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PBDEs, PCBs and organochlorine pesticides distribution in edible fish from Negro River basin, Argentinean Patagonia

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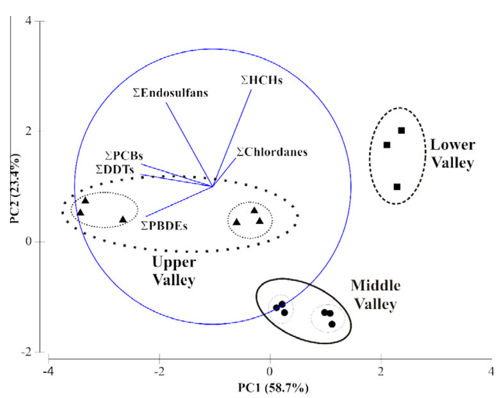
HIGHLIGHTS

- Patagonian silverside was a functional sentinel-organism of POPs in Negro River.
- OCPs, PCBs and PBDEs are ubiquitous contaminants in patagonian silverside tissues.
- Intensive agriculture, industries and dams represent sources of POPs in Negro River.
- PCBs levels in silverside muscles exceeded recommended limits for human consumption.

GRAPHICAL ABSTRACT



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ABSTRACT

DDTs, endosulfans, HCHs, chlordanes, PCBs and PBDEs levels were determined in different tissues of patagonian silverside (*Odontesthes hatcheri*) from the Upper (UV), Middle (MV) and Lower (LV) valleys of the Negro River, Argentina. Results showed a direct relation between pollutant levels in fish and land uses along the basin. All tissues showed decreasing levels from headwaters (UV) to downstream (LV). A significant predominance of organochlorine pesticides (306–3449 ng g^{-1} lipid) followed by ΣPCBs (65–3102 ng g^{-1} lipid) and ΣPBDEs (22–870 ng g^{-1} lipid) was observed in all tissues and valleys, suggesting agriculture as the main source of pollutants in this basin. Pesticides were dominated by DDTs (90% *pp′*-DDE) followed by endosulfan (α- > β- > sulfate), γ-HCH and γ-chlordane showing the prevalence of legacy compounds. Endosulfan levels point out the current use of technical endosulfan in the surrounding areas. The highest PCBs and PBDEs concentrations observed in fish from UV were associated to hydroelectric power plants and industries established upstream. PCB fingerprint presented a prevailing contribution of hexa-CBs (66 ± 7%) and penta-CBs (27 ± 9%), with a similar composition to Aroclor 1254–1260. The predominance of BDE-47 (69 ± 17%) among PBDEs, followed by BDE-100 and BDE-99, suggests possible debromination processes. These results were similar to worldwide trends found in fishes and environmental compartments. PCBs levels in silverside muscles along the Negro River exceeded the maximum limits for safe consumption, suggesting a possible human health risk related to silverside ingest. Therefore, a continued long-term monitoring of organic contaminants in fishes is needed in order to assess the potential risk for human health.

1. Introduction

Organochlorine Pesticides (OCPs), Polychlorinated Biphenyls (PCBs) and Polybrominated Diphenyl Ethers (PBDEs), among oth-

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ers, are included in the Persistent Organic Pollutants (POPs) group. POPs have been extensively studied from several decades, due to their persistence, bioaccumulation, long-range transport, toxicity and adverse effects on wildlife and human. For these reasons, most countries have restricted or banned their use (Wania and Mackay, 1996; Sabljic, 2001). In Argentina, Dichlorodiphenylethane (DDT) and endosulfan were used as agricultural products up to 1998 and 2012, respectively, when their application were officially phased out (SAGPyA, 1998; SENASA, 2011). PCBs, banned in 2001, were mainly used as dielectric fluid in transformers and capacitors (Colombo et al., 2007). On the other hand, PBDEs are mainly used in plastic, textile and electronic applications as fire retardant. Since these compounds are not chemically bound to the materials, they may leach out into the environment (de Wit, 2002).

The distinct land uses (i.e. rural, urban and industrial) lead to the contamination of aquatic environments by POPs mainly through runoff, direct discharges and wet/dry deposition (Roche et al., 2000). Due to their persistency and lipophilicity, POPs from the water column can easily be accumulated by biota. Particularly, fishes are able to uptake contaminants through gills and food intake and, eventually, transfer them to humans through consumption of these organisms (Zhou et al., 2008). Therefore, the accumulation of POPs in edible tissues is of concern from human health perspective since the fish body burden somehow reflects the contamination status of the environment. Despite being one of main sources to the human contamination, consumption of sea and freshwater organisms accounts for only 5–10% of Argentinean diet (www.sanutrición.org.ar).

The Negro River has the largest drainage basin (95,000 km^2) along the Argentinean Patagonia (Depetris et al., 2005). This river provides water for irrigation and urban, industrial and recreation use for a local population (~half a million). Economically speaking, 4% of worldwide production of apples and pears, with an intensive use of pesticides, and 30% of the electricity consumed in Argentina are being produced in this basin. In addition, chemical and oil/gas industries are a feature of Negro River (Arribére et al., 2003). As a consequence, a significant contamination by OCPs, PCBs and PBDEs has been detected in the Negro River basin (Isla et al., 2010; Gonzalez et al., 2010; Ondarza et al., 2012; Miglioranza et al., 2013). Thus, it is reasonable to believe that fish consumption might be relevant to the contamination of local population.

