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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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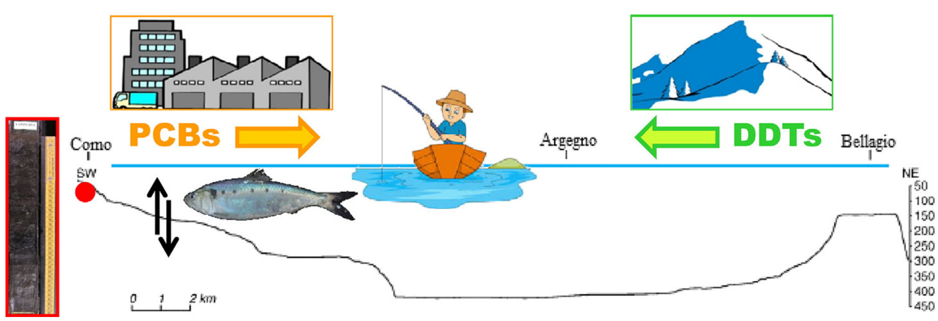
HIGHLIGHTS

- 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}).

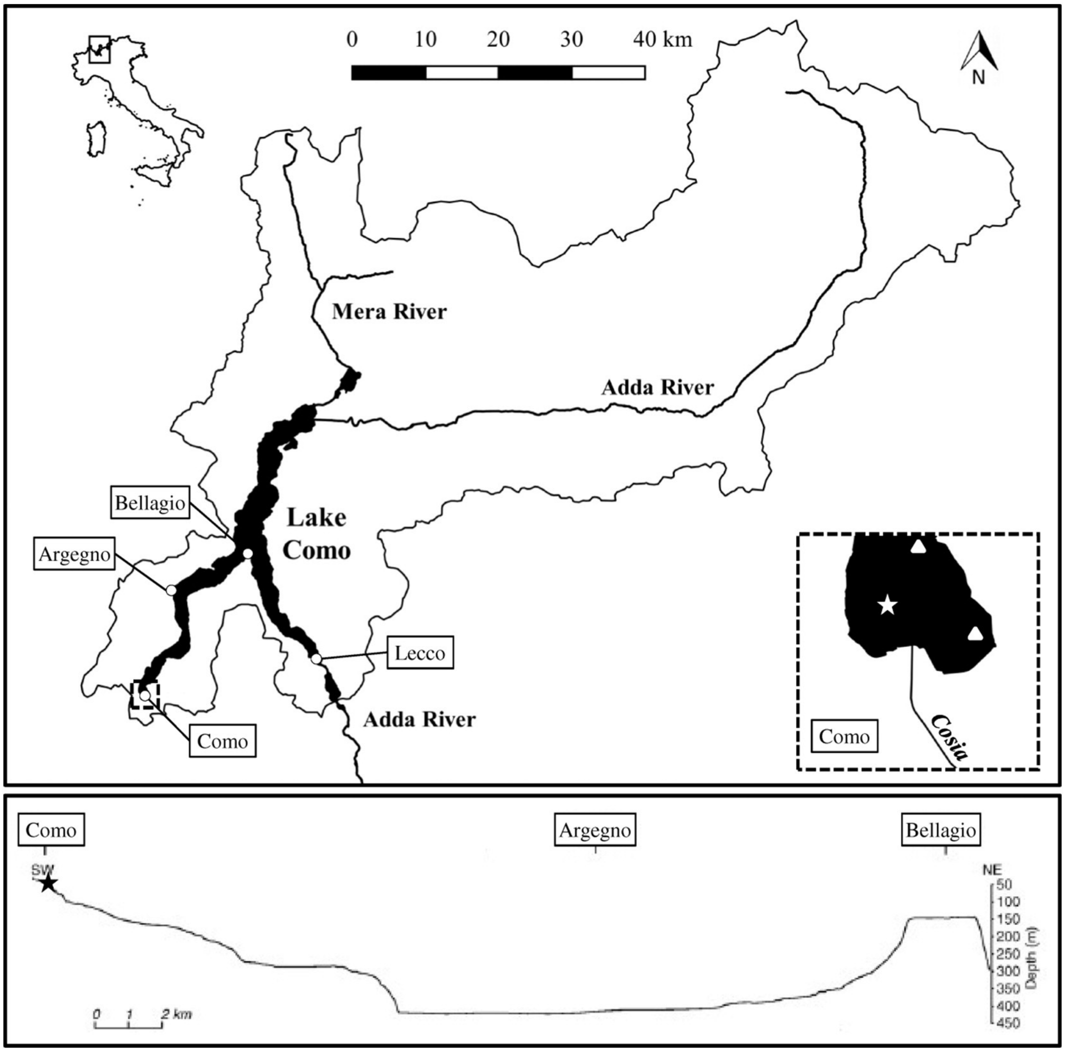

Fig. 1. Lake Como basin and topographic profile of the Como branch (modified from Fanetti et al., 2008). The star indicates the sediment core site, and the triangles are the superficial sediment sites in the Como Bay. Note that a superficial sediment was collected in the same site as the sediment core.

