



Multimatrix measurement of persistent organic pollutants in Mar Chiquita, a continental saline shallow lake



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HIGHLIGHTS

- OCPs, PCBs and PBDEs were found in water, sediments, SPM, and fish.
- Endosulfan was the main pesticide found in all matrixes.
- γ -HCH and endosulfans overpassed quality guidelines and represent a risk to aquatic biota.
- PCB levels overpassed the AID for human consumption being a risk for human health.

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ABSTRACT

RAMSAR sites are determined by specific characteristics of the environment in terms of ecological productivity as well services for human development, but they are also one of the most threatened ecosystems. Thus, the objective of this work was to evaluate the dynamic of Persistent Organic Pollutants (POPs) in different biotic and abiotic matrixes of the RAMSAR site (wetlands with international importance), Mar Chiquita Lake. Sampling was performed according to land use (agricultural, urban, and industrial) at two stations: Laguna del Plata and Campo Mare. POPs were analyzed in superficial water (Sw), suspended particulate material (SPM), bottom sediment (Bs) and fish tissues (*Odontesthes bonariensis*). Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) were analyzed by GC-ECD. HCHs, Endosulfans, DDTs, PCBs and PBDEs were found in all matrixes at both stations. The high persistence and transport processes are responsible for the occurrence of HCHs, DDTs and PCBs in Bs, SPM and fish tissues, even many years after their prohibition. PBDEs showed lower levels according to the scarcity of punctual sources in the area. Endosulfan showed variable amounts in agreement with application periods since this pesticide was used until a few years ago in this area. Finally, PCB levels overpassed the acceptable daily intake for human consumption being a risk for human health. Thus, the present report confirms the occurrence of POPs in Mar Chiquita lake, alerting on the contribution of agricultural and urban pollutants in a RAMSAR site. Current results also raise concerns on biomagnification processes through the food web.

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1. Introduction

Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) represent persistent, bioaccumulative and toxic compounds of global concern (UNEP, 2011). The production and intensive agricultural or industrial use of these compounds during decades have led to widespread contamination of the environment. Most of these substances have been restricted and

forbidden in most countries since the late 1970s, but some developing countries are still using them because of their low costs and versatility in the industry, agriculture, and public health (Loganathan and Kannan, 1994). In Argentina, most of the OCPs and PCBs uses have been banned since 1998 and 2005, respectively, although their residues are still found in aquatic environments. Particularly, technical grade and active ingredients of endosulfan were included in the Persistent Organic Pollutants (POPs) list on April 2011 (UNEP, 2011). This insecticide was highly used in agriculture during the last 15 decades in Argentina, until it was recently phased out in July 2013. So, endosulfan residues were found in several the aquatic ecosystems associated to environmental matrixes (Colombo et al.,

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2011; Ondarza et al., 2011; Gonzalez et al., 2013). On the other hand, PBDEs have received enhanced attention in the last years due to environmental concentrations and are increasing in the environment at worldwide level. Although, there is scarce information on PBDEs levels in aquatic environments of South America, the prevalence of BDE 47, 99 and 100 is observed possibly as a consequence of penta-congener mixture use in the region (Shaw and Kannan, 2009). The occurrence of OCPs, PCBs and PBDEs is frequently associated to many deleterious effects in the biota, such as reproductive toxicity, developmental effects, endocrine disruption, biochemical and histological effect (Black et al., 1998a, 1998b; Tjärnlund et al., 1998; Khessiba et al., 2005; Roche et al., 2007; Bacchetta et al., 2010; Ballesteros et al., 2007, 2009).

Wetlands are considered one of the most important ecosystems that have different functions, such as nutrient cycling, sediment retention, and flood control, and provide habitat for many aquatic and terrestrial wildlife. Residues of OCPs, PCBs and PBDEs have been determined in aquatic environments at worldwide level including different kind of wetlands (Ribeiro et al., 2005; Sapozhnikova et al., 2005; Quinete et al., 2011). Mar Chiquita Lake, located in the central region of Argentina, is the largest continental saline shallow lake of South America. Because of its high salinity ($>35 \text{ g L}^{-1}$), wildlife diversity and great extension, Mar Chiquita is considered since 1993 as an important wetland of Western Hemisphere Shorebird Reserve Network and it was declared of international importance upon the RAMSAR convention on wetland sites in 2002. Besides, this lake is a stop-over and final destination of around 60 migrant bird species (42 aquatic birds) from North America and other countries, including shorebirds of Charadriidae and Scolopacidae families (Osinaga-Acosta et al., 2006). Three rivers, Dulce, Xanaes and Suquía that runs over urban and agricultural areas discharge their waters on the lake. The increase of population, industrialization and agricultural activities, mainly related with soybean cultures in the surrounding areas, has been evident during the past decades, representing growing pollution sources to the Mar Chiquita Lake and its associated wetlands. Among fish, silverside (*Odontesthes bonariensis*) is one of the two fish species capable of living in these high-salinity waters additionally to *Jenynsia multidentata* (Haro and Bistoni, 2007). Particularly, fishing is one of the major activities in the lake, providing edible fish to the local market, therefore POPs could be biomagnified in the food web and the population be exposed. Besides, migrant bird species who inhabit Mar Chiquita Lake feed on fish and invertebrates, being exposed to POPs and also transporting these compounds at worldwide level.

