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Title: Multimatrix measurement of Persistent Organic Pollutants in Mar Chiquita, a continental saline shallow lake

Article Type: Research Paper

Keywords: Mar Chiquita Lake - Polychlorinated biphenyls - Polybrominated diphenyl ethers - organochlorine pesticides - *Odontesthes bonariensis*

Corresponding Author: Dr. Karina S. B. Miglioranza, Dr.

Corresponding Author's Institution: Laboratorio de Ecotoxicología y Contaminación Ambiental, Universidad Nacional de Mar del Plata. CONICET

First Author: Maria L Ballesteros

Order of Authors: Maria L Ballesteros; Karina S. B. Miglioranza, Dr.; Mariana Gonzalez; Gilberto Fillmann; Daniel A Wunderlin; Maria A Bistoni

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Response to Reviewers: The Science of the Total Environment
Associate Editor
Dr Damiá Barcelo

Dear Dr. Damiá Barcelo:

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FCEyN, Mar del Plata University
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Argentina
e-mail: kmiglor@mdp.edu.ar
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Mar del Plata, April 27th of 2014

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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.

1 Multimatrix measurement of Persistent Organic Pollutants in Mar Chiquita, a continental saline shallow
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3 Ballesteros, M.L.¹, Miglioranza K.S.B.^{2*} Gonzalez, M.², Fillmann Gilberto⁴ , Wunderlin, D.A⁵, Bistoni,
4 M.A¹.

5
6
7
8
9
10 ¹Instituto de Diversidad y Ecología Animal (CONICET-UNC), Universidad Nacional de Córdoba,
11 Facultad de Ciencias Exactas Físicas y Naturales –Av. Vélez Sársfield 299 (5000), Córdoba, Argentina.

12
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15 Ambiental – Funes 3350 (7600), Mar del Plata, Argentina.

16
17
18
19
20 ³Laboratório de Microcontaminantes Orgânicos e Ecotoxicologia Aquática, Universidade Federal do Rio
21 Grande, Rio Grande, RS, Brazil

22
23
24 ⁴Instituto de Ciencia y Tecnología de Alimentos Córdoba (CONICET-UNC), Universidad Nacional de
25 Córdoba, Facultad de Ciencias Químicas, Dto. Química Orgánica. Haya de la Torre y Medina Allende,
26 Ciudad Universitaria, (5000), Córdoba, Argentina.

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29 *Corresponding author. Tel.: +54-223-4752426 int 455. Fax: +54-223-47118.

30 *E-mail address:* kmiglor@mdp.edu.ar

1 Abstract

2 RAMSAR sites are determined by specific characteristics of the environment in terms of ecological
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23 21 Key words: Mar Chiquita Lake - Polychlorinated biphenyls – Polybrominated diphenyl ethers –
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25 22 organochlorine pesticides – *Odontesthes bonariensis*
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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 matrices (Colombo et al., 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 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; Black, et al., 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, 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, have 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 this 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 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 *Odontesthes 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°55'S y 62°-63°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 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 (Figure 1). The first station, Laguna del Plata (LP, S 30° 50' 09.6" / W 62° 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° 48' 49.4" / W 62° 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 mm 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 physicochemical 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±21.9 mm), weighted (average weight 29.7±13.9 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 (< 2-200 µm) and sand 200-2000 (µm).

2.4.2 OCPs, PCBs and PBDEs extraction procedure

a) 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 were 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, fractions were joined,

concentrated under vacuum and kept in sealed vials at -20°C. Results are reported as the mean of 3 independently replicated analysis from 3 liters per station and period.

b) 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 ± 0.31 g), LVR (0.33 ± 0.29 g), DTC (0.85 ± 0.59 g) and MCL (2.61 ± 1.24 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.

2.4.3 Analytical procedure

POPs were identified and quantified by GC-ECD using a Shimadzu 17-A chromatograph, equipped with a SPB-5 (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column. One microliter was splitless injected (275 °C), and detector at 290 °C. The oven temperature was held at 100 °C for 1 min, increased to 150 °C at 5 °C min⁻¹ (held for 1 min), further increased to 240°C at 1.5 °C min⁻¹, followed by a final heating up to 300°C at 10 °C min⁻¹ (held for 10 min). Ultrapure helium was used as carrier and nitrogen as make-up gas. Identification and quantification of compounds were performed by injection of OCPs, PCBs and PBDEs standard solutions “Bromodiphenyl Ethers-Lake Michigan Study” was obtained for AccuStandard Inc. and PCB #103 as internal standard (Ultra Scientific, USA).

2.4.4 Quality control

Procedural and instrumental blanks were analyzed throughout the procedure to check for interference and laboratory contamination. Concentrations in the samples were based on surrogate standards added. Analyte concentrations were calculated using the PCB 103 surrogate. The internal standard (TCMX) was used to calculate surrogate recoveries. It was greater than 80% (surface water) 90% (other matrixes). PCB #103 was also used for peaks identification through relative retention time. Detection limits were calculated according to (Keith et al., 1983), ranging between 0.03 and 0.05 ng mL⁻¹ for HCHs (α-, β-, γ- and δ- isomers) and between 0.08-0.33 ng mL⁻¹ for the rest of chlorinated compounds [Chlordanes (α- and γ- isomers and trans-nonachlor), DDTs (*pp'*-DDE, *pp'*-DDD and *pp'*-DDT), endosulfans (α- and β-

isomers and sulfate), aldrin, dieldrin, endrin, Heptachlors (heptachlor and heptachlor epoxide)], PCBs (IUPAC #8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 138, 126, 187, 128, 167, 156, 157, - 180, 169, 189, 195, 206 and 209) and PBDEs (IUPAC #28, 47, 66, 100, 99, 154, 153 and 138).

2.5 Statistical Analysis

Statistical analyses were carried out using the Infostat Software Package (Di Rienzo et al., 2011). Differences among sites and sampling periods were assessed by a one way analysis of variance (ANOVA), followed by a Multiple Comparison Test (Tukey). When parametric assumptions were not fulfilled, Kruskal-Wallis followed by multi-comparison Dunn's tests was used. Differences among fish organs were tested using a Friedman ANOVA analysis for multiple dependent samples. Significance level was set at $\alpha = 0.05$.

2.6 Contaminant levels in muscle: acceptable daily intake (ADI)

The quantity of pollutant in a 300 g filet (burden) was calculated using fresh weight concentration. The total amount that an individual of 70 kg could ingest per day without risk was obtained on the basis of the reference dose (RfD) that indicate the quantity of the compound per kilogram of weight that a human being could ingest per day without risk and has the units $\mu\text{g} \cdot \text{kg}^{-1} \cdot \text{d}^{-1}$. Then the burden was expressed as percentage of the amount allowed for a 70 kg individual.

3. Results and Discussion

3.1 Physical-chemical parameters of Sw and Bs:

Table 1 shows physicochemical parameters of Sw and Bs at both sites. In Bs, the percentage of Organic Carbon (OC) ranged between 0.46 and 0.69. Sw at both sites was alkaline with $\text{pH} > 8$. Also, high conductivity ($45\text{--}56 \text{ mS cm}^{-1}$) and dissolved oxygen (8 mg L^{-1}) values were observed which agree with a hypersaline lake, with high dissolved oxygen concentration. Bs was characterized as silty sand and silty loam in LP and CM, respectively and there was no relationship between sediment TOC content and total pollutant concentrations. Miglioranza et al., (2013) stated that other factors are involved in pollutant retention, such as punctual sources and/or differential partition of pollutants between BS and SPM.

3.2 POPs in the lake

Concentration and distribution of contaminants in Sw, SPM, Bs and fish organs/tissues are summarized in Tables 2 and 3. There were no statistical differences in residue levels of OCPs, PCBs and PBDEs between sampling stations at all studied matrixes. As a general trend, ratios of OCPs/(PCBs + PBDEs) > 1 at both stations, sampling periods and matrices showed the predominance of agricultural over industrial and urban pollution sources (Miglioranza et al., 2013).

3.2.1 HCHs

Sw and SPM showed the highest HCHs levels during post-rainy season at both LP (31.8 ng L⁻¹ and 17.8 ng g dry wt⁻¹) and CM (15.7 ng L⁻¹ and 28.8 dry wt⁻¹) (Table 2) while for Bs, the concentrations remained constant between 0.4 and 1 ng g dry weight⁻¹ during all the sampling periods. Among HCHs, 90% corresponded to the γ -HCH isomer (Lindane) followed by α - and β - isomers at all studied matrices. These results are not surprising for this area (Suquía River) considering the intensive past use of γ -HCH during decades in the study area. Moreover, although the use of HCHs was forbidden in 1998 for different activities, the γ -isomer was allowed until 2011 as active ingredient in lotions used for lice and scabies control (ANMAT, 2011). The maximum permitted levels of γ -HCH for aquatic biota protection in saline waters, proposed by the National Argentinean Water Council (INA, 2005) is 4 ng L⁻¹, and this value was exceeded during the post-rainy season at both LP and CM, where γ -HCH levels reached 21.7 ng L⁻¹ and 5.8 ng L⁻¹ respectively. Also, γ -HCH value in sediment from post-rainy season (0.77±0.13 ng g dw⁻¹) exceeded the Canadian reference value for sediments (0.32 ng g dw⁻¹, CCME 2001) whereas during dry and rainy seasons the γ -HCH levels were just slightly over this reference value (0.33±0.18 ng g dw⁻¹ and 0.35±0.13 ng g dw⁻¹, respectively).