Sample quantification was performed using the external reference standards 1,1-dichloro-2,2-bis(p-chlorophenyl)ethylene (pp′DDE), 1,1-dichloro-2,2-bis(p-chlorophenyl)ethane (pp′DDD) and 1,1,1-trichloro-2,2-bis(p-chlorophenyl)ethane (pp′DDT) (Pestanal, Sigma-Aldrich, Germany) in iso-octane (Carlo Erba, Italy, pesticide analysis grade). Aroclor 1260 (Alltech, IL, USA) with the addition of PCBs 28, 52 and 118 was used for PCB quantification. The sum of the analysed PCBs corresponds to approximately 97% by weight of the reference standard. The detection limit for each organochlorine compound was 0.1 ng g^{-1} d.w. The recovery efficiency was tested on a reference sediment that was previously used in an inter-calibration exercise (CIPAIS, 2003), and it was found to be within 80–100% for the three DDTs and approximately 90% for each PCB congener. The POP data are presented as the concentration per dry weight of the sediments (ng g^{-1} d.w.).

In total, 23 PCB congeners were measured and grouped on the basis of their chlorine content: tri-CB 28; tetra-CB 52; penta-CB 95, 101 and 118; hexa-CB 128, 138, 149, 151, 153, 156 and 158; hepta-CB 170, 174, 177, 180, 183 and 187; octa-CB 194, 195, 201 and 203; and nona-CB 206.

The detection and quantification limits of the method varied from 0.05 to 0.1 and from 0.1 to 0.5 ng g^{-1} d.w., respectively, depending on the organochlorine compound. The recovery efficiency was tested on a reference sediment that was previously used in an inter-calibration exercise (CIPAIS, 2003), and it was found to be within 80–100% for the three DDTs and approximately 90% for each PCB congener. The POP data are presented as the concentration per dry weight of the sediments (ng g^{-1} d.w.).

Trend estimation was used to discover trends in the LOI content and concentration levels of each investigated contaminant or class of contaminants along the core profile. The R^2 value produced by the least-squares fitting process was provided. Linear correlations between the LOI content and POP concentrations and between the analysed contaminants were investigated computing the Pearson product–moment correlation coefficient. Statistical analyses were performed using XLSTAT 2011 software.

2.3. Sampling and analyses of organisms

Zooplankton organisms were collected once in 2009 at the end of the winter from the same location where the fish were sampled (45°49′28″ N, 9°4′24″E; Fig. 1). The sampling was performed using a Clark–Bumpus plankton sampler (mesh: 200 μm), which vertically filtered the water column of 0–40 m corresponding to the layer where the majority of zooplankton live. Microscopic analysis showed that the sample was mainly composed of animals, although some large algal species were present.

Agone sampling was performed every year at the end of the winter from 2006 to 2009 in the southern part of the Lake Como branch (approximately from 45°49′28″N, 9°4′24″E to 45°50′47″N 9°5′47″E,

