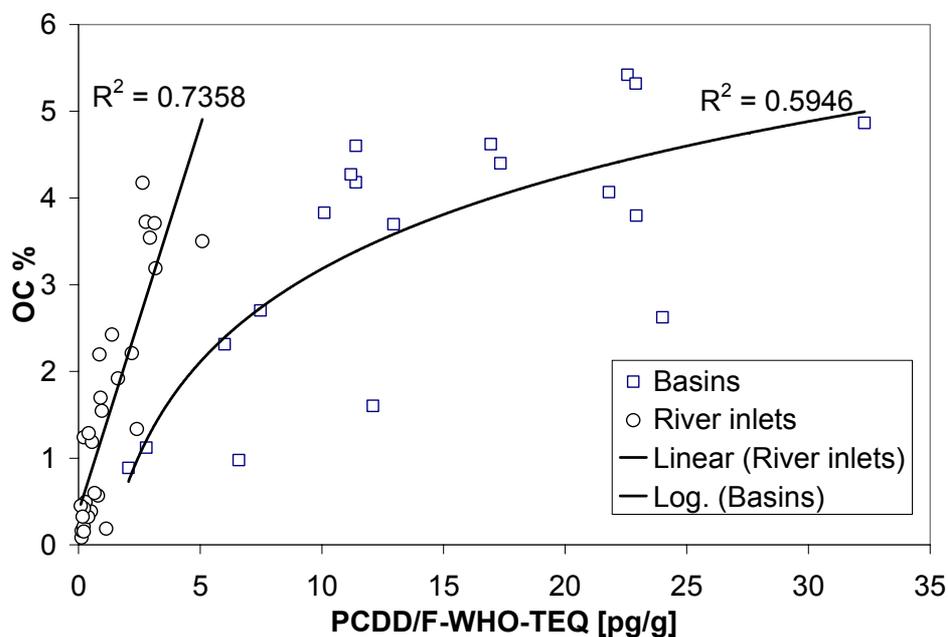


Figure 3: PCDD/Fs in the LM sediments in  $\text{pg WHO TEQ g}^{-1} \text{d.w.}$  versus Organic Carbon content (OC) in %

This observation is supported by the plot of total sedimentary OC versus PCDD/Fs concentrations for all sediments (Figure 3). Separating the concentrations observed in river inlet sediments from the settling basin sediments shows two distinct patterns: First, PCDD/Fs and OC in sediments close to the river inlets “o” show a linear relationship and a tendency of lower PCDD/F concentrations on an OC basis. Second, PCDD/Fs and OC in sediments from the basins “□” show a logarithmic relationship and OC based PCDD/F concentrations are considerably higher. This suggests that PCDD/F levels close to the river inlets are mainly determined by the settling of fresh OC as a local trap of contaminants. However, in the basins where organic matter rich in contaminants is continuously settling, decomposition of organic matter leads to a reduction of OC, while the more persistent PCDD/Fs are preserved in the sediments. This results in a higher PCDD/F load per unit TOC in the aged sediments of the LM basins.

### Conclusions

The PCDD/Fs present in LM sediments are a result of atmospheric deposition following long range transport of particulate matter. Riverine sources or diffuse local impacts are negligible. The broad range of PCDD/F concentrations found is a function of hydraulic focusing of OC present in the water column ( $\rightarrow$  different sedimentation rates of OC and the associated PCDD/Fs), determining the spatial distribution and resulting in high PCDD/F levels in sediments in the basins of LM and low levels close to the inlet of the tributary rivers and the Ticino river at the outlet of LM.

Another phenomena is “OC decomposition focusing”, visible in the big variations of PCDD/F concentration on an OC base. Thus, total OC concentrations in sediments do not reflect PCDD/F concentrations although OC is the main vehicle of lateral and horizontal transport of PCDD/Fs in LM. Since the atmospheric deposition of PCDD/Fs is mainly related to black carbon (subsequently associated with less persistent organic carbon of biological origin in the

water column), a better correlation between black carbon and PCDD/Fs in sediments can be expected. Therefore a speciation into biotic and abiotic OC fractions is needed in order to better understand the transport properties of PCDD/Fs in LM.

### References

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