Similar results were found in fish, where the highest levels were found during post-rainy season, although differences among periods were not significant (Table 3). The distribution pattern of pollutants among organs/ tissues was DTC≥LVR>GLS≥MCL (p<0.05). Lindane is a potent stimulant of the central nervous system, which produces biochemical and histological alterations in animals (Soengas et al., 1997; Pesce et al., 2008). Therefore, aquatic biota inhabiting Mar Chiquita Lake is exposed to risk levels of Lindane in water and sediments. Fish muscle does not represent a risk for human consumption since the levels of this contaminant did not overpass the daily allowed intake (ADI, Table 4),

3.2.2 Endosulfans:

1 The highest endosulfans levels in Sw were registered in rainy and post rainy seasons at both sites (Table
2 2). Those seasons are coincident with application and post-application periods of pesticides in the study
3 area. Since technical endosulfan was in use when samples were taken, aerial spraying on nearby soybean
4 crops, atmospheric wash out and, runoff from soils could be the major input pathways of this pesticide to
5 the lake (Leonard et al., 2000; Jergentz et al., 2004; Silva Barni et al., 2013).

6 The sum of α - and β - isomers was lower than the guideline proposed by INA for marine water ($\leq 8 \text{ ng L}^{-1}$
7 ¹) reaching up to 6.4 and 6.1 ng L^{-1} in rainy season (application period) at both LP and CM stations.
8 Besides α - and β - isomers, the main endosulfan metabolite, the endosulfan sulfate was found at levels
9 that ranged between 1.5 and 12.2 ng L^{-1} in Sw during dry and rainy seasons, respectively. This metabolite
10 is as toxic as, and also more persistent than the α - and β - isomers (Goswami et al., 2009). However, this
11 compound is not considered in the INA guideline of 8 ng L^{-1} for saline waters (INA, 2004). Therefore, if
12 endosulfan sulfate levels are included in the guidelines assuming a similar toxicity, the total levels of α , β
13 and sulfate of 11.6 and 9.73 ng L^{-1} in LP and 8.9 and 6.3 ng L^{-1} in CM, respectively, would surpass the
14 maximum limit. Gonzalez et al., (2012) registered similar levels of total endosulfans in a post-application
15 period in the Quequén River basin (Southern Pampa, Argentina). Also, Darko et al., (2008) reported
16 endosulfan levels of 0.064 ng L^{-1} in Lake Bosomtwi (Gahna). Those levels were much lower than those
17 registered in the present study even when both lake shores have similar uses such as agricultural
18 activities.

19 The highest concentrations of endosulfans found in SPM and Bs at the CM site, denote a clear influence
20 of the agricultural activities on the aquatic environment. Particularly these levels were significantly high
21 during rainy and post-rainy seasons, respectively compared with other sampling periods (Table 2). As it is
22 well known, endosulfans easily adsorb to soil particles, entering to aquatic ecosystems through runoff
23 during rain events. Thus, (Jergentz et al., 2005) found concentrations of 318 ng g^{-1} of endosulfans (sum of
24 α - and β - isomers) after a rainfall event in SPM of the Horqueta River, close to a soybean field in a
25 pampean region of Argentina. Also Gonzalez et al., (2013), found higher levels of endosulfan in SPM
26 than SS and Sw during application periods after rainfall period of 184 mm day^{-1} in Quequén River.
27 However, the levels registered by those authors were three order of magnitude higher (2000 ng g dry wt^{-1})
28 than those found in this study (Table 2).

29 In *O. bonaerensis*, endosulfan group accounted for 30-85% of the total contaminants in all tissues/organs
30 with the highest pesticide levels in samples from post rainy season (Table 3). The distribution pattern was

GLS=DTC>LVR≥MCL ($p<0.05$). Although endosulfan was recently forbidden, the residue levels in muscle were between 0.3 and 3% of the ADI, therefore do not represent a risk to human health. Similar findings were registered by Silva Barni, (2013) in Quequén River where the levels of endosulfans in silverside muscle were around 0.75% of ADI (Table 4). Although differences between sampling sites were not significant, the highest values of endosulfans were registered in fish from LP. This pattern was in agreement with the endosulfan level pattern found in Bs and SPM. Therefore this relationship between fish and sediment could indicate that the common endosulfan source for aquatic ecosystem is the runoff from agricultural fields to the lake. In the literature there are examples about changes at different levels of organization in aquatic environments related with the endosulfan impacts. In this regard, Leonard et al., (2000) found changes in the invertebrate community related with runoff of endosulfan in Naomi River (Australia). Also, studies about endosulfan effects on fish have been developed, including changes in biotransformation and oxidative stress enzymes (Bacchetta et al., 2010), increased levels of lipid peroxidation (Silva Barni et al., 2013) and, histopathological alterations in gills and liver (Ballesteros et al., 2007).

3.2.3 DDTs:

DDTs levels in Sw, ranged between 0.2 and 3.24 ng L⁻¹ (Table 2) with a predominance of *p,p'*-DDE (> 90%, 0.2-2.9 ng L⁻¹) followed by the parental compound, *p,p'*-DDT (0.5-1.7 ng L⁻¹). Besides at both stations, SPM had the highest levels of DDTs in post-rainy period (LP: 5.6 ng g dry wt⁻¹; CM 8.4 ng g dry wt⁻¹) whereas in Bs higher values were found in rainy season (Table 2). Only *p,p'*-DDT was found in SPM while both *p,p'*-DDE and *p,p'*-DDT in Bs. Additionally, *p,p'*-DDD was below detection limit at all abiotic matrices. In Bs, the *p,p'*-DDE/*p,p'*-DDT ratio was > 1 denoting aerobic metabolism in this matrix. Since *p,p'*-DDD is formed through an anaerobic degradation of *p,p'*-DDT and the Bs correspond to the upper five centimeters, aerobic metabolism would dominate (Hwang et al., 2006). Similar *p,p'*-DDE levels (0.9 ng g dry wt) and *p,p'*-DDE/*p,p'*-DDT ratios were registered by Miglioranza et al., (2013) in SS from the Lower Valley of Rio Negro River (Argentina). The authors indicated that these levels were the results of the historical DDT use in the area.

Although statistical differences of DDT residues in silverside tissues considering sampling date or periods of pesticide application were not found (Table 3), higher values of DDTs were found in CM compared with LP. The distribution pattern among organs/tissues was DTC=LVR>GLS>MCL ($p<0.05$). Moreover,

p,p'-DDE was the main metabolite present in all analyzed samples (at both CM and LP). Besides, there was a relation *p,p'*-DDE/*p,p'*-DDT ratio > 1, which is coincident with those results registered for abiotic compartments. This ratio was also reported by Silva Barni et al., (2013) in silverside of Quequén River. These authors explained that this ratio could be related with a *p,p'*-DDT biotransformation by fish as well as the uptake of *p,p'*-DDE from the environment. In this regard, Garcia et al., (2000) found similar distribution pattern and levels of DDT in fish (*Lepidorhombus boscii* and *Phycis blennoides*) in the North West Mediterranean. The values were 99.0 and 0.8 ng g wt w⁻¹ in liver and muscle, respectively. Although in Argentina the use of DDT was restricted in 1968 and was totally banned in 1990, the residues were also found in several environmental compartments (Miglioranza et al., 2003; Colombo et al., 2011; Ondarza et al., 2011 and 2014; Gonzalez et al., 2013; Miglioranza et al., 2013). The occurrence of the metabolite *p,p'*-DDE is a consequence of aerobic metabolism of *p,p'*-DDT and its higher persistence compared to parent compound (Hwang et al. 2006). Moreover, the occurrence of *p,p'*-DDT could be mainly related with the current use of the acaricide Dicofol in the area. Moreover atmospheric inputs of fresh DDT source is not discarded (Gonzalez et al., 2010).

3.2.4 PCBs:

PCBs were registered in Sw at all sampling periods and both sites without significant differences (Table 2). Although maximum permitted levels for saline water are not available, the total concentrations of PCBs did not overpass the maximum permitted levels for freshwater environments proposed by INA (≤ 9 ng L⁻¹). Considering these values, PCBs would not represent a risk for aquatic biota inhabiting the lake under these conditions.

The levels of PCBs in SPM and Bs were significantly higher in post-rainy season respect to the other sampling periods being 32.4 and 2.4 ng g dry wt⁻¹, respectively (Table 2). However, these values were lower than other reported for some Argentinean basins. Menone et al., (2001) reported higher PCBs levels (16-69 ng g dry wt⁻¹) in Bs of Mar Chiquita Lake tributaries (Buenos Aires) and Ondarza et al., (2012) reported environmental concentrations that reached up 1016.6 ng g dry wt⁻¹ in SPM of Río Negro River basin. Additionally the PCB levels in Bs were below Canadian Sediment Guidelines for protection of sediments (21.5 ng g⁻¹) at both stations and sampling periods (CCME, 2001). Despite these relative low PCBs values would represent a chronic contamination given by congener distribution pattern, with a predominance of penta (#110 and 118) and hexachlorobiphenyls (#138 and 153). The levels and

1 occurrence of such congeners agree with Arochlor 1254 and 1260 compositions which were historically
2 used in Argentina.