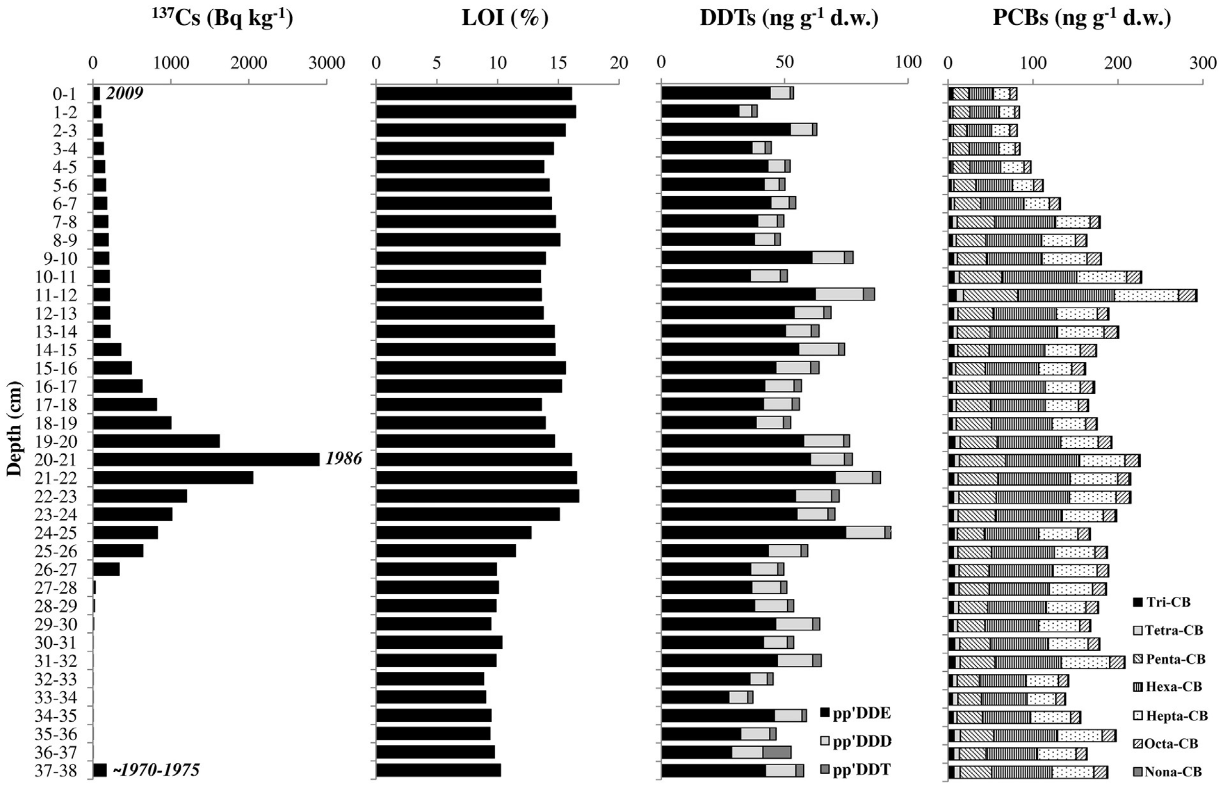

Fig. 2. ^{137}Cs, LOI, DDTs (pp′DDE, pp′DDD and pp′DDT), and PCBs (grouped by the number of chlorine substituents) in the sediment core profile.

which was close to the sediment sampling point), using pelagic gill nets. In 2007 and 2008, the agone were also sampled in the Lecco branch (Mandello, 45°54′46.96″N, 9°18′18.87″E).

The fish species was selected on the basis of several criteria: 1) its high lipid content, 2) its importance in the local diet and 3) the time spent in the deep areas of the lake, which, in turn, influences dietary habits. This species spends most of its lifetime far from the shores at variable depths, does not migrate for spawning and reproduces only once or twice. The agone are also zooplanktivorous, sometimes feeding on small fish. On average, 30,000 individual agone per year are fished in Lake Como; dried agone, known as "missoltino", are a valuable and popular gastronomic delicacy of the area. After capture (6 individuals of approximately 25–30-cm length, adult fish more than 3 years old) at the end of the winter (i.e., before the spawning period occurring in the summer), the fish were stored at 4 °C and subsequently measured and weighed.

The sample of zooplankton (0.5 g d.w.) and a pooled subsample of freeze-dried anterior dorsal muscle from homogenized fish (0.5 g d.w.) were extracted with 50 mL of an acetone/*n*-hexane v/v mixture as for sediments. The gravimetric determination of lipids was performed following solvent evaporation. The lipids were then suspended in 2 mL of *n*-hexane and digested with 5 mL of H_2SO_4 (98%, Carlo Erba, Italy). The organochlorine compounds were then recovered by several *n*-hexane washings. The hexane extracts were concentrated, cleaned-up on a Florisil column and analysed by gas-chromatography. The method detection and quantification limits varied from 0.1 to 0.5 and from 0.5 to 1 ng g^{-1} l.w., respectively, depending on the organochlorine compound. Good laboratory practices were used when testing the standard reference materials BCR-598 and BCR-349 (Community Bureau of Reference, Brussels) for DDT and PCB residues, respectively, analysing the samples in triplicate. The percentages of recovery for the DDTs were 107.5% ± 4% (pp′DDE), 106.2% ± 4% (pp′DDD), and 106.2% ± 3% (pp′DDT); the recoveries for the PCBs were between 91.3% ± 1.1% and 102.2% ± 1.6%.