Thus, the present work aimed to: (i) determine the contamination levels of PBDEs, PCBs and OCPs in different tissues of patagonian silverside (*Odontesthes hatcheri*) sampled along the Negro River; (ii) correlate the contamination results with land use, and (iii) reveal possible human health risk related to this fish consumption.

2. Materials and methods

2.1. Study area

The Negro River has 720 km of length, a mean discharge of 858 m^3 s^{-1} and 250 mm yr^{-1} of runoff. Its basin is divided into three valleys: Upper Valley (UV), Middle Valley (MV) and Lower Valley (LV) (Fig. 1). Land use along the river is characterized as follows: the UV has a considerable anthropogenic intervention where agriculture (fruits) encompass more than 80% of its surface together with dams, and industrial-urban settlements; in the MV agriculture is the main activity with tomatoes and soybean crops while in the LV livestock production, small industries and urban areas are equally relevant (Depetris et al., 2005).

2.2. Selected species

The patagonian silverside (*O. hatcheri*) is the most abundant native species along the Negro River, usually consumed by local residents and used in aquaculture. Silverside reproductive cycle runs from spring to summer, whilst their feeding preferences vary from insect larvae at young age to mollusks (*Aegla* sp.) at adulthood (Alvear et al., 2007).

2.3. Fish collection and treatment

In summer, a total of 29 adults (22 females and 7 males) of silverside were collected, using multifilament gillnets. In LV, only females were sampled. All fishes were measured (mm), weighed (g) and the sex was determined. Muscle, liver, gills and gonads were removed and stored at −20 °C prior to analysis. Tissues were pooled according to sampling area and sex. Condition (KI = total weight × 100/total length^3) and hepatosomatic (HI = liver weight × 100/total weight) indexes were calculated.

2.4. Analytical procedures

2.4.1. Reagents and standard materials

Dichloromethane and *n*-hexane (pesticide grade), anhydrous sodium sulfate and silica gel were employed (Merck Inc.). Standard solutions of organochlorine compounds and PCB-103 (internal standard) were used (Absolute Standards and Ultra Scientific, respectively). DSJ PCB standard solution was purchased from Cambridge Isotopes Laboratories (Andover, MA, USA). Reference standard BDEs mixture containing BDE-28, 47, 66, 85, 99, 100, 138, 153 and 154, was purchased from AccuStandard (“Bromodiphenyl Ethers-Lake Michigan Study” New Haven, CT, USA).

2.4.2. Extraction and cleanup

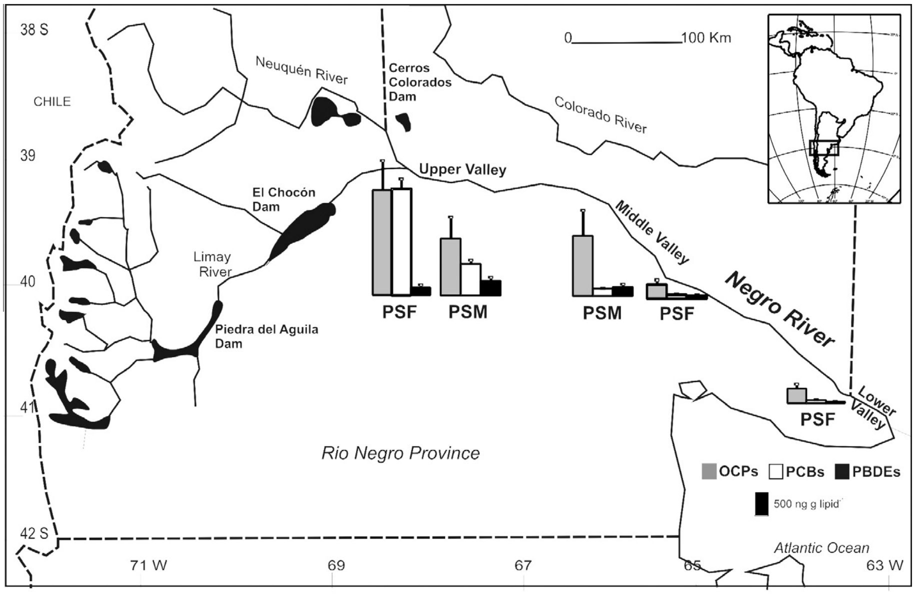
OCPs (endosulfans, DDTs, HCHs and chlordanes), PCBs and PBDEs were extracted according to Metcalfe and Metcalfe (1997) and modified by Miglioranza et al. (2003a). Subsamples ($n = 3$ for each tissue) of muscle (5 g), liver, gonads and gills (3 g) were homogenized with anhydrous sodium sulfate and Soxhlet extracted with dichloromethane and *n*-hexane (1:1 v/v) for 8 h. Lipid content was gravimetrically determined after removal by gel permeation chromatography. The contaminants fraction was further purified with a silica gel column.

2.4.3. Gas chromatographic analyses

OCPs and PCBs were analyzed by gas chromatography (GC) with electron-capture detector using a Shimadzu 17-A chromatograph (Miglioranza et al., 2003a). PBDEs were analyzed with a GC–MS Perkin Elmer-Clarus-500, operated under electron impact mode with the selecting ion and full ion scanning mode (Ondarza et al., 2011).

