



Trophic transfer of persistent organic pollutants through a pelagic food web: The case of Lake Como (Northern Italy)

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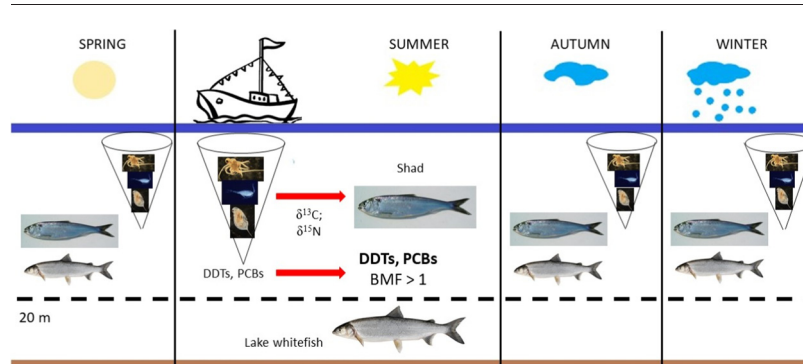
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HIGHLIGHTS

- Zooplankton and pelagic fish in Lake Como were analysed for DDT and PCB.
- Stable Isotopes Analysis indicates that the diet of landlocked shad is not always pelagic.
- Landlocked shad bioaccumulate contaminants from zooplankton in summer.
- BMF_{TL} (Biomagnification Factor) zooplankton/shad is in the range 0.9–1.9 for DDTs.
- BMF_{TL} pelagic zooplankton/shad is within the range 1.6–4.9 for PCB congeners.

GRAPHICAL ABSTRACT



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ABSTRACT

Despite DDT and PCB having been banned for about 40 years, they are still detectable in the environment. In the present research we specifically investigated the trophic transfer of these organochlorine contaminants (OC) through a pelagic food web of a deep lake in Northern Italy (Lake Como) over time. Zooplankton and fish were sampled each season of a year and OC concentrations and the carbon and nitrogen isotopic ratios were measured. By using stable isotopes, the direct trophic relationship between pelagic zooplankton and zooplanktivorous fish was confirmed for *Alosa agone* only in summer. Based on this result, the biomagnification factor normalized on the trophic level (BMF_{TL}) for organic contaminants was calculated. BMF_{TL} values were within the range 0.9–1.9 for DDT isomers and 1.6–4.9 for some PCB congeners (PCB 95, PCB 101, PCB 149, PCB 153, PCB 138 - present both in zooplankton and in fish and representing >60% of the PCB contamination), confirming the biomagnification of these compounds in one of the two zooplanktivorous fish species of the lake.

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1. Introduction

Legacy persistent organic pollutants, such as dichloro-diphenyl-trichloroethane and its metabolites (DDT) and poly-chlorinated-biphenyls (PCB), extensively used for sanitary, agricultural and/or industrial purposes from the mid-1940s and then banned/restricted, are

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still present in the environment for their long-time persistence. Organochlorine compounds (OC) are known to have effects on development, metabolism and reproduction of aquatic organisms (Berg et al., 2016; Gauthier et al., 2018; Jenkins et al., 2018). Sorption and distribution of these hydrophobic compounds in biota are influenced by their *n*-octanol/water partition coefficients and by the elimination rates being lower than the accumulation rates, which in turn results in their trophic accumulation along the food web (Coelhan et al., 2006; Bettinetti et al., 2016; Jurgens et al., 2016; Corsolini and Sarà, 2017; Zhang et al., 2017).

The biomagnification approach can be used to describe the potential bioaccumulation of toxicants in an organism relating it to its trophic position (Conder et al., 2012). A specific metric has to be used (as for example the biomagnification factor normalized on the trophic level – BMF_{TL}) (Conder et al., 2012), and the trophic position of each species within a food web and its temporal and spatial variations must be known too (Post, 2002).

Stable isotope analysis (SIA) of carbon (C) and nitrogen (N) signatures allows the understanding of the structure of the trophic webs, prey-predator relationships, and the nature of trophic relationships among organisms. The description of the trophic relationships and the organisms' diet reconstruction can be carried out using the difference between isotopic ratios of the consumer and its diet (i.e. the diet discrimination factors). The stable carbon isotope ratio ($\delta^{13}\text{C}\%$) reveals the contributions of different food sources, while the N isotope ratio ($\delta^{15}\text{N}\%$) indicates the trophic role since a consumer is typically enriched compared to its diet (Caut et al., 2009; Post, 2002; Visconti and Manca, 2011).

In lake ecosystems, SIA can reveal seasonal changes in $\delta^{13}\text{C}\%$ and $\delta^{15}\text{N}\%$ of zooplankton and fish, due to changes in food sources (Grey et al., 2001) or changes in taxonomic composition of pelagic communities, with different species having variable isotopic signatures (Matthews and Mazumder, 2003) that transfer this variability up to the food chain. The analysis can also underline the spatial variation in a single lake ecosystem (Syväranta et al., 2006), particularly when lakes are large and deep. Grey et al. (2001) reported that the pelagic phytoplankton has a more negative $\delta^{13}\text{C}$ value than littoral producers. Therefore, when evaluating the biomagnification in an aquatic ecosystem, it seems scientifically relevant to know the specific relationships among the different organisms of the trophic web, which can change with seasons.