3 The PCBs levels in fish from LP were higher than CM, although differences were not statistically
4 significant. Moreover, as was observed for abiotic matrices, the highest levels were registered in post-
5 rainy season. The distribution pattern of total PCBs concentrations was LVR=DTC=GLS>MCL ($p<0.05$)
6 indicating that both gills and diet are important uptake routes for these contaminants. Despite the low
7 PCBs levels in all abiotic matrices, muscle tissue of silverside exceeded the ADI at both sampling stations
8 (Table 4) during post-rainy season representing a risk to human health. The levels registered in the
9 present study were much higher than those found in silverside from Quequén River ($0.22 \text{ ng g dry wt}^{-1}$)
10 from (Silva Barni., 2013).

11 The congener pattern was similar to those reported to abiotic matrices, but it is important to remark the
12 presence of congener #118. This is a molecule mono-ortho substituted and due to this chemical structure,
13 it has the ability to trespass on biological membranes easily and it is considered as highly toxic to
14 organisms. Therefore the presence of PCB #118 could cause a potential damage for fish and humans.
15 Thus, several authors have reported reduced survival, food consumption, fecundity, growth and pituitary
16 gonadotropin content, in fish exposed to a mixture of mono-ortho and non-ortho PCBs at 0.76, 3.8, and
17 $19 \mu\text{g g wt wt}^{-1}$ (Black, et al., 1998 a and b).

19 3.2.5 PBDEs:

20 The concentrations of PBDEs were similar in the abiotic matrices with no statistical differences between
21 both site and sampling periods. An exception was the higher PBDEs levels in Sw from CM dry season
22 (1.34 ng L^{-1}), (Table 2). This increasing of PBDEs during dry season could be a consequence of the lower
23 water inputs into the lake and therefore lower contaminant dilution. Particularly, the BDE-47 was the
24 unique congener detected in water samples. By other hand, PBDE levels, in Bs and SPM, ranged between
25 $0.6 - 3.0$ and $0.2 - 14.3 \text{ ng g dw}^{-1}$, respectively. There is not a sediment quality guidelines available for these
26 chemicals, however the PBDE levels were similar to sediments from China ($0.15 - 2.4 \text{ ng dry wt}^{-1}$; Xu et
27 al., 2009) and much lower than sediment from Korean marine sediments ($27.8 \text{ ng dry wt}^{-1}$; Moon et al.,
28 2007). The distribution pattern in both Bs and SPM was BDE-47>BDE-100>BDE-99>BDE-154.
29 Moreover, the predominance of these congeners suggests a possible penta- BDE source in the area in
30 addition to atmospheric deposition.

Regarding to fish organs (Table 3), the PBDEs levels in post-rainy season were higher than the other periods with significant differences in GLS (6.7 and 4.7 ng g w wt⁻¹ for LP and CM, respectively) and LVR from LP fish among sampling periods (3.8 and 0.7 ng g w wt⁻¹ for post-rainy and dry season, respectively). Although no significant differences between sampling stations were found, PBDEs levels in LP were higher than CM suggesting the influence of the vicinity of Cordoba City. The distribution pattern was GLS=DTC=MCL>LVR, and as was observed for PCBs compounds, GLS and DTC constitute the main uptake routes for PBDEs. The residue levels found in this study were much higher than those registered by Silva Barni et al., (2013) in silverside muscle from Quequén River (0.22 ng g wet wt⁻¹). Although Mar Chiquita Lake and Quequén rivers are agricultural systems, the levels of PBDEs registered in the present study suggest an important source of industrial contaminants from the tributaries, such as Suquía River, which run along an important urban. In this regard, Ondarza et al., (2012) reported similar levels and congeners distribution of PBDEs in tissues of *Oncorhynchus mykiss* from Río Negro River ranging from 1.21 ng g wet wt⁻¹ in muscle up to 31.29 ng g wet wt⁻¹ in gonads. Also, Colombo et al. (2011) registered PBDE concentrations up to 220 ng g wet wt⁻¹ in tissues of farmed *Prochilodus lineatus* from an urban area of Buenos Aires city. Besides Guo et al., (2008) reported PBDE concentrations in fish ranged of 1.9 ng g wet w⁻¹ and the distribution was similar to those reported in this study. Also, Montory and Barra, (2006) registered PBDEs concentrations up to 1.46 ng g wet wt⁻¹ in tissues of farmed *Salmo salar*. In the present work, fish muscle does not represent a risk for human consumption since the levels of this contaminant do not overpass the ADI (Table 4).

PBDEs congener pattern in fish was coincident with those observed in SPM and Bs. The relatively higher concentrations of BDE-47 and BDE-99 at all matrices could be due to the debromination of higher brominated BDEs (Eljarrat et al., 2005). Also, Stapleton et al., (2004) found a decrease in BDE-99 and a rapid increase of BDE-47 in fish fed with BDE-99. Moreover, these authors pointed out that because their physicochemical properties, BDE-47 and BDE-99 are expected to be more bioavailable to uptake from the environment than higher brominated congeners and therefore more susceptible to biomagnification in the food web. PBDEs have been widely recognized as emergent contaminants and recent toxicological studies in fish have suggested that feeding with BDE-47 and BDE-99 induced inhibition of EROD and Glutathione reductase activities after 22 days (Tjärnlund et al., 1998).

3.2.6 Heptachlors, Aldrin, Dieldrin, Endrin and Chlordanes:

1 Total concentrations of Heptachlors, Drins, and Chlordanes represented less than 20 % of total pollutant
2 residues in the studied matrices, with concentrations ranging between <DL and 2.6 ng L⁻¹ in Sw, 0.08 and
3 1.6 ng g dw⁻¹ in Bs and SPM and <DL and 6.3 for fish organs/tissues. These results could be consequence
4 of chronic pollution of legacy recalcitrant pesticides, showing therefore low concentrations in all
5 matrices.

6 7 8 9 10 11 12 Conclusions

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9 The occurrence of legacy (DDTs, PCBs, HCHs) and recently banned compounds such as endosulfans and
10 PBDEs, in different matrices from Mar Chiquita lake, a RAMSAR site of Argentina was determined. In
11 summary:

12 1. OCPs/ (PCBs + PBDEs) > 1 ratios at both stations showed the predominance of agriculture over
13 industrial and urban pollution sources. The enhanced precipitation during spring and summer periods,
14 coincident with pesticide application period, leads to high water inputs from tributaries and runoff from
15 surrounding agricultural fields to the Mar Chiquita lake. Thus, the high loads of endosulfans, is indicative
16 of the recent and massive use of this agrochemical. Besides, during the dry season, levels of contaminants
17 were concentrated in Sw as a consequence of evaporation and lower water inputs to the lake.

18 2. The highest levels of OCPs, PCBs and PBDEs in SPM and Bs, were registered in the post-rainy
19 season at both sampling stations. Pollutant levels in SPM were one order of magnitude higher than those
20 of BS leading to a risk for filter feeders..

21 3. The high γ - HCH and endosulfan levels overpassed national and international quality guidelines of
22 water and sediments and therefore represent a risk to aquatic biota.

23 4. The distribution pattern of contaminants in fish tissues/organs shows a predominance of endosulfans
24 and PCBs, followed by PBDEs, DDTs and HCHs as the consequence of the recent use of endosulfan and
25 the influence of industrial activities primarily provided by the Suquía River.

26 5. The levels of OCPs, and PBDEs in *O. bonariensis* muscle were below ADI, whereas PCB levels
27 overpassed the ADI for human consumption being a risk for human health.

28 6. PBDEs also showed lower levels as emerging pollutants with no punctual sources in the surrounded
29 area. However, owing to the currently lack of specific regulations for PBDEs in environmental samples in

Argentina, a nationwide survey of PBDEs concentration is recommended, as to establish a quality standard for PBDE control in the future.

Mar Chiquita lake represent a unique and particular environment that deserves to be preserved, hence action toward minimizing inputs from Suquía river and soil management strategies should be established. The role of police-makers on pesticide sprays and soil cultivation should be enhanced in order to protect populated or reserve areas with buffer zones, like vegetated barriers and therefore minimize the pollutants arrival to the lake.

Conflict of Interest

All the authors have no conflicts of interest.