2.4.4. Quality Assurance and Quality Control (QA and QC)

Procedural and instrumental blanks were extracted with every batch of samples and OCPs, PCBs and PBDEs levels were below the detection limits. Surrogate recovery was greater than 89% and the results were not corrected for recovery efficiency. Instrumental detection limits, calculated according to Keith et al. (1983), ranged between 0.3 to 1.3 ng g^{-1} for HCHs (α-, β-, γ-, δ-), chlordanes (α-, γ-, trans-nonachlor), DDTs (*pp*′-DDE, *pp*′-DDD, *pp*′-DDT), endosulfans (α-, β-, endosulfan sulfate) and PCBs (#8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 138, 187, 128, 167, 156, 157, 180, 169, 189, 195, 206, 209), whilst ranged from 0.8 to 4.4 ng g^{-1} for PBDEs (#28, 49, 47, 66, 100, 99, 154, 153 and 183).



PSF: patagonian silverside female, PSM: patagonian silverside male.

Fig. 1. Sampling locations in the Negro River basin and levels of OCPs, PCBs and PBDEs (average ± standard deviation) (ng g^{-1} lipid) in muscles of males and females of the patagonian silverside.

2.5. Statistical analysis

The results were expressed as ng g^{-1} lipid weight (ng g^{-1} lipid). Statistical analyses were performed using the software InfoStat 2008 (Di Rienzo et al., 2008). The relationship between contaminant levels, expressed as ng g^{-1} wet weight, and lipid content in each tissues was assessed using correlation. Comparisons of contaminant levels (ng g^{-1} lipid) among tissues were done with Friedman ANOVA analyses for multiple dependent samples, while Wilcoxon test was used to compare differences between sexes. Kruskal–Wallis ANOVA test were used to compare differences among sampling sites. Significance level was set at $p < 0.05$. Additionally, a principal component analysis (PCA) was performed to reveal the relationship among sampling sites and the accumulation of contaminants in each fish tissues.

3. Results and discussion

3.1. Biological and biochemical parameters

Patagonian silverside total length varied between 230 and 405 mm in females, and 345 to 375 mm in males. Total weight ranged between 90.5–606.8 and 347.6–493.6 g in females and males, respectively. KI and HI values higher than 1 indicate healthy fishes and any changes in these indexes might be related to environmental stress (Tricklebank et al., 2002). Silverside exhibited a great overlap in KI and HI between gender and valleys. KI ranged from 0.7 to 1.1, while the HI of females (1.6–5.4) was higher than those of males (1.6–2.6). These results showed a healthy condition and a good reserve of energy for both genders.

Patagonian silverside is a lean species and liver had the highest levels of lipid content in both genders ($p < 0.05$) in comparison to the other tissues, followed by gonads, gills and muscle (Table 1). Lipid contents were significantly correlated with total contaminant levels (ng g^{-1} wet weight) in muscle ($r = 0.5$, $p < 0.05$), liver ($r = 0.7$, $p < 0.05$), gonads and gills ($r = 0.8$, $p < 0.05$), independently of the sampling site.

3.2. Levels and distribution of contaminants in fish

The levels of contaminants in patagonian silverside tissues showed a clear general decrease from the upper valley (UV) towards the middle (MV) and lower valley (LV) (Fig. 1). A predominance of OCPs followed by PCBs and PBDEs was found in all tissues along the river, showing that agriculture was the main source of contamination along the Negro River environment (Table 1). OCPs composition was dominated by DDTs (75 ± 9.6%) and lower proportions of endosulfans (21 ± 8.3%), HCHs (2 ± 1.4%) and chlordanes (2 ± 1.3%) (Table 1). It is well known that contaminants from surrounding lands runoff towards the aquatic environments, mainly adsorbed onto soil particles (Miglioranza et al., 2003b; Katayama et al., 2010), and cause an increase of streamwater levels which could, sometimes, exceed the limits for protection of aquatic biota (Ondarza et al., 2012). This tissue distribution agrees with the historic use of legacy compounds such as DDT, chlordane and lindane in the surrounding environment, in addition to the current use of endosulfans (INTA, 2004). It is also interesting to note that PCBs and DDTs levels, two of the most relevant compounds that represent the background contamination in this area (Isla et al., 2010; Gonzalez et al., 2010; Miglioranza et al., 2013), were significantly correlated in all tissues of silverside ($r = 0.8$, $p < 0.05$). This could be due to their similar chemical properties and environmental behavior (Sabljic, 2001).

In both genders, gills showed the highest total contaminants levels followed by liver, gonads and muscle, with the exception of muscle of females from UV and gonads of males from MV (Table 1). Since, gills are in direct contact with the aquatic environment, they play an important role in the contaminants uptake. This pattern was already seen for common carp (*Cyprinus carpio*) in this river (Ondarza et al., 2010).

Liver levels provide an insight into the fresh contamination due to its role in detoxification and biotransformation of xenobiotics. The PCA were helpful in reducing the complexity of the data set and also provided a visual representation of the spatial differences in current contaminant distribution in liver of silverside from the Negro River (Fig. 2). The first two components of the PCA explained

Table 1
Lipid content (%) and levels of organic contaminants (average ± standard deviation) (ng g^{-1} lipid) in the patagonian silverside collected along the Negro River.