To reduce interspecific variation due to the lipid content in the different analysed tissues (whole body of zooplankton and muscle of the fish), the POP concentrations were expressed on a lipid weight basis (ng g^{-1} l.w.).

The biomagnification factors (ng g^{-1} l.w.$_{predator}$/ng g^{-1} l.w.$_{prey}$) were calculated, and the values for each DDT homologue and PCB group are reported in the text.

3. Results and discussion

3.1. Sediment dating

The ^{137}Cs activity versus depth profile (Fig. 2) has a relatively well-resolved peak at the depositional layer 20–21 cm, corresponding to the Chernobyl accident event in 1986. As already observed in other cores collected in European freshwater environments (Klaminder et al., 2012), despite the fact that the collected core preserves a very clear and well-resolved peak corresponding to 1986, the years immediately around the fallout event present a re-distribution of ^{137}Cs away from the peak. Klaminder et al. (2012) have described that a fraction of the Chernobyl caesium is mobile in sediments, allowing it to migrate through diffusion in sediments mainly during the first 10 years of sediment diagenesis.

No fallout maximum due to the atmospheric testing of nuclear weapons from the 1960s has been recorded; only a slight increase at the bottom of the sampled core is present, likely indicating the back end of the period of radioactive weapon experiments. Because the sampled core is relatively short, a mean post-1986 sedimentation rate of 1.1 cm year^{-1} can be inferred, confirming what Provini et al. (1995) already observed in the Como sub-basin of Lake Como. Considering a constant sedimentation rate over time, the bottom of the analysed core can be dated back to the 1970s.

Table 1
Agone length (pooled average value in cm ± s.d.), lipid content (%) and concentrations (ng g^{-1} l.w.) of DDTs and PCBs in the years 2006–2009 for the Como branch and in 2007–08 for the Lecco branch. The concentrations are of different DDT metabolites and PCBs grouped on the basis of their number of chlorines. In 2009, the zooplankton lipid content (%) and the DDT and PCB concentrations are reported.

	Como branch					Lecco branch	
	2006	2007	2008	2009		2007	2008
	Agone	Agone	Agone	Zooplankton	Agone	Agone	Agone
Average length	22.6 ± 2.5	30.6 ± 1.4	29.3 ± 1.8		28.7 ± 0.9	27.1 ± 1.2	29.1 ± 1.4
Lipids	8.4	11.5	4.6	7.1	8.1	13.0	8.7
Total DDT	1010.0	840.0	1168.0	131.2	799.0	610.0	1122.0
pp′DDE	510.0	580.0	879.4	81.4	534.6	440.0	804.4
pp′DDD	260.0	130.0	108.1	15.9	96.8	80.0	129.7
pp′DDT	240.0	130.0	180.2	33.7	167.2	90.0	187.6
Total PCB	1009.0	1225.0	1214.0	981.2	2944.9	528.0	1637.0
Tri-CB	<1	<1	1.1	<1	12.9	<1	<1
Tetra-CB	23.5	44.8	20.0	15.0	21.7	19.1	24.9
Penta-CB	303.1	310.0	330.3	203.4	570.3	146.8	439.5
Hexa-CB	465.0	598.6	587.1	449.7	1672.1	257.7	825.9
Hepta-CB	172.2	231.9	213.9	287.5	631.1	91.8	296.6
Octa-CB	44.9	39.3	61.8	32.1	70.0	12.4	50.5
Nona-CB	<1	<1	<1	<1	<1	<1	<1

3.2. Temporal trend of LOI in sediments

The sediment organic matter content plays an important role in trapping hydrophobic contaminants from the overlying water column. The percentage of LOI in superficial sediments of the Como Bay is between 13.9% and 15.4%.

The profile of organic matter as a percentage of LOI (Fig. 2) in sediments indicates that a significant increase in content ($R^2 = 0.62$) has occurred since the mid-1980s (approximately 10%), towards the surface sediments (average value of 15–16%). However, no significant ($p > 0.05$) correlation exists between the contaminants and the percentage of LOI.