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8 Figure Captions

10 Fig. 1 Study area and location of sampling stations in Mar Chiquita Lake

1 1 Multimatrix measurement of Persistent Organic Pollutants in Mar Chiquita, a continental saline shallow
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5 3 Ballesteros, M.L.¹, Miglioranza K.S.B.^{2*} Gonzalez, M.², ~~Gilberto~~ Fillmann⁴ Gilberto⁴, Wunderlin, D.A.⁵,
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7 4 Bistoni, M.A.¹.
8
9 5
10 6 ¹Instituto de Diversidad y Ecología Animal (CONICET-UNC), Universidad Nacional de Córdoba,
11
12 7 Facultad de Ciencias Exactas Físicas y Naturales –Av. Vélez Sársfield 299 (5000), Córdoba, Argentina.
13
14 8 ²Instituto de Investigaciones Marinas y Costeras (CONICET-UNMdP), Universidad Nacional de Mar del
15
16 9 Plata, Facultad de Ciencias Exactas y Naturales, Laboratorio de Ecotoxicología y Contaminación
17
18 10 Ambiental – Funes 3350 (7600), Mar del Plata, Argentina.
19 11 ³Laboratório de Microcontaminantes Orgânicos e Ecotoxicologia Aquática, Universidade Federal do Rio
20
21 12 Grande, Rio Grande, RS, Brazil
22
23 13 ⁴Instituto de Ciencia y Tecnología de Alimentos Córdoba (CONICET-UNC), Universidad Nacional de
24
25 14 Córdoba, Facultad de Ciencias Químicas, Dto. Química Orgánica. Haya de la Torre y Medina Allende,
26
27 15 Ciudad Universitaria, (5000), Córdoba, Argentina.
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42 29 *Corresponding author. Tel.: +54-223-4752426 int 455. Fax: +54-223-47118.
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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 allowed intake (DAIs-ADI-Acceptable daily intake) for human consumption being a risk for human health Thus, the present report confirm 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.

Key words: Mar Chiquita Lake - Polychlorinated biphenyls – Polybrominated diphenyl ethers – organochlorine pesticides – *Odontesthes bonariensis*

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 matrices (Colombo et al., 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 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 ~~possible~~ 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; Black, et al., 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, 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, have 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 this 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 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 *Odontesthes 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°55'S y 62°-63°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 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 (Figure 1). The first station, Laguna del Plata (LP, S 30° 50' 09.6" / W 62° 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° 48' 49.4" / W 62° 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.

2.23. Sampling collection:

2.23.1. 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 mm 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.

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

2.23.3. Fish: ~~A total of 50~~ 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±21.9 mm), weighted (average weight 29.7±13.9 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

2.34 Chemical analysis

~~2.34.1~~ 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 (< 2-200 µm) and sand 200-2000 (µm).

~~2.34.2~~ 2.4.2 OCPs, PCBs and PBDEs extraction procedure:

~~2.34.2.1a)~~ Sw:

Pollutants were liquid- liquid extracted according to Gonzalez et al., (2012). Compounds were extracted from Sw by the liquid – liquid method. 4 Briefly, 500 mL of water ~~were~~ spiked with 20 ng of PCB

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#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 keep~~ing~~ 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, fractions were joined, concentrated under vacuum and kept in sealed vials at -20°C. Results are reported as the mean of 3 independently replicated analysis from 3 liters per station and period.

~~2.34.2.2.b)-~~ 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 ± 0.31 g), LVR (0.33 ± 0.29 g), DTC (0.85 ± 0.59 g) and MCL (2.61 ± 1.24 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.

~~2.34.3, 2.4.3~~ Analytical procedure

POPs were identified and quantified by GC-ECD using a Shimadzu 17-A chromatograph, equipped with a SPB-5 (30 m x 0.25 mm i.d. x 0.25 µm film thickness) capillary column. One microliter was splitless injected (275 °C), and detector at 290 °C. The oven temperature was held at 100 °C for 1 min, increased to 150 °C at 5 °C min⁻¹ (held for 1 min), further increased to 240°C at 1.5 °C min⁻¹, followed by a final heating up to 300°C at 10 °C min⁻¹ (held for 10 min). Ultrapure helium was used as carrier and nitrogen as make-up gas. Identification and quantification of compounds were performed by injection of OCPs, PCBs and PBDEs standard solutions “Bromodiphenyl Ethers-Lake Michigan Study” was obtained for AccuStandard Inc. and PCB #103 as internal standard (Ultra Scientific, USA).

~~2.34.4, 2.4.4~~ Quality control and quality assurance

Procedural and instrumental blanks were analyzed throughout the procedure to check for interference and laboratory contamination Concentrations in the samples were based on surrogate standards added. Analyte concentrations were calculated using the PCB 103 surrogate. The internal standard (TCMX) was

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used to calculate surrogate recoveries. ~~Procedural and instrumental blanks were analyzed throughout the procedure to check for interference and laboratory contamination. Surrogate recovery (PCB #103)~~ It was greater than 80% (surface water) 90% (other matrixes) ~~using TCMX as internal standard.~~ PCB #103 was also used for peaks identification through relative retention time. Detection limits were calculated according to (Keith et al., 1983), ranging between 0.03 and 0.05 ng mL⁻¹ for HCHs (α -, β -, γ - and δ - isomers) and between 0.08-0.33 ng mL⁻¹ for the rest of chlorinated compounds [Chlordanes (α - and γ - isomers and trans-nonachlor), DDTs (*p,p'*-DDE, *p,p'*-DDD and *p,p'*-DDT), endosulfans (α - and β - isomers and sulfate), ~~Dins~~ (aldrin, dieldrin, endrin), Heptachlors (heptachlor and heptachlor epoxide)], PCBs (IUPAC #8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 138, 126, 187, 128, 167, 156, 157, - 180, 169, 189, 195, 206 and 209) and PBDEs (IUPAC #28, 47, 66, 100, 99, 154, 153 and 138).

2.5 Statistical Analysis

Statistical analyses were carried out using the Infostat Software Package (Di Rienzo et al., 2011). Differences among sites and sampling periods were assessed by a one way analysis of variance (ANOVA), followed by a Multiple Comparison Test (Tukey). When parametric assumptions were not fulfilled, Kruskal-Wallis followed by multi-comparison Dunn's tests was used. Differences among fish organs were tested using a Friedman ANOVA analysis for multiple dependent samples. Significance level was set at $\alpha = 0.05$.

2.6 Contaminant levels in muscle: acceptable daily intake (ADI)

~~Daily Intake Allowed (DIA) were calculated as~~ 70 kg individual ~~The quantity of pollutant in a 300 g filet (burden) was calculated using fresh weight concentration. The total amount that an individual of 70 kg could ingest per day without risk was obtained on the basis of the reference dose (RfD) that indicate the quantity of the compound per kilogram of weight that a human being could ingest per day without risk and has the units ug. kg⁻¹. d⁻¹. Then the burden was expressed as percentaje of the amount allowed for a 70 kg individual.~~

3. Results and ~~discussion~~ Discussion

3.1 Physical-chemical parameters of Sw and Bs:

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Table 1 shows physicochemical parameters of Sw and Bs at both sites. In Bs, the percentage of [Organic Carbon \(OC\)](#) ranged between 0.46 and 0.69. Sw at both sites was alkaline with pH > 8. Also, high conductivity (45-56 mS cm⁻¹) and dissolved oxygen (8 mg L⁻¹) values were observed which agree with a hypersaline lake, with high dissolved oxygen concentration. Bs was characterized as silty sand and silty loam in LP and CM, respectively and there was no relationship between sediment TOC content and total pollutant concentrations. Miglioranza et al., (2013) stated that other factors are involved in pollutant retention, such as punctual sources and/or differential partition of pollutants between BS and SPM.

3.2 POPs in the lake

Concentration and distribution of contaminants in Sw, SPM, Bs and fish organs/tissues are summarized in Tables 2 and 3. There were no statistical differences in residue levels of OCPs, PCBs and PBDEs between sampling stations at all studied matrixes. As a general trend, ratios of OCPs/(PCBs + PBDEs) > 1 at both stations, sampling periods and matrices showed the predominance of agricultural over industrial and urban pollution sources ([Miglioranza et al., 2013](#)).

3.2.1 HCHs

Sw and SPM showed the highest HCHs levels during post-rainy season at both LP (31.8 ng L⁻¹ and 17.8 ng g dry wt⁻¹) and CM (15.7 ng L⁻¹ and 28.8 dry wt⁻¹) (Table 2) while for Bs, the concentrations remained constant between 0.4 and 1 ng g dry weight⁻¹ during all the sampling periods. Among HCHs, 90% corresponded to the γ -HCH isomer (Lindane) followed by α - and β - isomers at all studied matrices. These results are not surprising for this area (Suquía River) considering the intensive past use of γ -HCH during decades in the study area. Moreover, although the use of HCHs was forbidden in 1998 for different activities, the γ -isomer was allowed until 2011 as active ingredient in lotions used for lice and scabies control (ANMAT, 2011). The maximum permitted levels of γ -HCH for aquatic biota protection in saline waters, proposed by the National Argentinean Water Council (INA, 2005) is 4 ng L⁻¹, and this value was exceeded during the post-rainy season at both LP and CM, where γ -HCH levels reached 21.7 ng L⁻¹ and 5.8 ng L⁻¹ respectively. Also, γ -HCH value in sediment from post-rainy season (0.77±0.13 ng g dw⁻¹) exceeded the Canadian reference value for sediments (0.32 ng g dw⁻¹, CCME 2001) whereas during dry and rainy seasons the γ -HCH levels were just slightly over this reference value (0.33±0.18 ng g dw⁻¹ and 0.35±0.13 ng g dw⁻¹, respectively).