Sampling site	Upper Valley (UV)							
Sex	F	M						
Tissue	Mu	L	Go	Gi	Mu	L	Go	Gi
% lipid	0.7 ± 0.04	34.0 ± 1.4	3.3 ± 0.4	2.3 ± 0.06	0.5 ± 0.2	40.1 ± 0.8	2.6 ± 0.1	1.5 ± 0.4
Total pollutants	6,349 ± 395	1,729 ± 232	1,614 ± 168	2,348 ± 223	2,714 ± 223	3,047 ± 393	2,141 ± 216	5,505 ± 539
OCPs								
α-HCH	<dl	0.8 ± 0.04	<dl	<dl	7.8 ± nd	0.6 ± 0.1	<dl	<dl
γ-HCH	21.1 ± 7.9	2.8 ± 0.5	8.8 ± 3.9	9.7 ± 1.6	54.1 ± 5.3	1.8 ± 0.4	5.7 ± 1.5	18.6 ± 0.3
γ-chlordane	15.8 ± 5.6	9.4 ± 2.2	10.8 ± 3.4	9.5 ± 8.4	33.3 ± 17.6	9.9 ± 1.5	10.2 ± 1.5	29.5 ± 11.6
α-chlordane	<dl	6.3 ± 0.6	<dl	<dl	<dl	6.4 ± nd	<dl	<dl
Transnonachlor	<dl	<dl	<dl	<dl	<dl	<dl	<dl	<dl
α-endosulfan	1,358.7 ± 161.8	17.5 ± 7.9	164.0 ± 106.6	226.9 ± 112.9	34.6 ± 10.5	21.7 ± 8.8	258.0 ± 91.7	445.4 ± 77.9
β-endosulfan	272.6 ± 291.6	8.7 ± 3.7	141.5 ± 122.8	105.2 ± 29.5	53.1 ± 10.0	12.2 ± 5.1	184.2 ± 11.4	192.6 ± 36.2
endosulfan sulfate	144.5 ± 13.3	47.4 ± 5.2	56.9 ± 17.2	44.4 ± 16.4	122.3 ± 28.3	68.3 ± 39.7	85.9 ± 3.3	79.0 ± 5.9
pp′-DDE	1,129.3 ± 90.2	1,134.9 ± 162.6	788.5 ± 132.2	1,086.8 ± 85.3	988.8 ± 297.6	1,912.2 ± 269.1	1,003.9 ± 30.0	2,498.5 ± 653.3
pp′-DDD	20.0 ± 3.1	41.8 ± 13.0	16.7 ± 5.6	28.7 ± 9.0	35.0 ± 8.4	65.2 ± 13.8	22.8 ± 0.3	32.3 ± 13.7
pp′-DDT	86.3 ± 13.9	3.5 ± 1.8	56.9 ± 17.2	139.9 ± 38.0	168.7 ± 67.6	3.1 ± 3.3	75.4 ± 15.2	153.2 ± 46.7
PCBs								
52	64.0 ± 28.0	15.9 ± 1.3	25.9 ± 3.2	38.3 ± 10.2	<dl	15.7 ± 1.7	27.5 ± nd	170.4 ± 105.4
44	31.1 ± 13.5	4.5 ± 2.4	21.3 ± 4.7	32.9 ± 4.7	37.2 ± 3.8	6.1 ± 0.6	17.9 ± 7.8	133.7 ± 116.5
66	<dl	13.4 ± 3.0	26.3 ± 3.0	83.9 ± 13.9	<dl	14.7 ± 4.0	42.1 ± 8.6	212.8 ± 91.4
101	428.8 ± 7.2	48.2 ± 15.1	32.6 ± 5.7	39.1 ± 1.7	<dl	94.2 ± 43.1	39.6 ± 4.3	97.5 ± 24.7
110	291.3 ± 14.5	28.6 ± 3.4	32.7 ± 16.4	52.7 ± 14.3	284.3 ± 20.5	35.6 ± 19.7	36.4±	91.6 ± 15.5
149	607.1 ± 1.9	29.2 ± 5,7	23.4 ± 6.1	32.9 ± 5.8	81.2 ± 16.9	49.5 ± 11.8	32.5 ± 4.3	82.7 ± 8.9
118	110.0 ± 21.4	52.9 ± 14.9	39.5 ± 3.7	58.4 ± 5.6	103.0 ± 32.9	136.3 ± 27.9	54.3 ± 7.7	134.2 ± 39.1
153	785.5 ± 31.1	98.6 ± 41.8	49.3 ± 3.6	62.4 ± 20.6	193.0 ± 33.4	244.4 ± 46.4	74.0 ± 2.7	386.2 ± 241.2
138	656.7 ± 51.3	81.5 ± 31.3	54.4 ± 9.1	98.5 ± 19.6	132.6 ± 36.9	187.7 ± 31.9	85.0 ± 2.7	384.9 ± 220.4
187	127.6 ± 14.1	10.1 ± 3.0	6.5 ± 3.3	17.2±4.3	<dl	19.9 ± 1.6	8.2 ± 2.0	30.5 ± 1.0
PBDEs								
47	184.8 ± 20.4	45.6 ± 18.8	40.3 ± 2.0	134.3 ± 11.8	251.1 ± 90.4	97.9 ± 4.7	57.5 ± 11.9	293.4 ± 122.5
100	23.8 ± 10.7	13.6 ± 8.3	11.3 ± 1.8	25.0 ± 4.8	97.9 ± 33.5	29.7 ± 3.7	12.6 ± 1.9	38.4 ± 6.8
99	20.9 ± 2.6	14.2 ± 8.0	6.7 ± 1.2	21.5 ± 1.9	35.7 ± 13.1	13.7 ± 2.4	6.9 ± 0.9	<dl