The present work reports on the occurrence and distribution of OCPs, PCBs and PBDEs in the environment of Mar Chiquita Lake particularly focusing on superficial water, suspended particulate material, bottom sediments and different organs/tissues of *O. bonariensis* in order to know the dynamics of these pollutants in this RAMSAR site.

2. Material and methods

2.1. Study area

The Mar Chiquita Lake (30° – $30^{\circ}55'S$ and 62° – $63^{\circ}W$) is located at 150 km NE from Cordoba City, Argentina. It presents a surface of 5770 km² and has been classified as hypersaline lake ($>35 \text{ g L}^{-1}$) (Bucher 2006). The climate is temperate with a mean rainfall of 740 mm concentrated on spring and summer seasons.

2.2. Sampling

Two monitoring stations were selected at the south coast of the lake (Fig. 1). The first station, Laguna del Plata (LP, $S 30^{\circ} 50'09.6''/W 62^{\circ} 53' 21.6''$), is located close to the Suquía River mouth. This freshwater system contributes with both urban and industrial wastes to Mar Chiquita Lake (Wunderlin et al., 2001). The second station, Campo Mare (CM, $S 30^{\circ}48'49.4''/W 62^{\circ}52'02.8''$) is surrounded mainly by crops. Three

temporal samplings at each station were carried out, covering dry (September), rainy (March) and post-rainy (May) seasons.

2.3. Sampling collection

2.3.1. Superficial water (Sw) and suspended particle material (SPM)

Sw samples were collected for OCPs, PCBs, and PBDEs analyses in 1-L pre-cleaned glass amber bottles, with Teflon-lined screw caps from each site. Water temperature, dissolved oxygen (DO), conductivity, and pH were recorded in situ, during sampling, using a multiparametric probe Multiline F/SET3 (WTW, Weilheim, Germany). From each Sw sample, suspended particle materials (SPMs) were obtained by passing the water sample through a 0.45- μm cellulose nitrate membrane filter (model HA 0.45 μm , Millipore, USA) under vacuum. SPMs were air dried at room temperature until they reached a constant weight and kept wrapped in aluminum foil at -20°C until analysis.

2.3.2. Bottom sediments (Bs)

Surface bottom sediments (0–5 cm) were collected with a stainless steel corer, air dried at room temperature, subsampled for physico-chemical and pollutants analyses and kept at -20°C until analysis.

2.3.3. Fish

Fifty individuals of *O. bonariensis* (considering station and time period) were sampled following standard fishing procedures. At the laboratory, fish were measured (average length $147.9 \pm 21.9 \text{ mm}$), weighted (average weight $29.7 \pm 13.9 \text{ g}$) and dissected to obtain gills (GLS), liver (LVR), muscle (MCL) and digestive tract content (DTC), which were wrapped in aluminum foil and stored at -20°C until chemical analysis.

2.4. Chemical analysis

2.4.1. Physical–chemical parameters of Bs

Total organic carbon (OC) was determined by wet oxidation (Walkley and Black, 1965). Particle size distribution of the sediments was determined by the pipette method (Galehouse, 1971); two sizes were estimated: silt + clay ($<2\text{--}200 \mu\text{m}$) and sand $200\text{--}2000 \mu\text{m}$.

2.4.2. OCPs, PCBs and PBDEs extraction procedure

- Sw: Pollutants were liquid–liquid extracted according to Gonzalez et al. (2012). Compounds were extracted from Sw by the liquid–liquid method. Briefly, 500 mL of water was spiked with 20 ng of PCB #103 as an internal standard and was shaken with 300 mL of hexane/dichloromethane for 2 h in a Teflon-lined cap glass amber bottle. After keeping overnight at 4°C , the organic layer was evaporated to 2 mL. Clean-up was performed by chromatography on activated (200°C , 24 h) silica gel. Elution was carried out with hexane and hexane/dichloromethane (50:50) mixtures, and fractions were joined, concentrated under vacuum and kept in sealed vials at -20°C . Results are reported as the mean of three independently replicated analysis from 3 liters per station and period.
- Bs, SPM and fish: Contaminants were extracted according to Metcalfe and Metcalfe, (1997) with modifications reported by (Miglioranza et al., 2003). Briefly, subsamples of Bs (6 g), filters containing the SPM were directly introduced into the Soxhlet extractor and fish organs, GLS ($0.57 \pm 0.31 \text{ g}$), LVR ($0.33 \pm 0.29 \text{ g}$), DTC ($0.85 \pm 0.59 \text{ g}$) and MCL ($2.61 \pm 1.24 \text{ g}$) were homogenized with anhydrous sodium sulfate, spiked with PCB #103 as internal standard and Soxhlet extracted with *n*-hexane: dichloromethane (50:50) for 8 h. Lipids from biota were removed by gel permeation chromatography using Bio-Beads S-X3 (200–400 mesh) and content was gravimetrically determined. POPs fraction was further purified using activated silica gel and extracts were concentrated and stored in 1 mL vials at -20°C prior to GC analyses.

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