Similar results were found in fish, where the highest levels were found during post-rainy season, although differences among periods were not significant (Table 3). The distribution pattern of pollutants among organs/ tissues was $DTC \geq LVR > GLS \geq MCL$ ($p < 0.05$). Lindane is a potent stimulant of the central nervous system, which produces biochemical and histological alterations in animals (Soengas et al., 1997; Pesce et al., 2008). Therefore, aquatic biota inhabiting Mar Chiquita Lake is exposed to risk levels of Lindane in water and sediments. Fish muscle does not represent a risk for human consumption since the levels of this contaminant did not overpass the daily allowed intake (DAIADI, Table 4),

3.2.2 Endosulfans:

The highest endosulfans levels in Sw were registered in rainy and post rainy seasons at both sites (Table 2). Those seasons are coincident with application and post-application periods of pesticides in the study area. Since technical endosulfan was in use when samples were taken, aerial spraying on nearby soybean crops, atmospheric wash out and, runoff from soils could be the major input pathways of this pesticide to the lake (Leonard et al., 2000; Jergentz et al., 2004; Silva Barni et al., 2013).

The sum of α - and β - isomers was lower than the guideline proposed by INA for marine water ($\leq 8 \text{ ng L}^{-1}$) reaching up to 6.4 and 6.1 ng L^{-1} in rainy season (application period) at both LP and CM stations. Besides α - and β - isomers, the main endosulfan metabolite, the endosulfan sulfate was found at levels that ranged between 1.5 and 12.2 ng L^{-1} in Sw during dry and rainy seasons, respectively. This metabolite is as toxic as, and also more persistent than the α - and β - isomers (Goswami et al., 2009). However, this compound is not considered in the INA guideline of 8 ng L^{-1} for saline waters (INA, 2004). Therefore, if endosulfan sulfate levels are included in the guidelines assuming a similar toxicity, the total levels of α , β and sulfate of 11.6 and 9.73 ng L^{-1} in LP and 8.9 and 6.3 ng L^{-1} in CM, respectively, would surpass the maximum limit. Gonzalez et al., (2012) registered similar levels of total endosulfans in a post-application period in the Quequén River basin (Southern Pampa, Argentina). Also, Darko et al., (2008) reported endosulfan levels of 0.064 ng L^{-1} in Lake Bosomtwi (Gahna). Those levels were much lower than those registered in the present study even when both lake shores have similar uses such as agricultural activities.

The highest concentrations of endosulfans found in SPM and Bs at the CM site, denote a clear influence of the agricultural activities on the aquatic environment. Particularly these levels were significantly high during rainy and post-rainy seasons, respectively compared with other sampling periods (Table 2). As it is

well known, endosulfans easily adsorb to soil particles, entering to aquatic ecosystems through runoff during rain events. Thus, (Jergentz et al., 2005) found concentrations of 318 ng g⁻¹ of endosulfans (sum of α- and β- isomers) after a rainfall event in SPM of the Horqueta River, close to a soybean field in a pampean region of Argentina. Also Gonzalez et al., (2013), found higher levels of endosulfan in SPM than SS and Sw during application periods after rainfall period of 184 mm day⁻¹ in Quequén River. However, the levels registered by those authors were three order of magnitude higher (2000 ng g dry wt⁻¹) than those found in this study (Table 2).

In *O. bonaerensis*, endosulfan group accounted for 30-85% of the total contaminants in all tissues/organs with the highest pesticide levels in samples from post rainy season (Table 3). The distribution pattern was GLS=DTC>LVR≥MCL (p<0.05). Although endosulfan was recently forbidden, the residue levels in muscle were between 0.3 and 3% of the ~~DAIADI~~, therefore do not represent a risk to human health. Similar findings were registered by Silva Barni, (2013) in Quequén River where the levels of endosulfans in silverside muscle were around 0.75% of ~~DAIADI~~ (Table 4). Although differences between sampling sites were not significant, the highest values of endosulfans were registered in fish from LP. This pattern was in agreements with the endosulfan level pattern found in Bs and SPM. Therefore this relationship between fish and sediment could indicate that the common endosulfan source for aquatic ecosystem is the runoff from agricultural fields to the lake. In the literature there are examples about changes at different levels of organization in aquatic environments related with the endosulfan impacts. In this regard, Leonard et al., (2000) found changes in the invertebrate community related with runoff of endosulfan in Naomi River (Australia). Also, studies about endosulfan effects on fish have been developed, including changes in biotransformation and oxidative stress enzymes (Bacchetta et al., 2010), increased levels of lipid peroxidation (Silva Barni et al., 2013) and, histopahtological alterations in gills and liver (Ballesteros et al., 2007).

3.2.3 DDTs:

DDTs levels in Sw, ranged between 0.2 and 3.24 ng L⁻¹ (Table 2) with a predominance of *p,p'*-DDE (> 90%, 0.2-2.9 ng L⁻¹) followed by the parental compound, *p,p'*-DDT (0.5-1.7 ng L⁻¹). Besides at both stations, SPM had the highest levels of DDTs in post-rainy period (LP: 5.6 ng g dry wt⁻¹; CM 8.4 ng g dry wt⁻¹) whereas in Bs higher values were found in rainy season (Table 2). Only *p,p'*- DDT was found in SPM while both *p,p'*-DDE and *p,p'* DDT in Bs. Additionally, *p,p'*-DDD was below detection limit at all

abiotic matrices. In Bs, the p,p' -DDE/ p,p' -DDT ratio was > 1 denoting aerobic metabolism in this matrix. Since p,p' -DDD is formed through an anaerobic degradation of p,p' -DDT and the Bs correspond to the upper five centimeters, aerobic metabolism would dominate (Hwang et al., 2006). Similar p,p' -DDE levels (0.9 ng g dry wt) and p,p' -DDE/ p,p' -DDT ratios were registered by Miglioranza et al., (2013) in SS from the Lower Valley of Rio Negro River (Argentina). The authors indicated that these levels were the results of the historical DDT use in the area.

Although statistical differences of DDT residues in silverside tissues considering sampling date or periods of pesticide application were not found (Table 3), higher values of DDTs were found in CM compared with LP. The distribution pattern among organs/tissues was $DTC=LVR>GLS>MCL$ ($p<0.05$). Moreover, p,p' -DDE was the main metabolite present in all analyzed samples (at both CM and LP). Besides, there was a relation p,p' -DDE/ p,p' -DDT ratio > 1 , which is coincident with those results registered for abiotic compartments. This ratio was also reported by Silva Barni et al., (2013) in silverside of Quequén River. These authors explained that this ratio could be related with a p,p' -DDT biotransformation by fish as well as the uptake of p,p' -DDE from the environment. In this regard, Garcia et al., (2000) found similar distribution pattern and levels of DDT in fish (*Lepidorhombus boscii* and *Phycis blennoides*) in the North West Mediterranean. The values were 99.0 and 0.8 ng g wt w^{-1} in liver and muscle, respectively.

Although in Argentina the use of DDT was restricted in 1968 and was totally banned in 1990, the residues were also found in several environmental compartments (Miglioranza et al., 2003; Colombo et al., 2011; Ondarza et al., 2011 and 2014; Gonzalez et al., 2013; Miglioranza et al., 2013). The occurrence of the metabolite p,p' -DDE is a consequence of aerobic metabolism of p,p' -DDT and its higher persistence compared to parent compound (Hwang et al. 2006). Moreover, the occurrence of p,p' -DDT could be mainly related with the current use of the acaricide Dicofol in the area. Moreover atmospheric inputs of fresh DDT source is not discarded (Gonzalez et al., 2010).

3.2.4 PCBs:

PCBs were registered in Sw at all sampling periods and both sites without significant differences (Table 2). Although maximum permitted levels for saline water are not available, the total concentrations of PCBs did not overpass the maximum permitted levels for freshwater environments proposed by INA (≤ 9 ng L^{-1}). Considering these values, PCBs would not represent a risk for aquatic biota inhabiting the lake under these conditions.

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The levels of PCBs in SPM and Bs were significantly higher in post-rainy season respect to the other sampling periods being 32.4 and 2.4 ng g dry wt⁻¹, respectively (Table 2). However, these values were lower than other reported for some Argentinean basins. Menone et al., (2001) reported higher PCBs levels (16-69 ng g dry wt⁻¹) in Bs of Mar Chiquita Lake tributaries (Buenos Aires) and Ondarza et al., (2012) reported environmental concentrations that reached up 1016.6 ng g dry wt⁻¹ in SPM of Río Negro River basin. Additionally the PCB levels in Bs were below Canadian Sediment Guidelines for protection of sediments (21.5 ng g⁻¹) at both stations and sampling periods (CCME, 2001). Despite these relative low PCBs values would represent a chronic contamination given by congener distribution pattern, with a predominance of penta (#110 and 118) and hexachlorobiphenyls (#138 and 153). The levels and occurrence of such congeners agree with Arochlor 1254 and 1260 compositions which were historically used in Argentina.

The PCBs levels in fish from LP were higher than CM, although differences were not statistically significant. Moreover, as was observed for abiotic matrices, the highest levels were registered in post-rainy season. The distribution pattern of total PCBs concentrations was LVR=DTC=GLS>MCL (p<0.05) indicating that both gills and diet are important uptake routes for these contaminants. Despite the low PCBs levels in all abiotic matrices, muscle tissue of silverside exceeded the ~~DAIADI~~ at both sampling stations (Table 4) during post-rainy season representing a risk to human health. The levels registered in the present study were much higher than those found in silverside from Quequén River (0.22 ng g dry wt⁻¹) from (Silva Barni., 2013).