	Middle valley								Lower valley			
Sex	F	M	F									
Tissue	Mu	L	Go	Gi	Mu	L	Go	Gi	Mu	L	Go	Gi
% lipid	0.8 ± 0.2	34.5 ± 0.1	57.4 ± 7.0	2.2 ± 0.2	0.7 ± 0.1	35.9 ± 1.3	1.3 ± 0.2	0.9 ± 0.4	1.8 ± 0.1	37.3 ± 0.3	64.1 ± 4.2	4.1 ± 0.1
Total pollutants	481 ± 46	739 ± 104	1,305 ± 165	5,320 ± 382	2,020 ± 281	1,450 ± 203	6,442 ± 697	4,153 ± 297	560 ± 45	678 ± 87	423 ± 55	805 ± 43
OCPs												
α-HCH	<dl	0.6 ± 0.1	1.2 ± 0.1	<dl	<dl	0.4 ± 0.3	<dl	24.7 ± 14.0	1.5 ± 0.6	1.3 ± 0.2	1.1 ± 0.3	<dl
γ-HCH	8.6 ± 3.1	3.5 ± 3.9	3.6 ± 1.4	146.3 ± 81.1	14.0 ± 8.1	1.3 ± 0.1	63.2 ± 4.2	150.5 ± 74.3	21.4 ± 1.2	5.9 ± 1.4	3.0 ± 1.6	22.9 ± 7.3
γ-Chlordane	9.9 ± 3.9	6.3 ± 0.3	19.2 ± 3.1	87.1 ± 58.7	15.7 ± 9.7	6.1 ± 0.6	95.2 ± 14.4	68.8 ± 44.7	11.9 ± 0.8	10.7 ± 0.8	6.7 ± 1.2	15.5 ± 3.0
α-Chlordane	3.1 ± nd	3.5 ± 0.8	7.5 ± 3.7	45.7 ± 10.3	14.6 ± 12.1	4.1 ± 0.1	14.3 ± 3.0	16.4 ± 14.1	3.9 ± 0.3	4.4 ± 0.6	3.5 ± 0.4	9.4 ± 7.1
Transnonachlor	<dl	3.9 ± 1.3	<dl	<dl	9.3 ± nd	8.2 ± 0.8	<dl	<dl	<dl	2.5 ± nd	<dl	<dl
α-Endosulfan	12.4 ± 1.9	6.9 ± 2.9	16.8 ± 5.6	1,213.9 ± 1,034.0	31.4 ± 19.1	2.3 ± 0.4	517.6 ± 241.8	120.5 ± 0.9	36.6 ± 5.1	22.0 ± 3.7	1.0 ± 0.9	168.0 ± 126.7
β-Endosulfan	20.1 ± 15.8	3.3 ± 1.5	2.5 ± 0.4	558.2 ± 359.2	25.7 ± 28.2	3.5 ± 0.9	77.2 ± 26.4	477.9 ± 107.6	13.9 ± 3.9	2.9 ± 0.8	2.2 ± 0.2	57.9 ± 24.2
Endosulfan sulfate	8.9 ± 5.2	18.9 ± 3.4	42.1 ± 7.3	523.1 ± 274.2	53.2 ± 60.6	19.8 ± 3.9	149.5 ± 18.2	262.6 ± 91.2	42.4 ± 12.8	48.4 ± 5.1	32.6 ± 3.0	77.5 ± 67.2
pp′-DDE	211.0 ± 56.4	508.9 ± 96.5	758.5 ± 243.3	1,368.3 ± 609.4	1,340.4 ± 342.5	1,008.1 ± 128.7	3,064.2 ± 283.7	1,357.7 ± 28.1	215.8 ± 41.5	423.7 ± 28.3	264.5 ± 56.2	135.1 ± 36.4
pp′-DDD	2.9 ± 1.1	13.1 ± 2.8	32.7 ± 16.9	25.6 ± 9.6	4.5 ± 2.2	18.3 ± 2.2	41.9 ± 10.7	89.1 ± 12.3	15.1 ± 7.0	19.7 ± 2.0	11.8 ± 0.6	13.3 ± 7.2
pp′-DDT	29.2 ± 20.2	0.7 ± 0.4	36.7 ± 4.0	169.8 ± 104.8	66.4 ± 47.9	1.7 ± 0.1	127.9 ± 24.8	268.7 ± 18.9	41.4 ± 5.0	11.1 ± nd	17.7 ± 2.3	10.4 ± 2.5
PCBs												
52	<dl	<dl	<dl	<dl	<dl	3.3 ± nd	<dl	<dl	<dl	1.1 ± nd	<dl	<dl
44	8.4 ± 3.6	1.9 ± 0.5	3.8 ± 1.7	65.6 ± 40.8	3.9 ± 0.1	1.9 ± 0.2	<dl	101.9 ± 30.0	6.3 ± 4.4	1.9 ± nd	1.5 ± 0.6	15.9 ± 11.5
66	<dl	2.0 ± 0.7	<dl	85.4 ± 92.1	11.4 ± 5.0	3.3 ± 1.2	<dl	<dl	10.2 ± 4.2	<dl	2.2 ± 0.2	20.0 ± 13.5