It is well-known that a relationship between the organic matter content in sediments and productivity exists (Meyers and Ishiwatari, 1993). The total phosphorous (TP) in the water column, which is directly correlated with algal productivity, is usually used to evaluate the trophic status. While TP analyses at circulation show a recovery of the water quality in the deepest area of the lake (Argegno, Como basin, depth = 425 m; Salmaso et al., 2007), the levels of production, which are evaluated as the LOI in sediments (Fig. 1) in the Como Bay, are not decreasing. This indicates that this area of the lake is still eutrophic.

3.3. Temporal trend of POPs in sediments

The levels of DDT and PCB in superficial sediments showed a homogeneity of contamination, whereas the variability was negligible among the sampled sites in the Como Bay and the levels were comparable to

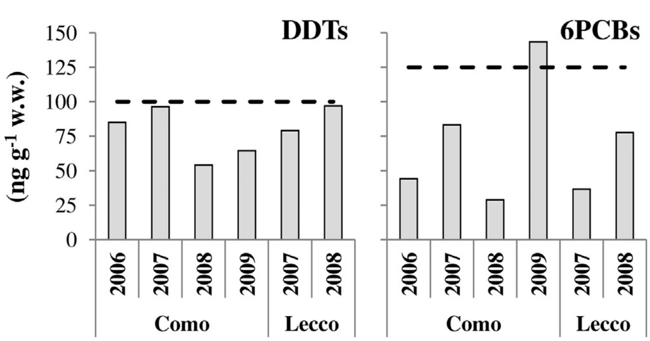

Fig. 3. The agone concentrations of DDTs and the sum of the six PCBs reported in EU 1259/2011 during the years 2006–2009 for the Como branch and in 2007–08 for the Lecco branch. The dashed lines indicate the human consumption limits.

the corresponding areas in the core sample. The DDTs were within the range of 50 to 63 ng g^{-1} d.w., and the PCBs were between 84 and 101 ng g^{-1} d.w.

The sediment core showed a DDT average concentration of 60 ng g^{-1} d.w., and in the profile, two main periods of major contamination can be underlined (Fig. 2), from 14–15 cm to 9–10 cm (average contamination: 70 ng g^{-1} d.w.) and from 24–25 cm to 19–20 cm (average contamination: 80 ng g^{-1} d.w.). The DDTs have never experienced a significant ($p < 0.05$) decrease over time, notwithstanding the ban of the parent compound. The most abundant DDT homologue in the sediment core samples was pp′DDE, with concentrations ranging from 27 to 75 ng g^{-1} d.w., followed by pp′DDD, with concentrations of 5 to 20 ng g^{-1} d.w. and pp′DDT (1–11 ng g^{-1} d.w.). The concentration increase observed around 1986 (from 24–25 cm to 19–20 cm) is likely due to the landslide that occurred in Valtellina in 1987, causing the input of a huge amount of sediments and soils from high altitude zones to the lake through the Adda River (Alexander, 1988).

Regarding the PCBs (Fig. 2), a significant ($p < 0.05$) decreasing trend is recognizable towards the top of the core from the first 10 cm ($R^2 = 0.86$), following the sharp increase in the period 2000–2002 (11–12 cm), when three flood events occurred and the lake overflowed at the city of Como (Como Municipality, pers. comm.). The most abundant group of PCBs, on the basis of the number of chlorine substituents in the molecule, is represented by the hexa-CB followed by the hepta- and penta-CB.

The persistence of high levels of hydrophobic organic contaminants in surface sediments, even though they were banned at the end of the 1970s (in Italy, DDT and PCB uses were stopped in 1978 and 1983, respectively), indicates that pollution sources are still present in the watershed. A local source of DDT residues has been detected in melting glaciers that released the pollutants accumulated in past years (Bettinetti et al., 2011). This fact was considered to be the cause of the dramatic increase in pp′DDE levels in the mussel *D. polymorpha* collected in the northern part of the Como branch in 2005. On the contrary, no sharp increases have been recorded in the Como Bay sediments that correspond to that period, likely because most of the pollutants, which were released by the melting glaciers and transported into the lake by the suspended solids, settled in the central part of the lake—a part that is separated from the left southern branch by a submerged step at Bellagio ("Bellagio plateau", Fig. 1; Fanetti et al., 2008). However, the lack of DDT residue pollution recovered from the sediments located in the part of the basin that is farthest from the pollution source seems to indicate that the entire lake was impacted by the glacial release.