The congener pattern was similar to those reported to abiotic matrices, but it is important to remark the presence of congener #118. This is a molecule mono-ortho substituted and due to this chemical structure, it has the ability to trespass on biological membranes easily and it is considered as highly toxic to organisms. Therefore the presence of PCB #118 could cause a potential damage for fish and humans. Thus, several authors have reported reduced survival, food consumption, fecundity, growth and pituitary gonadotropin content, in fish exposed to a mixture of mono-ortho and non-ortho PCBs at 0.76, 3.8, and 19 µg g wt⁻¹ (Black, et al., 1998 a and b).

3.2.5 PBDEs:

The concentrations of PBDEs were similar in the abiotic matrices with no statistical differences between both site and sampling periods. An exception was the higher PBDEs levels in Sw from CM dry season

(1.34 ng L⁻¹), (Table 2). This increasing of PBDEs during dry season could be a consequence of the lower water inputs into the lake and therefore lower contaminant dilution. Particularly, the BDE-47 was the unique congener detected in water samples. By other hand, PBDE levels, in Bs and SPM, ranged between 0.6 -3.0 and 0.2-14.3 ng g dw⁻¹, respectively. There is not a sediment quality guidelines available for these chemicals, however the PBDE levels were similar to sediments from China (0.15-2.4 ng dry wt⁻¹; Xu et al., 2009) and much lower than sediment from Korean marine sediments (27.8 ng dry wt⁻¹; Moon et al., 2007). The distribution pattern in both Bs and SPM was BDE-47>BDE-100>BDE-99>BDE-154. Moreover, the predominance of these congeners suggests a possible penta- BDE source in the area in addition to atmospheric deposition.

Regarding to fish organs (Table 3), the PBDEs levels in post-rainy season were higher than the other periods with significant differences in GLS (6.7 and 4.7 ng g w wt⁻¹ for LP and CM, respectively) and LVR from LP fish among sampling periods (3.8 and 0.7 ng g w wt⁻¹ for post-rainy and dry season, respectively). Although no significant differences between sampling stations were found, PBDEs levels in LP were higher than CM suggesting the influence of the vicinity of Cordoba City. The distribution pattern was GLS=DTC=MCL>LVR, and as was observed for PCBs compounds, GLS and DTC constitute the main uptake routes for PBDEs. The residue levels found in this study were much higher than those registered by Silva Barni et al., (2013) in silverside muscle from Quequén River (0.22 ng g wet wt⁻¹). Although Mar Chiquita Lake and Quequén rivers are agricultural systems, the levels of PBDEs registered in the present study suggest an important source of industrial contaminants from the tributaries, such as Suquía River, which run along an important urban. In this regard, Ondarza et al., (2012) reported similar levels and congeners distribution of PBDEs in tissues of *Oncorhynchus mykiss* from Río Negro River ranging from 1.21 ng g wet wt⁻¹ in muscle up to 31.29 ng g wet wt⁻¹ in gonads. Also, Colombo et al. (2011) registered PBDE concentrations up to 220 ng g wet wt⁻¹ in tissues of farmed *Prochilodus lineatus* from an urban area of Buenos Aires city. Besides Guo et al., (2008) reported PBDE concentrations in fish ranged of 1.9 ng g wet w⁻¹ and the distribution was similar to those reported in this study. Also, Montory and Barra, (2006) registered PBDEs concentrations up to 1.46 ng g wet wt⁻¹ in tissues of farmed *Salmo salar*. In the present work, fish muscle does not represent a risk for human consumption since the levels of this contaminant do not overpass the ~~DAIADI~~ (Table 4).

PBDEs congener pattern in fish was coincident with those observed in SPM and Bs. The relatively higher concentrations of BDE-47 and BDE-99 at all matrices could be due to the debromination of higher

brominated BDEs (Eljarrat et al., 2005). Also, Stapleton et al., (2004) found a decrease in BDE-99 and a rapid increase of BDE-47 in fish fed with BDE-99. Moreover, these authors pointed out that because their physicochemical properties, BDE-47 and BDE-99 are expected to be more bioavailable to uptake from the environment than higher brominated congeners and therefore more susceptible to biomagnification in the food web. PBDEs have been widely recognized as emergent contaminants and recent toxicological studies in fish have suggested that feeding with BDE-47 and BDE-99 induced inhibition of EROD and Glutathione reductase activities after 22 days (Tjärnlund et al., 1998).

3.2.6. Heptachlors, ~~Drins~~ Aldrin, Dieldrin, Endrin and Chlordanes:

Total concentrations of Heptachlors, Drins, and Chlordanes represented less than 20 % of total pollutant residues in the studied matrices, with concentrations ranging between <DL and 2.6 ng L⁻¹ in Sw, 0.08 and 1.6 ng g dw⁻¹ in Bs and SPM and <DL and 6.3 for fish organs/tissues. These results could be consequence of chronic pollution of legacy recalcitrant pesticides, showing therefore low concentrations in all matrices.

Conclusions

~~This study attempted to determined concentrations of POPs such as PCBs, PBDEs, HCHs, DDTs and endosulfans in aquatic compartments from Mar Chiquita lake, a RAMSAR site of Argentina. Particularly, it contribute to knowledge of human activities impact on the Mar Chiquita Lake. Results showed the~~
~~The occurrence of legacy (DDTs, PCBs, HCHs) and recently banned compounds such as endosulfans and PBDEs, in different matrices from Mar Chiquita lake, a RAMSAR site of Argentina was determined this aquatic environment.~~ In summary:

1. OCPs/ (PCBs + PBDEs) > 1 ratios at both stations showed the predominance of agriculture over industrial and urban pollution sources. The enhanced precipitation during spring and summer periods, coincident with pesticide application period, leads to high water inputs from tributaries and runoff from surrounding agricultural fields to the Mar Chiquita lake. Thus, the high loads of ~~pesticides like~~ endosulfans, is indicative of the recent and massive use of this agrochemical, ~~with the major inputs expected during rainy and post rainy sampling periods.~~ Besides, during the dry season, levels of contaminants were concentrated in Sw as a consequence of evaporation and lower water inputs to the lake.

2. ~~The highest Levels-levels~~ of OCPs, PCBs and PBDEs in SPM and Bs, were registered in the post-rainy season ~~where higher than those corresponding to rainy season~~ at both sampling stations. ~~It is worthy to remark that total pollutant~~ Pollutant levels in SPM were one order of magnitude higher than those of BS ~~leading to a risk for filter feeders. This is important because some fish and bird incorporate contaminants through diet, therefore high levels of contaminants would be biomagnified at the food web.~~

3. The high γ - HCH and endosulfan levels overpassed national and international quality guidelines of water and sediments and therefore represent a risk to aquatic biota.

4. The distribution pattern of contaminants in fish tissues/organs shows a predominance of endosulfans and PCBs, followed by PBDEs, DDTs and HCHs as the consequence of the recent use of endosulfan and the influence of industrial activities primarily provided by the Suquía River.

5. The levels of OCPs, and PBDEs in *O. bonariensis* muscle were below ~~DAIADI~~, whereas PCB levels overpassed the ~~DAIADI~~ for human consumption being a risk for human health.

6. PBDEs also showed lower levels as emerging pollutants with no punctual sources in the surrounded area. However, owing to the currently lack of specific regulations for PBDEs in environmental samples ~~currently~~ in Argentina ~~at present~~, a nationwide survey of PBDEs concentration is recommended, as to ~~provide better risk assessment and to~~ establish a quality standard for PBDE control in the future.

Mar Chiquita lake represent a unique and particular environment that deserves to be preserved, hence action toward minimizing inputs from Suquía river and soil management strategies should be established. The role of police-makers on pesticide sprays and soil cultivation should be enhanced in order to protect populated or reserve areas with buffer zones, like vegetated barriers and therefore minimize the pollutants arrival ~~of these pollutants~~ to the lake.

Conflict of Interest

All the authors have no conflicts of interest.

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Figure Captions

Fig. 1 Study area and location of sampling stations in Mar Chiquita Lake

Table 1: Physicochemical characteristics of bottom sediments (Bs) and superficial water (Sw) at the two sampling stations of Mar Chiquita Lagoon. Abbreviations: LP= Laguna del Plata; CM= Campo Mare

			Post-rainy		Dry		Rainy	
			LP	CM	LP	CM	LP	CM
Bs	Particle size (%)	sand (200-2000 µm)	27.5	80.0	46.3	96.0	42.7	78.8
		silt + clay (<2-200 µm)	72.5	20.0	53.7	3.0	57.3	21.2
		Total Organic Carbon	0.6	0.7	0.5	0.5	0.6	1.1
	Texture		Silty loam	Silty sand	Silty loam	Silty sand	Silty loam	Silty sand
Sw	Conductivity (ms cm ⁻¹)		48.5	56.9	53.0	55.7	45.3	48.1
	pH		8.7	8.6	8.9	9.0	8.4	9.0
	Dissolved oxygen (mg L ⁻¹)		13.5	12.4	10.3	10.6	8.1	9.2
	Temperature (°C)		17.5	16.7	17.4	15.5	26.8	15.5
	Salinity (g L ⁻¹)		33.0	38.7	36.0	37.9	30.8	32.7

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Table 2. Mean contaminant levels in superficial water (ng L⁻¹), suspended particulate matter (ng g dry wt⁻¹) and bottom sediments (ng g dry wt⁻¹) from Mar Chiquita Lake.