101	8.0 ± nd	9.0 ± 4.5	17.4 ± 3.0	46.8 ± 49.5	14.7 ± 1.1	19.5 ± 3.6	54.2 ± 3.6	<dl	3.3 ± 1.2	6.8 ± 3.2	2.7 ± 0.1	<dl
110	22.4 ± 7.2	31.7 ± 1.3	54.6 ± 7.9	299.4 ± 192.6	19.2 ± 1.1	50.7 ± 9.4	542.5 ± 67.5	285.6 ± 125.3	19.2 ± 3.9	24.2 ± 2.2	17.8 ± 3.3	39.8 ± 18.9
149	9.5 ± 2.1	6.9 ± 1.9	24.8 ± 3.5	90.6 ± 49.9	16.7 ± 0.8	14.4 ± 2.8	118.8 ± 10.1	116.0 ± 69.3	11.3 ± 0.3	9.9 ± 1.2	6.3 ± 1.0	16.7 ± 14.1
118	8.4 ± 1.2	13.1 ± 4.6	36.0 ± 6.0	117.6 ± 64.4	28.3 ± 0.2	32.1 ± 4.6	275.2 ± 38.2	139.7 ± 89.3	15.9 ± 3.4	10.4 ± 0.9	7.1 ± 2.2	15.6 ± 11.6
153	22.1 ± 4.6	22.1 ± 9.3	65.6 ± 9.5	182.2 ± 148.3	43.7 ± 3.4	73.2 ± 7.4	189.9 ± 38.6	129.5 ± 65.3	15.6 ± 3.8	22.0 ± 2.0	14.2 ± 1.9	43.8 ± 30.7
138	19.4 ± 4.4	23.2 ± 8.6	59.4 ± 9.4	193.2 ± 100.0	55.7 ± 3.1	56.9 ± 10.5	231.3 ± 28.4	195.3 ± 94.9	22.4 ± 5.4	17.9 ± 1.7	12.9 ± 1.1	27.0 ± 27.5
187	<dl	3.4 ± 0.4	<dl	<dl	6.0 ± 1.9	7.2 ± 0.9	<dl	<dl	<dl	3.6 ± 0.5	1.2 ± 1.7	<dl
PBDEs												
47	16.8 ± 9.9	45.3 ± 12.4	105.5 ± 53.0	34.2 ± 16.7	169.1 ± 45.3	99.8 ± 9.7	565.9 ± 31.4	211.7 ± 45.7	37.1 ± 1.9	22.4 ± 3.4	18.7 ± 2.8	45.8 ± 2.4
100	34.4 ± 3.4	7.2 ± 0.9	12.4 ± 7.9	33.9 ± 11.5	52.2 ± 23.1	12.1 ± 2.4	142.2 ± 11.6	56.8 ± 8.9	8.2 ± 0.2	3.7 ± 0.3	2.7 ± 0.4	25.7 ± nd
99	25.3 ± 8.8	4.1 ± 1.9	5.2 ± 1.5	33.4 ± 10.2	24.4 ± 15.6	1.9 ± 0.4	170.9 ± 61.6	79.8 ± 74.1	7.1 ± 4.3	1.3 ± 1.0	1.2 ± 0.05	44.7 ± nd

F: female. M: male. Mu: muscle. L: liver. Go: gonad. Gi: gills. OCPs: organochlorine pesticides. Total pollutants: Σ(OCPs + PCBs + PBDEs). <dl: below the detection limit. nd: not determinated.

82.1% of the total variance, with DDTs, PCBs, HCHs and chlordanes as the most significant variables. The UV group showed the highest levels of DDTs, PCBs and PBDEs. The variance in the UV group, predominantly across PC1, may be partially explained by the fish gender. Moreover, the LV group differs from UV and MV in lower HCHs and chlordanes levels.

The levels of POPs in liver was always higher than gonad (liver/gonad ratio = 1.1–1.4) in all fish along the river. Moreover, liver and gonads of females presented significantly lower contaminant levels than males ($p < 0.05$, Table 1). These could be explained by the elimination of lipids bound-hydrophobic compounds, such as POPs, during spawning (Serrano et al., 2008). This was previously reported for the Argentinean silverside (*Odontesthes bonariensis*, Menone et al., 2000) and gilthead sea bream (*Sparus aurata*, Serrano et al., 2008).

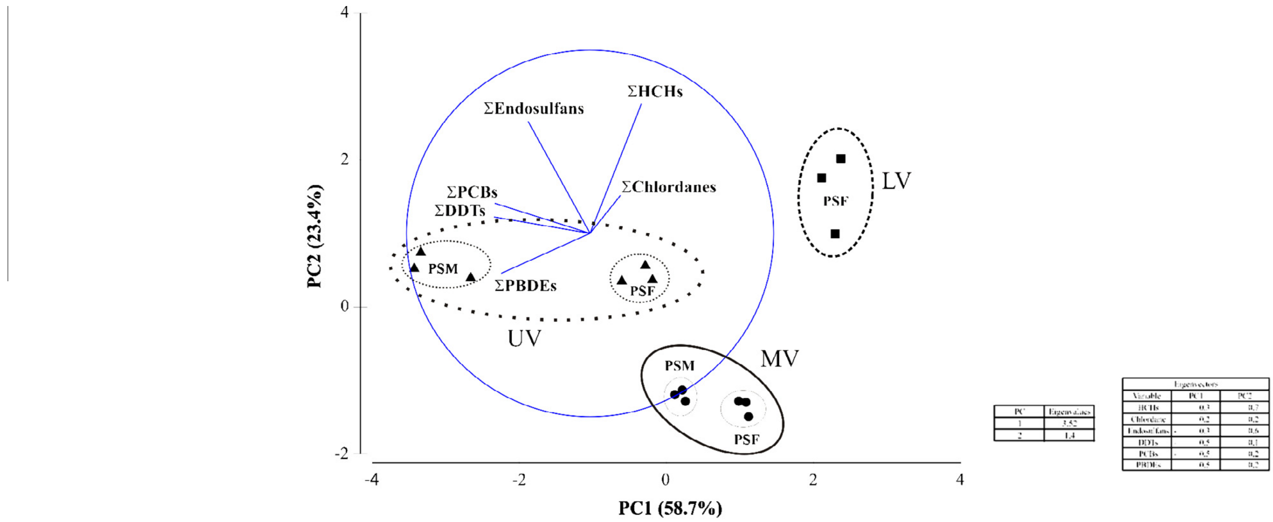
Among all analyzed tissues, muscle is of concern due to the implications for human consumption. Muscle of females from UV had significantly higher contaminants levels (6341 ng g^{-1}, $p < 0.05$) than those from MV (459 ng g^{-1}) and LV (522 ng g^{-1}, Fig. 1). Although males from MV have shown high levels (1966 ng g^{-1}), the contamination of muscles from UV was still significant higher (2618 ng g^{-1}, $p < 0.05$, Fig. 1).

