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Recent DDT and PCB contamination in the sediment and biota of the Como Bay (Lake Como, Italy)☆

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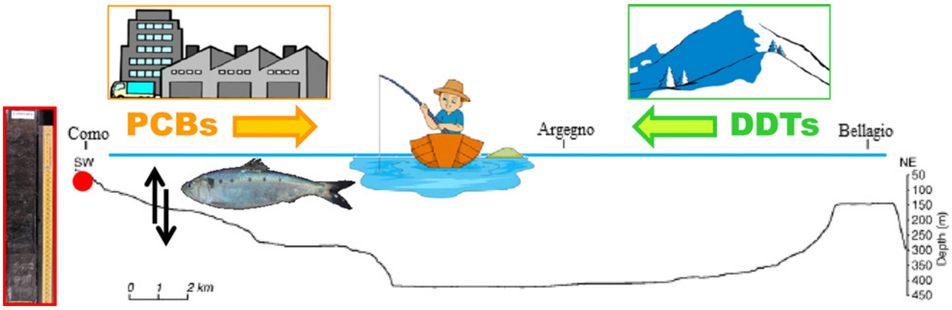
HIGHLIGHTS

- Deposition of DDT and PCB (1970s-2009) was recorded in a sediment core in Como Bay.
- A decreasing trend was observed for PCB whose main source is the city of Como.
- DDT showed no significant change over time because of input from glacier releases.
- Biomagnification was recorded between zooplankton and a zooplanktivorous fish.
- Concentrations of PCB exceeded human health recommendations in one fish samples.

GRAPHICAL ABSTRACT



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ABSTRACT

Due to its peculiar geographical and morphological characteristics, Lake Como (Northern Italy) represents an interesting study-case for investigating the sub-basin scale circulation of persistent organic pollutants (POPs) that, despite being banned since the 1970s, have reached surprisingly high concentrations in some southern alpine lakes as a consequence of their release from melting glaciers in recent years. In particular, the Como Bay, which is located in the city of Como, seems noteworthy because its waters have a longer residence time than the other areas of the lake. The analyses of the historical concentration of PCBs, pp′DDT and its metabolites in a sediment core sampled from the Como Bay covering a time-period from their ban to recent times, showed that the DDTs have never experienced a significant ($p < 0.05$) decrease over time, with concentrations of the most abundant homologue, pp′DDE, ranging from 27 to 75 ng g^{-1} d.w. Conversely PCBs significantly ($p < 0.05$) decreased towards recent times, reaching concentrations around 80 ng g^{-1} d.w. The contribution of high altitude and local sources was recorded also in the food web: both zooplankton and the zooplanktivorous fish agone were mainly contaminated by pp′DDE (81.4 ng g^{-1} w.w. and 534.6 ng g^{-1} w.w. respectively) and by the PCB metabolite hexa-CB (449.7 ng g^{-1} w.w. and 1672.1 ng g^{-1} w.w. respectively). The DDT concentrations in the agone (sampled during the years 2006–2009) never exceeded the limits for human consumption in Italy, while concentrations of six selected PCBs exceeded human health advisory recommendations in one of the fish samples analysed, when it was approximately two times higher than the recommended value of 125 ng g^{-1} w.w.

☆ To the memory of my beloved Prof. Ettore Grimaldi, an enthusiastic ichthyologist, a bright scientist, and a native of Como who loved his lake and the lakes. Roberta.

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1. Introduction

The historical record captured by lake sediments represents a useful archive of the "past to present" environmental changes. Sediments integrate information from the water column, catchment area and atmosphere, and they can help in assessing the baseline conditions for different biological, chemical and physical systems as well as the impacts and recovery times following any type of disturbance. They are repositories for physical and biological debris and sinks for a wide variety of persistent chemicals. When linked to sediments, chemicals can be in a dynamic exchange with the water column and can enter the food-chain through the organisms that spend a portion or their whole life-cycle in the benthic environment. The direct transfer of chemicals from sediments to organisms can be considered a major route of exposure for many species (Zoumis et al., 2001). The high persistence of certain contaminants justifies their presence notwithstanding their long-time bans; in general, persistent organic pollutants (POPs) are characterized by low water solubility and high lipid solubility. These pollutants are semi-volatile, have a high molecular mass and are stable to biological and photolytic degradation. These properties allow for their bioaccumulation in the fatty tissues of living organisms and, thus, their accumulation along the food webs.

In Italy, unexpected pollution by "old" POPs, such as DDT (dichloro-diphenyl-trichloroethane) and PCBs (poly-chlorinated-biphenyls), has been found in the biota and the sediments of some great lakes of the subalpine area decades after the banning of these compounds (Bettinetti et al., 2008; Bettinetti et al., 2011). In the case of Lake Maggiore, DDT contamination was mainly traceable to a manufacturing plant located on one of its major inlets (Bettinetti et al., 2005), while in the case of Lakes Como and Iseo, a "glacier release hypothesis" was proposed to explain this phenomenon, as this was already observed in other mountain regions around the world where a strong retreat of glaciers and release of trapped contaminants has been observed in recent years, due to climatic warming (Blais et al., 1998, 2001; Donald et al., 1999; Bettinetti et al., 2008, 2011; Bogdal et al., 2009, 2010). This secondary pollution source affected the littoral benthic fauna (*Dreissena polymorpha*) in correspondence with a water-column recirculation event, causing peak of DDT residues in mussel tissues in 2005. The study indicated that the input of PCBs due to melting glaciers was lower than that of the DDT homologues, whose parent compound was particularly used for fruit-tree pest control in the valleys below the glaciers' zone (Bettinetti et al., 2008).