SITE		Superficial water			Suspended Particulate Material			Bottom Sediments		
Laguna del Plata	Season	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy
	Σ HCHs	31.8 ^b	2.9 ^a	7.3 ^a	17.8 ^b	4.7 ^a	2.0 ^{ab}	1.3 ^a	0.4 ^a	0.9 ^a
			(2.5-3.4)	(3.1-11.8)	(14.2-21.1)	(0.5- 12.0)	(1.4-2.7)		(0.1-0.6)	(0.5-1.4)
	Σ ENDO	9.7 ^a	0.9 ^a	11.6 ^a	37.5 ^b	1.5 ^a	12.3 ^{ab}	1.8 ^{ab}	0.5 ^a	2.2 ^b
			(0.5-1.3)	(<LD-22.2)	(25.8-54.9)	(0.3-4.0)	(11.5-13.1)		(0.4-0.5)	(1.8-2.8)
	Σ DDTs	3.2 ^a	0.2 ^a	0.2 ^a	5.6 ^b	0.2 ^a	<LD	0.03 ^a	0.3 ^{ab}	0.3 ^a
			(0.1-.22)		(2.5-7.3)	(0.1-0.2)			(0.2-0.3)	(0.2-0.4)
Campo Mare	Σ PCBs	7.3 ^a	3.2 ^a	3.3 ^a	32.4 ^a	2.6 ^a	2.3 ^a	1.4 ^c	0.4 ^a	0.9 ^b
			(2.5-3.9)	(0.3-7.0)	(23.9-41.2)	(0.4-5.9)	(0.8-3.9)		(0.3-0.5)	(0.7-1.0)
	Σ PBDEs	0.3 ^a	1.3 ^a	0.2 ^a	2.9 ^a	4.0 ^a	0.2 ^a	3.0 ^b	0.6 ^a	1.0 ^{ab}
			(1.1-1.6)	(<LD-0.3)	(0.1-5.0)	(<LD-6.8)	(0.2-0.2)		(0.5-0.8)	(0.3-1.9)
	Σ HCHs	15.7 ^a	3.8 ^a	4.6 ^a	25.8 ^a	6.8 ^a	4.5 ^a	0.9 ^b	0.5 ^a	0.5 ^a
			(0.6-7.0)	(3.2-6.1)	(20.1-31.1)	(1.3-17.2)	(3.4-6.7)	(0.7-1.1)	(0.5-0.6)	(0.3-0.9)
	Σ ENDO	6.3 ^a	3.1 ^a	8.9 ^a	57.3 ^a	3.3 ^a	22.5 ^a	2.1 ^b	0.8 ^a	1.3 ^{ab}
Campo Mare			(1.2-4.9)	(0.2-15.7)	(38.1-95.3)	(2.6-3.7)	(8-34.3)	(1.4-2.8)	(0.6-1.0)	(0.8-2.1)
	Σ DDTs	0.2 ^a	0.8 ^a	1.6 ^a	4.8	<LD	<LD	0.1 ^b	0.2 ^a	0.3 ^a
			(0.4-1.2)	(0.2-3.3)	(4.3-5.6)			(0.03-0.1)	(0.1-0.3)	(0.1-0.4)
	Σ PCBs	1.9 ^a	8.8 ^a	0.9 ^a	21.6 ^a	6.1 ^a	3.2 ^a	1.2 ^b	0.4 ^a	0.5 ^a
			(2.1-15.4)	(0.2-3.0)	(17.5-27.9)	(3.7-8.3)	(1.3-4.7)	(1.2-1.2)	(0.2-0.5)	(0.2-1.0)
Campo Mare	Σ PBDEs	0.2 ^{ab}	1.1 ^b	0.4 ^a	14.3 ^a	2.2 ^a	1.1 ^a	0.9 ^a	1.4 ^a	0.7 ^a
			(0.2-1.9)		(1.0-27.9)	(1.4-3.0)	(0.2-2.9)	(0.6-1.3)	(0.2-2.7)	(<LD-1.5)

Range levels in brackets. Means not sharing the same superscript (a, or b) in each column are significantly different at P <0.05. ΣHCHs: α-, β- and γ- isomers; ΣENDO: α- + β- isomers + endosulfan sulfate; ΣDDTs: *p p'*-DDT+ *p p'*-DDE; ΣPCBs: #18, #44, #66, #101, #110, #118, #138, #153, #156, 167, #180 and #187; ΣPBDEs: #47, #100, #99 and #154; <LD: Below detection limit.

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Table 3. Mean concentrations of fish contaminants (ng g wet wt⁻¹) from Mar Chiquita Lake.

SITE		Gills			Liver			Stomach content			Muscle		
Laguna del Plata	season	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy
	Σ HCHs	1.3a (<LD-4.5)	0.8a (0.2-1.3)	NA	0.7a (0.1-21)	1.8a (0.2-3.7)	NA	5.6a (0.2-29.1)	1.3a (0.2-3.4)	NA	1.4a (<LD-2.5)	0.2a (<LD-0.4)	NA
	Σ ENDO	86.2a (54.0-150.9)	55.5a (27.9-83.8)	NA	87.8a (<LD-166.3)	10.6a (<LD-24.1)	NA	230.0b (55.6-562.7)	39.8a (25.3-62.0)	NA	24.1b (12.1-51.4)	3.5a (1.3-6.4)	NA
	Σ DDTs	2.7a (<LD-8.6)	0.9a (<LD-2.3)	NA	2.7a (0.2-13.8)	5.8b (4.3-6.9)	NA	2.3a (<LD-6.4)	1.31a (0.2-3.8)	NA	1.0a (0.1-1.8)	0.7a (0.1-2.1)	NA
	Σ PCBs	61.8a (23.3-121.2)	23.8a (7.2-47.9)	NA	14.8 (<LD-43.9)	23.4 (<LD-68.0)	NA	30.3a (11.8-57.6)	10.6a (5.4-23.5)	NA	2.3a (0.4-6.2)	10.8a (1.7-14.4)	NA
	Σ PBDEs	6.7b (3.5-10.6)	3.2a (1.9-4.8)	NA	3.8b (1.1-7.4)	0.7a (0.2-1.0)	NA	5.9a (2.4-13.6)	2.2a (1.0-4.3)	NA	3.4a (<LD-7.3)	7.2a (4.5-12.0)	NA
	Σ HCHs	1.6a (0.4-4.0)	1.0a (0.6-1.8)	1.7a (0.33.6)	2.2a (0.1-8.4)	2.4a (<LD-5.1)	11.2a (<LD-31.0)	8.5a (0.7-23.4)	3.4a (0.4-8.3)	19.3a (4.6-53.3)	0.9a (0.1-3.1)	0.6a (<LD-2.5)	0.5a (<LD-2.5)
	Σ ENDO	237.2b (48.5-475.8)	36.6a (15.2-65.7)	127.9ab (65.2-234.0)	60.2ab (28.8-92.1)	13.5a (<LD-32.5)	126.8b (23.5-226.7)	126.2a (75.5- 208.9)	27.1a (15.0-48.1)	196.7a (13.8-362.8)	2.7ab (2.5-3.5)	1.3a (0.5-2.5)	10.5b (1.2-21.7)
	Σ DDTs	1.8a (0.5-5.3)	1.9a (<LD-5.6)	1.5a (<LD-3.8)	8.4a (6.8-10.0)	2.9a (0.5-4.7)	16.7a (0.1-60.9)	13.9a (<LD-41.4)	12.8a (0.4-27.7)	19.4a (<LD-76.2)	1.5a (0.2-2.5)	0.2a (0.1-0.2)	0.9a (0.1-2.5)
	Σ PCBs	51.1a (48.2-53.6)	25.3a (12.5-48.9)	36.6a (13.8-82.1)	48.1ab (36.7-73.9)	4.5a (3.0-7.5)	33.5b (10.6-70.1)	17.8ab (14.0-23.2)	11.6a (5.9-21.6)	88.9b (27.9-134.6)	10.9a (1.9-32.7)	2.1a (0.2-5.3)	5.8a (2.6-13.2)
	Σ PBDEs	4.7a (<LD-8.4)	3.2a (2.2-4.4)	2.7a (<LD-5.8)	1.2a (<LD-3.2)	0.8a (0.2-1.7)	0.8a (<LD-1.9)	4.6a (4.0-5.1)	2.4a (1.08-3.8)	3.4a (2.3-6.1)	1.4a (0.4-2.9)	1.4a (0.6-2.4)	4.9a (1.0-8.1)
	% Lipid	2.6 (0.6-8.8)			6.3 (0.7-17.0)			2.9 (1.0-7.7)			1.3 (0.2-5.3)		
Campo Mare	Σ HCHs	1.6a (0.4-4.0)	1.0a (0.6-1.8)	1.7a (0.33.6)	2.2a (0.1-8.4)	2.4a (<LD-5.1)	11.2a (<LD-31.0)	8.5a (0.7-23.4)	3.4a (0.4-8.3)	19.3a (4.6-53.3)	0.9a (0.1-3.1)	0.6a (<LD-2.5)	0.5a (<LD-2.5)
	Σ ENDO	237.2b (48.5-475.8)	36.6a (15.2-65.7)	127.9ab (65.2-234.0)	60.2ab (28.8-92.1)	13.5a (<LD-32.5)	126.8b (23.5-226.7)	126.2a (75.5- 208.9)	27.1a (15.0-48.1)	196.7a (13.8-362.8)	2.7ab (2.5-3.5)	1.3a (0.5-2.5)	10.5b (1.2-21.7)
	Σ DDTs	1.8a (0.5-5.3)	1.9a (<LD-5.6)	1.5a (<LD-3.8)	8.4a (6.8-10.0)	2.9a (0.5-4.7)	16.7a (0.1-60.9)	13.9a (<LD-41.4)	12.8a (0.4-27.7)	19.4a (<LD-76.2)	1.5a (0.2-2.5)	0.2a (0.1-0.2)	0.9a (0.1-2.5)
	Σ PCBs	51.1a (48.2-53.6)	25.3a (12.5-48.9)	36.6a (13.8-82.1)	48.1ab (36.7-73.9)	4.5a (3.0-7.5)	33.5b (10.6-70.1)	17.8ab (14.0-23.2)	11.6a (5.9-21.6)	88.9b (27.9-134.6)	10.9a (1.9-32.7)	2.1a (0.2-5.3)	5.8a (2.6-13.2)
	Σ PBDEs	4.7a (<LD-8.4)	3.2a (2.2-4.4)	2.7a (<LD-5.8)	1.2a (<LD-3.2)	0.8a (0.2-1.7)	0.8a (<LD-1.9)	4.6a (4.0-5.1)	2.4a (1.08-3.8)	3.4a (2.3-6.1)	1.4a (0.4-2.9)	1.4a (0.6-2.4)	4.9a (1.0-8.1)
	% Lipid	2.6 (0.6-8.8)			6.3 (0.7-17.0)			2.9 (1.0-7.7)			1.3 (0.2-5.3)		