3.2.1. Organochlorine pesticides: DDTs, endosulfans, HCHs and chlordanes

The 90% of DDTs residues in silverside tissues from the three valleys was *pp′*-DDE. Ratios *pp′-DDE* + *pp′*-DDD/*pp′*-DDT ranged between 6 and 630, reflecting a high rate of DDT degradation in the environment or in fish, after a historic application of DDT (Shailaja and Sen Gupta, 1989). The anaerobic metabolite of DDT, *pp′*-DDD, was found at significant lower concentrations than *pp′*-DDE and *pp′*-DDT, except in liver where their levels were higher than *pp′*-DDT ($p < 0.05$), probably by a direct uptake of this compound from the environment as well as in situ metabolism within fish. When comparing all valleys, liver, muscle and gills of females from UV had the highest *pp′*-DDE levels ($p < 0.05$), whilst ovaries had the lowest ($p < 0.05$). In males, gills showed also the highest *pp′*-DDE levels in UV (2498 ng g^{-1}) followed by liver (1912 ng g^{-1}), while muscle and gonads showed the lowest levels along the river, without significant differences between them (Table 1). Although DDT is not currently used in agricultural applications, DDTs profiles in silverside agree with those found in soils of the UV, which are recognized as a hot spot of *pp′*-DDE (0.5 μg g^{-1} dry weight) due to the intensive use of DDT insecticide during long time (Gonzalez et al., 2010).

Lower DDTs levels in silverside from MV might be expected considering changes in land use along valleys, where an increase of tomatoes, olive and soybean productions, together with livestock development is observed in MV, instead of the intensive fruit culture from the UV. Differently from UV, soils of MV had lower DDTs levels (3.2 ng g^{-1} dry weight, Miglioranza et al., 2013). However, fish from MV had slightly lower DDTs levels than those from UV although differences were not significant. Therefore, DDTs levels in fish tissues from MV, are probably under the influence of contaminants transported from upstream areas. On the other hand, LV females had a significant decrease in DDTs levels (up to 10 times lower), range from 158.8 to 454.5 ng g^{-1} in gills and liver, respectively ($p < 0.05$), in comparison to UV and MV females. DDTs burden in 300 g of muscle was 1.9 μg (range 1.4–2.4 μg) reaching only 5.5% of the guideline levels for safe human consumption (35 μg), considering a chronic reference dose of 0.5 μg $kg^{-1}d^{-1}$ and an body weight of 70 kg (www.epa.gov/IRIS; www.atsdr.cdc.gov).

Average DDTs levels in muscle of silverside from Negro River (871 ng g^{-1} lipid) were higher than levels in sabalos (*Prochilodus lineatus*) from the Río de La Plata, Argentina (460 ng g^{-1} lipid, Co-



UV: upper valley ( ). MV: middle valley ( ). LV: lower valley ( ). PSF: patagonian silverside female. PSM: patagonian silverside male.

Fig. 2. Principal component analysis (PCA) for organic contaminants in liver of the patagonian silverside collected along the Negro River.

lombo et al., 2011), but lower than fish from China (3624 ng g^{-1} lipid, Zhou et al., 2008), which is probably one of the most DDT-contaminated areas in the world.

Although endosulfans levels in UV were higher than in MV and LV ($p < 0.05$), the α-/β- ratio > 1 found in silverside tissues from all valleys, indicates exposure to technical mixture of α- and β-isomers (70:30) along the whole basin. The highest levels of endosulfan sulfate were found in liver of both sexes along the river ($p < 0.05$), suggesting a biotransformation process of the parent isomers as well as uptake from the environment (Leonard et al., 2001).

Average endosulfans burden in a 300 g fillet of silverside was 1.8 μg (0.15–3.5 μg) which indicate no significant risk to the consumers since it contributes 30% of the reference dose (6.0 μg kg^{-1} d^{-1}) in an individual of 70 kg (www.epa.gov/IRIS; www.atsdr.cdc.gov).

In contrast to other pollutants, an increasing gradient from UV to LV was found for HCHs and chlordanes, with a predominance of γ-chlordane and γ-HCH (Lindane) in all tissues of silverside (Table 1, Fig. 2). Lindane and chlordanes were widely used as domestic pesticides, such as poisons for lice and ants, respectively (SAGPyA, 1998). The deviation of the α-/γ-chlordane ratio from the technical mixture (α-/γ- > 1, Mattina et al., 1999), suggests a selective preservation of the γ-isomer as has been previously observed in Negro River soils, sediments and fish (Ondarza et al., 2010; Miglioranza et al., 2013). Lindane and chlordanes burden in silverside fillet (300 g) were 0.07 μg (0.03–0.1 μg) and 0.07 μg (0.05–0.09 μg), respectively, which were much lower than their respective daily intake values of 21 μg d^{-1} (lindane) and 4.2 μg d^{-1} (chlordanes), in an individual of 70 kg (www.epa.gov/IRIS; www.atsdr.cdc.gov).