The complete mixing of the water column at the end of the winter occurs quite rarely in the deepest areas of the southern alpine large lakes, usually in the years when air temperatures are particularly low; however, this phenomenon involves the shallower waters of these deep/large lakes every winter. This is the case for the Como Bay in the southern part of the Como branch of Lake Como, where the average depth is approximately 50 m (Fanetti et al., 2008). This area represents a heavily anthropized water system without outlets nearby (the outlet is Adda River originating in the south of the other branch of the lake — Fig. 1), particularly impacted by industrial, agricultural and urban activities. The Como Bay, located at the front of the city, is supplied by the surface water of one main tributary, the Cosia River. In its final part, the river passes through the city, canalized and mainly underground, and receives water from a sewage treatment plant. The waters of the basin are subjected to intensive exploitation to meet the water demands of the Como urban district, even for potable uses (Bettinetti et al., 2014).

The aim of the present work is to evaluate the levels of "old contaminants" detected in recent sediments in the Como Bay and determine their levels in zooplankton and in a fish which lives far from the shores. Therefore, superficial sediments and a sediment core were sampled in the Como Bay basin, in an area not directly disturbed by the inlet of rivers, and the concentrations of DDTs and PCBs were determined. Zooplankton and the agone (*Alosa agone*) were analysed to evaluate the extent of biomagnification and the possible risk for human consumption.

2. Materials and methods

2.1. Sediment sampling and dating

For a preliminary evaluation of the homogeneity/variability of contamination of the Como Bay sediments, three superficial sediments (the upper 2 cm, 250-μm sieved) were collected in 2008 (Fig. 1). Therefore, at the end of the winter in 2009, a sediment core of 38 cm was collected with a gravity corer (inner diameter: 6.3 cm) in the Como Bay at a depth of 70 m (Fig. 1 — 45°49′3.38″N, 9°4′14.60″E).

The sediment core was long enough to detect the recent period of contamination, the last 20–25 years, as contamination data of sediment cores collected in the same area and covering the period from 1977 to 1991 were already available (Galassi et al., 1995; Provini et al., 1995).

The core was stored in the dark at 4 °C; once opened longitudinally, it was visually inspected and subsampled into 1-cm slices based on the observation by Provini et al. (1995) on a sedimentation rate of 1.1 cm year^{-1} in the study area. A total of 38 slices were thus targeted for analysis.

Age dating of the core was performed by analysing the ^{137}Cs content. ^{137}Cs is produced during nuclear fission; therefore, its presence in the environment is due to nuclear testing or releases from nuclear reactors. In the northern hemisphere, the major periods of global deposition of ^{137}Cs fallout were in 1958 and 1963/1964. Moreover, an evident peak can be observed that corresponds to the Chernobyl accident in 1986 (Ritchie and McHenry, 1990; Klaminder et al., 2012). Radiocaesium measurements were made using an HPGe co-axial y-ray detector coupled to a multi-channel analyser. The dried samples were gently ground with a mortar and pestle and passed through a 2-mm sieve before being placed in plastic pots of similar diameter to the detector end cap for y-spectrometry. Counting times were typically in the range of 28,000 to 58,000 s. The detector was calibrated with standard reference materials and radionuclide standards.

2.2. Sediment analyses

The dry mass and organic matter content were determined by weight Loss-On-Ignition (LOI) (Dean, 1974) at 80 °C and 550 °C, respectively, and are expressed as a percentage of wet weight (% w.w.) and dry weight (% d.w.). For POP determination, extraction of the freeze-dried and homogenized sediments (1 g) was performed in glass microfibre thimbles (19-mm internal diameter × 90-mm external length, Whatman, England) for 2 h with 60 mL of *n*-hexane (Carlo Erba, Italy, pesticide analysis grade) using a modified Soxhlet apparatus (Velp Scientifica — ECO 6 thermoreactor). Organochlorine compounds were recovered by several *n*-hexane washings, and the extracts were concentrated down to approx. 2 mL and passed through a Florisil column (4 cm × 0.7 cm) with Cu powder (0.1 g) on the top. The Cu powder was previously activated by HCl (18%, Carlo Erba, Italy) and washed with water, acetone and *n*-hexane. The Florisil column was eluted with 25 mL of *n*-hexane-dichloromethane (Carlo Erba, Italy, pesticide analysis grade) using an 85:15 (v/v) mixture, and the eluate was concentrated to exactly 0.5 mL. The purified extracts were analysed by gas-chromatography (GC Carlo Erba, Top 8000) coupled with a ^{63}Ni electron capture detector (Carlo Erba, ECD 80), heated at 320 °C, using an on-column injection system (volume injected: 1 μL). The column was a WCOT fused silica CP-Sil-8 CB (50 m × 0.25 mm, film thickness: 0.25 μm, Varian, USA). The temperature programme used was from 60 °C to 180 °C at 20 °C min^{-1}, followed by a run from 180 °C to 200 °C at 1.5 °C min^{-1}. A further run was implemented from 200 °C to 270 °C at 3 °C min^{-1}, followed by a final isothermal maintenance at 270 °C for 20 min, with helium as the carrier gas (1 mL min^{-1}) and nitrogen as the auxiliary gas (30 mL min^{-1}).