Range levels in brackets. Means not sharing the same superscript (a, or b) in each column are significantly different at P <0.05. ΣHCHs: α-, β- and γ- isomers; ΣENDO: α- + β- isomers + endosulfan sulfate; ΣDDTs: *p p*´-DDT+ *p p*´-DDE; ΣPCBS: #18, #44, #66, #101, #110, #118, #138, #153, #156, 167, #180 and #187; ΣPBDEs: #47, #100, #99 and #154; <LD: Below detection limit. N/A: Not analyzed. Fish were not captured at this station during rainy season.

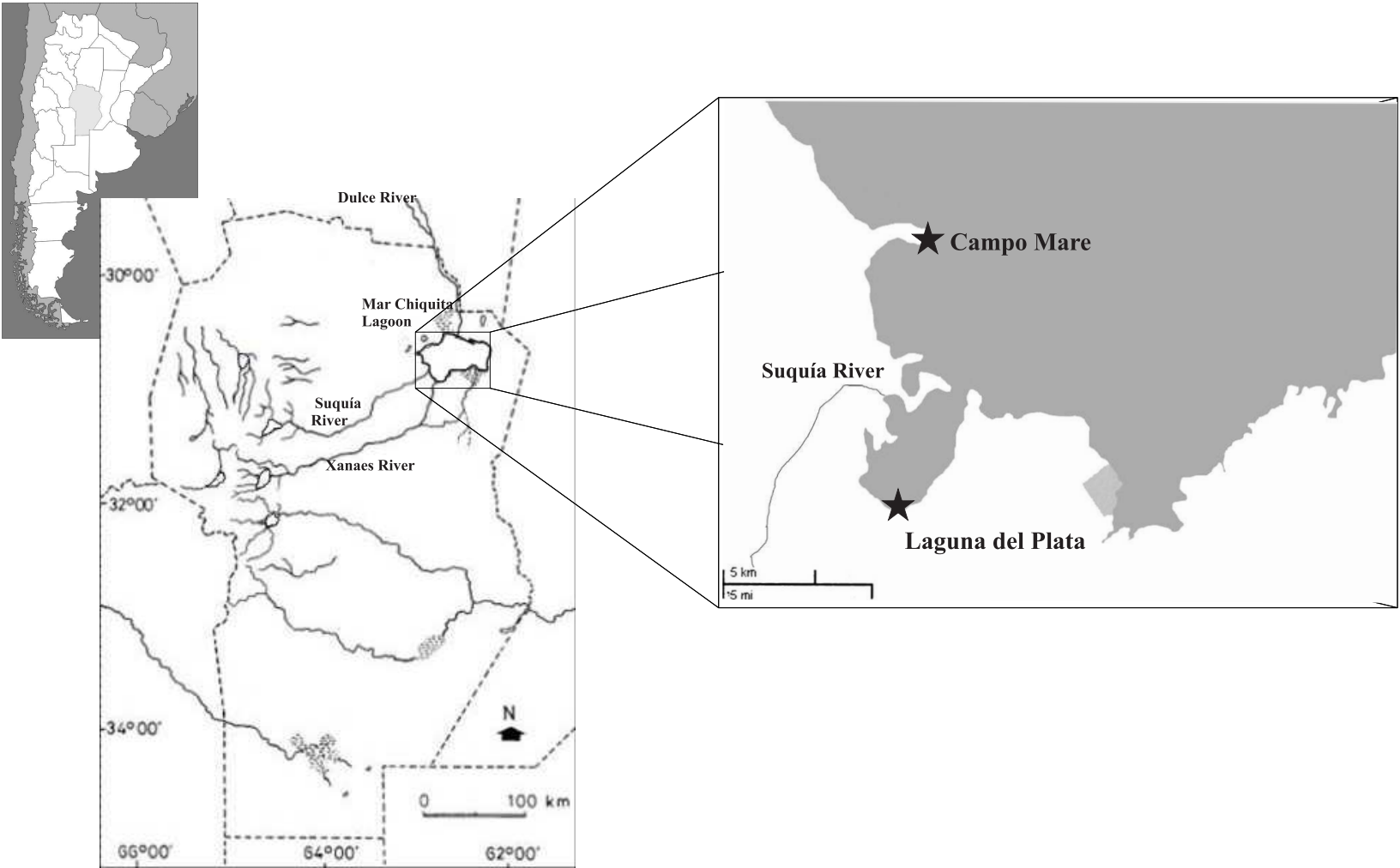
Table 4. Contaminant levels in muscle of silverside from the Mar Chiquita Lake, burden in a 300 g filet, percentage of allowed ingest, oral reference dose (RfD) values for each contaminant group and total daily allowed ingest for a 70 kg individual.

SITE	POPs	POPs levels in silverside muscle			Burden (µg)			% of daily allowed ingest for a 70 kg individual			RfD (µg kg ⁻¹ d ⁻¹)	µg in a 70 kg individual
		Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy	Post-rainy	Dry	Rainy		
Laguna del Plata	γ-HCH [#]	1.4	0.2	N/A	0.4	0.1	N/A	1.9	0.5	N/A	0.3	21.0
	ΣENDO [#]	24.1	3.5	N/A	7.2	1.0	N/A	1.7	0.2	N/A	6.0	420.0
	ΣDDTs [#]	1.0	0.7	N/A	0.3	0.2	N/A	0.8	0.6	N/A	0.5 ^(d)	35.0
	ΣPCBs [#]	2.3	10.8	N/A	0.7	3.2	N/A	50	231.0	N/A	0.02 ^(c)	1.4
	ΣPBDEs*	3.4	7.2	N/A	1.0	2.2	N/A	14.2	30.1	N/A	0.1 ^(a) , 2 ^(b)	7.0
Campo Mare	γ-HCH [#]	0.9	0.6	0.5	0.3	0.1	0.2	1.4	0.5	0.1	0.3	21.0
	ΣENDO [#]	2.7	1.3	10.5	0.8	0.4	3.2	0.2	0.1	0.8	6.0	420.0
	ΣDDTs [#]	1.5	0.2	0.9	0.5	0.1	0.3	1.4	0.3	0.9	0.5 ^(d)	35.0
	ΣPCBs [#]	10.9	2.1	5.8	3.3	0.6	1.7	235.7	42.9	121.4	0.02 ^(c)	1.4
	ΣPBDEs*	1.4	1.4	4.9	0.4	0.4	1.5	5.7	5.7	21.4	0.1 ^(a) , 2 ^(b)	7.0

* IRIS EPA database (<http://www.epa.gov/IRIS/> accessed may 2012); [#] ATSDR (<http://www.atsdr.cdc.gov/accessed> may 2012); ^(a)BDE-47, ^(b)Penta BDE, ^(c)Arochlor 1254/1248, ^(d)*p p'*-DDT.

ΣHCHs: α–, β– and γ– isomers; ΣENDO: α– + β– isomers + endosulfan sulfate; ΣDDTs: *p p'*-DDT+ *p p'*-DDE; ΣPCBs: #18, #44, #66, #101, #110, #118, #138, #153, #156, 167, #180 and #187; ΣPBDEs: #47, #100, #99 and #154; N/A: Not analyzed. Fish were not captured at this station during rainy season.

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Conflict of Interest

All the authors have no conflicts of interest.