The specific goals of the present study were: (i) to describe the pelagic trophic web structure of Lake Como, one of the deepest lake in Europe, located in Northern Italy; (ii) to assess the DDT and PCB contamination in the organisms; (iii) to estimate the BMF_{TL} of DDT and PCB in two pelagic fish species considering their real trophic relationships with the other organisms throughout the year.

2. Materials and methods

2.1. Study site

Lake Como (Northern Italy, 198 m a.s.l., Fig. 1) is the third largest Italian lake by both volume (22.5 km³) and surface area (145 km²) and the deepest one with the maximum depth of 425 m at Argegno. It is characterised by an upside down “Y” shape, where three sub-basins can be identified. It is a warm monomictic lake, with a complete circulation of the water column at temperatures around 6.5 °C in late winter. However, water mixing typically involves the first 150–200 m and complete turnover happens only periodically, after particularly cold and windy winters. The lake is therefore defined as olo-oligomictic (Ambrosetti et al., 1992). As concern its trophic status, Lake Como is classified as meso-eutrophic, with total phosphorus concentrations of about 25 µg L⁻¹ (at the maximum depth in spring) (Salmaso et al., 2014).

Lake Como is located in a heavily industrialized area. It has been of interest for several decades because of water quality problems, in

particular its south-western branch, where the major city (the city of Como) is located, no river outlet is present and the theoretical time of water renewal is 12.7 years. The city of Como represents a PCB hotspot (Bettinetti et al., 2014, 2016). Moreover, in recent years unexpected high levels of DDT in the lake were best explained by glacial release (Bettinetti et al., 2008): DDT, previously used for fruit tree pest control in the valleys below glaciers, was carried up to mountain in the air and fell on glaciers trapped in snow. As climate warming has caused glaciers to retreat, the trapped contaminants were released back into the environment in melt water, flowing through streams and rivers and accumulating in lake organisms and sediments.

2.2. Sampling of zooplankton and fish

Zooplanktonic pelagic samples (N = 4) were collected close to Argegno (45° 56' 36" N, 9° 7' 42" E, Fig. 1) seasonally from spring 2013 to winter 2014, following the main changes in zooplankton biomass and density. Live crustacean zooplankton were gathered in the late morning with a 200 µm-mesh nylon net with a diameter of 58 cm by several vertical hauls (in the range 4–20, depending on the season) at 0–20 m depth, in order to reach around 1 g dry weight (d.w.) for each sample. Since the average transparency of Lake Como is 6.43 m within the year this depth range seems to be representative of the whole zooplankton community.

Each sample was divided in three parts: one part was fixed and preserved in alcohol 95% until the identification of taxa using compound microscopy at 40× and the calculation of biomass from length–weight regression equations (Manca and Comoli, 2000; McCauley, 1984); a second part was allocated for SIA; the rest of each sample was filtered on a 2 µm pore glass–fibre filters (GF/C, 4.7 cm of diameter) and then frozen at –20 °C until OC analysis.

Six specimens of landlocked shad (*Alosa agone*) (Volta et al., 2011) and six specimens of lake whitefish (*Coregonus morpha hybrida*) were collected by professional fishermen near Argegno in the central part of the lake using pelagic gillnets, every season. After capture, fish were stored at 4 °C and subsequently measured (Table S11). Muscle fillets were collected from the dorsal region, between head and dorsal fin, both for the OC determination and SIA. For both the analysis the six fillets of each species were then pooled (N = 4 for both landlocked shad and lake whitefish). Fish species were selected for their dietary habits, since they are known as zooplanktivorous fish (Berg and Grimaldi, 1965, 1966).

2.3. C and N SIA

To determine C and N isotopic compositions of zooplankton, samples were defrosted and specimens for each taxon were isolated. Each group of zooplankton organisms and the fish tissue were oven-dried at 60 °C for 48 h and ground into fine powder. A subsample of 1 mg dry weight (d.w.) was weighed in aluminium capsules (5 × 9 mm) and sent to G:G Hatch Stable Isotope Laboratory (University of Ottawa, Canada). Stable isotopes were determined using a Carlo Erba 1110 Elemental Analyzer coupled with Thermo Finnigan DeltaPlus Advantage IRMS with a ConFlo III interface. The analytical precision of analysis (i.e. standard deviation), based on laboratory internal standard, was usually <0.2‰ for both elements.

Isotope ratios were calculated according to the following Eq. (1):

$$\delta^{13}\text{C} \text{ and } \delta^{15}\text{N} = \left[\left(\frac{R_{\text{sample}}}{R_{\text{standard}}} \right) - 1 \right] * 1000 \quad (1)$$

where, R equalled ¹³C/¹²C for $\delta^{13}\text{C}$ and ¹⁵N/¹⁴N for $\delta^{15}\text{N}$ and standards were PeeDee Belemnite and atmospheric N₂ for C and N respectively.

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