Previous studies (Binelli et al., 2001) indicate that the main source of PCBs is the city of Como rather than the melting of the glaciers (Bettinetti et al., 2008), whereas the pollutants enter the bay through fallout and water inlets and waste water treatment discharges. This hypothesis is confirmed by the increase in PCBs observed after flood events that transported solid materials from soils and other solid surfaces directly from the city of Como into the lake.

The contamination data for the present core can be compared with those of another core that was collected in 1991 in the same area of the lake and analysed for DDTs and PCBs by the same laboratory with the same methodological techniques (Galassi et al., 1995; Provini et al., 1995). A perfect overlapping of the two cores can be observed for the levels of DDTs and PCBs during the same sedimentation periods (1977–1991), and it is reasonable that the present sediment core can be considered a historical continuation of the previous core for the period 1991–2009. While the decreasing trend observed for PCBs in the previous work can be confirmed by the present data, an absence of a decline in the input of DDTs is shown for DDTs, likely due to the glacial release that would have started in the early nineties (Bettinetti et al., 2011).

3.4. Organism contamination

The zooplankton concentrations of organochlorine contaminants at the end of winter in 2009 and the agone concentrations collected in the deep areas of the Como (2006–09) and Lecco (2007–08) branches are reported in Table 1.

The zooplankton was mainly contaminated by the DDT metabolite pp′DDE and by the PCB metabolite hexa-CB, followed by hepta-CB and penta-CB.

The DDT concentrations in the agone of the Como branch were generally lower or similar to those of PCB. In 2009 the total PCB concentrations were 3.7 times higher than the total DDTs and in the zooplankton the ratio was 7.5. In this case at least the ratio of PCBs and DDTs is apparently not conservative within this food web. The concentration of DDTs was relatively constant over time, while the concentration of PCBs increased in 2009.

In the Lecco branch, which is directly influenced by the Adda River outlet, the concentrations of both the PCBs and DDTs measured in the agone were lower in 2007 and were comparable/slightly higher in 2008.

The fish in all years and sites were generally contaminated by pp′ DDE among the types of DDTs, while among the PCBs, the hexa-CB prevailed, followed by penta-CB, with the only exception occurring in 2009 when hepta-CB was more concentrated. In 2009, the octa- and nona-CB were less prevalent in the zooplankton and fish than they were in the sediments, perhaps due to the higher octanol–water coefficients, which would mean lower ratios of these PCBs in the pore-waters to those associated with the organic material of the sediments.

The pp′DDE exhibited the highest biomagnification factor (6.6). Among the PCBs, the biomagnification increased from the least chlorine substituted compounds towards the hexa-CB (3.7), and then it decreased with the increasing number of chlorines, confirming the hypothesis previously mentioned.

Considering that the coregonids represent one group of the two species inhabiting the deepest areas of Lake Como, with different behaviour (feeding and reproductive period) compared to the agone, it seems worth highlighting that in 2007, the contaminant levels in the northernmost part of the lake were lower than in the southwestern branch (PCBs: 0.34 and 0.40 mg kg^{-1} l.w.; DDTs: 0.10 and 0.11 mg kg^{-1} l.w.; Villa et al., 2011). Moreover, a previous study carried out in the early 1990s (Chiaudani and Premazzi, 1993) confirmed that the sediments and fish collected in the southern-west branch of Lake Como were the most polluted.

The DDT concentrations in the agone that were sampled during the years 2006–2009 never exceeded the limits for human consumption in Italy (Ordinanza Ministero della Sanità del 18 luglio 1990), which is 100 ng g^{-1} w.w. when the lipid content is 5–20%, as in this case (Fig. 3). Regarding the limit of PCBs for human consumption, the sum of the six PCBs (PCBs 28, 52, 101, 138, 153 and 180) cannot exceed 125 ng g^{-1} w.w. as stipulated by the EU 1259/2011 rule. This limit for the concentration of the six PCBs was only exceeded in 2009, where it was approximately two times higher than the recommended value (Fig. 3).

4. Conclusions

On the basis of our results, a public health risk may exist for the consumption of fish living in the southernmost part of the left branch of Lake Como due to PCB contamination. Presently, the elevated trophic status of the bay can play an important role in mitigating the contamination of the water column because lipophilic toxicants link to the particulate matter and are stored in sediments through the sedimentation process. However, the situation might worsen further before the trophic status can improve as a result of the measures undertaken to reach the standards requested by the EU Water Framework Directive 2000/60/EC. Therefore, POPs must be monitored in the future, both in fish and in water, and the pollution sources should be better identified and reduced.

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