3.2.2. PCBs and PBDEs

The high concentrations of PCBs and PBDEs observed in UV might be linked to the presence of numerous hydroelectric power plants and several industries established in the upper stream, such as petro-chemical industries, paper factories, storage battery and a chlor-alkali plant. These activities produce a large quantity of wastes and deliver their effluents into the Negro River, usually untreated, representing additional potential sources of these pollutants. The distance to source could explain the diminished values of PCBs and PBDEs from UV to LV.

PCBs levels in muscle of female from UV (3102 ng g^{-1}) were 6–10 times higher than the rest of analyzed tissues ($p < 0.05$, Table 1). In males, gills showed the maximum concentrations (1724 ng g^{-1}), muscle and liver reached more than 800 ng g^{-1}, while testicles presented the lowest levels ($p < 0.05$, Table 1).

Particularly, an ingestion of only 300 g of silverside muscle from UV represents a mean input of 3.9 μg of PCBs (range 1.3–6.8 μg), which gives and excess at about 180% (0.9–4.8 times) than the maximum levels allowed for human consumption (1.4 μg), considering a chronic reference dose of 0.02 μg kg^{-1} d^{-1} and an average body weight of 70 kg (www.epa.gov/IRIS; www.atsdr.cdc.gov). On the other hand, beside PCBs uptake through muscle of silverside from MV and LV (0.5 μg each one) was lower than the limit, it also accounts for the 36% of the thresholds levels. Therefore, the daily consumption of patagonian silverside muscle from this watershed, mainly from UV, should be restricted in order to avoid high PCBs intake and reduce risk to populations. However, this estimation of dietary exposure to PCBs might be slightly overestimated since are referred to fresh unprocessed muscle residues. It is known that the loss of fat during cooking processes (boiling, baking, and fried) diminished the residues of PCBs or other organochlorine compounds in raw trout muscle (Zabik et al., 1996).

PCB fingerprints were dominated by hexa-CBs (153, 138, 149) and penta-CBs (110, 101, 118) congeners, consistent with used Aroclor 1254 and 1260 mixtures as well as with their high lipophilicity, stability and persistence, which facilitate accumulation in fish. Particularly, congeners 138 and 153 are more resistant to metabolism, being more slowly eliminated (Storelli et al., 2009). The congener pattern agree with previous reports about soils, sediments, macrophytes and fish from Argentina showing an enrichment in heavier PCBs (Menone et al., 2000; Colombo et al., 2007; Ondarza et al., 2011). However, an increasing contribution of tetra-chlorinated congeners (average 21%) was found in gills of both sexes. This PCB group is less hydrophobic and has a lower steric hindrance consequently, could remain in the water column and be more available for fish uptake (Colombo et al., 2007).

The highest PBDEs levels were found in muscle from UV (229.5 and 384.7 ng g^{-1} in females and males, respectively, $p < 0.05$). These values were substantially higher than those found in Arctic fish (30.7 ng g^{-1} lipid) and similar to sabalo (*P. lineatus*) muscle from Río de La Plata (243 ng g $lipid^{-1}$, Colombo et al., 2011). These results would correspond to the activities in the area and the subsequent release from several sources such as wastes, plastics and electronic equipments.

PBDEs congener composition in patagonian silverside of both sexes was relatively homogeneous with a predominance of BDE-47 (69 ± 17.8%), followed by BDE-100 (18 ± 8.5%) and BDE-99 (14 ± 10.8%). Moreover, this pattern reflects the world wide trend observed in many aquatic ecosystems (Ikonomou et al., 2006; Colombo et al., 2011; Ondarza et al., 2011). The enriched composition in tetra-congener together with ratios BDE-47/BDE-99 = 7.3 ± 5.6 and BDE-99/BDE-100 = 0.7 ± 0.3, suggest a possible selective debromination from penta- to tetra-congeners (Voorespoels et al., 2003). Moreover, due to its smaller size (8.1 and 9.6 Å in BDE-100 and BDE-99, respectively) (Luross et al., 2002), other plausible explanation is that BDE-100 could enter through biological membranes more easily than BDE-99. Furthermore, the BDE-99/BDE-100 ratios < 1 found in fish from the present study can be also explained by a less biodegradability of BDE-100 compared to BDE-99 due to its differences in bromine substitutions (stereospecific hindrance) (Christensen et al., 2002). The PCBs/PBDEs ratios ranged between 2 and 13 in fish tissues along the Negro River, showing the persistence and historical use of PCBs in industries and hydroelectric power plants, as well as untreated sewage and washout from dumps. On the other hand, it is not surprisingly the increase of PBDEs levels reflect the extensive use of these compounds in electronics products (de Wit, 2002).

4. Conclusions

The present work showed that patagonian silverside from the Negro River basin was a suitable biomonitor of OCPs, PCBs and PBDEs. The result revealed that land use in surrounding areas (intensive agriculture, industrial activity, hydroelectric power plants) represent current sources of OCPs, mainly DDTs, and PCBs to fish from the basin. The high DDTs and PCBs levels in fish were an example of how banned chemicals can still represent a hazard to aquatic organisms and subsequently to human health. The concentrations of PCBs in silverside muscles, mainly those from the Upper Valley, were at unsafe levels for human consumption. In the case of PBDEs, the predominance of BDE-47, although at low levels, denotes the worldwide tendency in the area.

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