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## Assessment of Argentinean Patagonia pollution: PBDEs, OCPs and PCBs in different matrices from the Río Negro basin

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### HIGHLIGHTS

- ▶ OCPs, PCBs and PBDEs were found in soils, sediments, SPM, streamwater and macrophytes.
- ▶ Pesticides represented 70% of the total pollutants and *pp'*-DDE was the main pesticide found in all matrixes.
- ▶ The relation PCBs/PBDEs > 1 agrees with worldwide tendency.
- ▶ Macrophytes played a key role in reducing pollutant levels in the river.
- ▶ Monitoring critical points of legacy contamination is crucial for watershed management.

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### ABSTRACT

This work reports the occurrence and distribution of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in soil, sediment, suspended particle matter (SPM), streamwater and macrophytes, along the Río Negro basin, Argentinean Patagonia. The clear predominance of OCPs among all matrixes indicates the impact of agriculture on the watershed. The highest levels were found for *pp'*-DDE which represented up to 95% in agricultural soils ( $42.0\text{--}1.27 \times 10^3$  ng/g d.w) from the Upper Valley (upstream), where long and historical intensive fruit cultures have been settled and represent a hot spot of legacy pesticides for the environment. The insecticide endosulfan, currently in use, was also found in all matrixes. Levels ranged between 0.3 and 708.0 ng/g d.w, being the highest concentrations those of SPM from the Middle Valley, just before the delta area, where pesticides would be retained leading to lower concentrations as was observed downstream. PCB (#153, 138, 110, 101) and PBDE (BDE-47) levels were directly related with the presence of hydroelectric power plants, dams and dumping sites, mainly settled in the Upper Valley (0.8 ng/g and 15.1 ng/g d.w for PBDEs and PCBs, respectively). Although there was a decreasing gradient of these pollutant concentrations through the river flow, downstream urban areas enhanced PCB concentrations in the aquatic environment. More efforts and monitoring programs are highly required to control and reduce soil erosion in order to prevent the availability of forbidden pollutants in the environment.

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### 1. Introduction

The occurrence of persistent organic pollutants (POPs) in environmental compartments has received attention due to their persistence, biomagnification potential, long-range transport capacity and toxicity. The use and production of most of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) have been internationally

regulated by the Stockholm Convention since 2004. Restrictions for the endosulfan insecticide and the polybrominated diphenyl ethers (PBDEs) were recently implemented (UNEP, 2004, 2011). Particularly, OCPs have been restricted and forbidden in most countries since the late 1970s, while some developing countries are still using them for public health (Wania and Mackay, 1996; Sabljic, 2001; Borghesi et al., 2008). PCBs were banned three decades ago, and PBDEs, used as flame retardants since 1970, have received attention recently due to their persistence and toxic effects (de Wit, 2002; Hites, 2004).

These pollutants can reach the aquatic environment from non-point and punctual sources depending on land use and contaminant delivery, and due to their hydrophobic character they associate to organic matter

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of sediments and/or lipids of organisms. Although the toxicity of weathered organic compounds is generally thought to decline with residence time in the environment (Semple et al., 2003), their long half-lives with their potential for bioaccumulation and biomagnification through food chains, present a significant threat to the environment. Agricultural activities, urban settlements, industries and dams are potential sources of PBDEs, OCPs and PCBs to large basins. To determine pollutant levels and distribution patterns as well as to identify the sources of these compounds are essential to prevent or mitigate accurately risks to the aquatic environment.

Río Negro is the most important river with the largest drainage basin (140,000 km<sup>2</sup>) and water discharge (600 m<sup>3</sup>/s) to the coastal area of Argentinean Patagonia. The basin provides 4% of the worldwide production of apples, pears and peaches concomitantly with an intensive use of pesticides from 50 years ago. Moreover, the settlement of hydroelectric power plants in the upstream zone generates 30% of the electricity consumed in Argentina. In addition, the occurrence of chemical industries and petroleum facilities has been reported by Arribère et al. (2003). Due to the different anthropogenic activities developed in the basin, river discharge could be an important source of contamination to the adjacent coastal environment.

This work reports the occurrence and distribution of OCPs, PCBs and PBDEs in several environmental matrices (soil, sediment, suspended particle matter and macrophytes) along the Río Negro basin in relation to land use. Research was sponsored by the United Nations Environment Programme (UNEP), as part of the Project "Argentinean Patagonia Pollution", which aimed to study the role of Patagonian basins on the POP contamination in the southeastern coast of the Atlantic Ocean.

## 2. Materials and methods

### 2.1. Study area

The study was conducted along the Río Negro basin which is located across the northern region of Argentinean Patagonia (Fig. 1, S 39° 04.9' 14"; W 67° 02.9' 59"). The area is included in the Patagonian plateau (east side) characterized by a dry continental climate, low rainfall, good insolation, and a high thermal amplitude with a mean annual temperature between 14 °C and 16 °C (Coronato et al., 2008). Rainfall in most of the plateau is below 200 mm/year, increasing up to 800 mm/year close to the Andes (Coronato et al., 2008). These climate

characteristics and the sandy alluvial mollisol type soils (Coronato et al., 2008), allow the cultivation of fruits (e.g. grapes, apples, peaches, plums, pears) and vegetables.

Río Negro basin transports a great burden of dissolved solids which are delivered into the Patagonian coast (Depetris et al., 2005). Based on land use, the basin is divided in three areas: the upper valley (UV), mostly concerned to fruit production with several dams installed upstream; the middle valley (MV) with animal farming and less intense fruit production, and the lower valley (LV) dedicated mainly to animal farming and has also some natural areas. Moreover, the main urban settlements are concentrated in UV (e.g. Roca, Villa Regina, Cipolletti) and LV (e.g. Viedma, Conesa).

### 2.2. Sampling

Samples of soil, bottom sediment, streamwater, suspended particulate matter (SPM) and macrophytes were collected along the river basin between February and April 2006, which coincides with the period of the highest pesticide application (Fig. 1).

#### 2.2.1. Soils

Surface soils were sampled covering seven sites according to land use: Hidronor (HN), Villa Regina (VR) and La Josefa (LJ), as representative of agricultural areas; Villarino (VI) and Limay (LI) as development of recreational activities; and Chelforo (CH) and Criadero (CR) as natural soils (Fig. 1). Soil sampling sites were mostly selected to 300–500 mts from river margin. Samples were randomly taken in triplicate from the top soil (0–10 cm). Soils from HN and VR in the UV and VI from LV were also sampled for profile analyses. Soil cores ( $\leq 30$  cm) were obtained using steel core samplers of 10 cm of diameter and 40 cm of length. Three equidistant samples were obtained for each soil along a 100 m transects and transported to the laboratory. The cores were opened to characterize the profile and subsampled in three or four sections as appropriate from 0–4 to 20–30 cm. Subsamples were placed in aluminum boxes covered with aluminum foil (in order to avoid contamination) and kept at room temperature until they reached constant weight. All samples were sieved (2 mm) to remove coarse organic fragments and homogenized. Subsamples for residue analyses were kept at  $-20$  °C wrapped in aluminum foil until analysis, while subsamples for physicochemical properties were kept at room temperature.

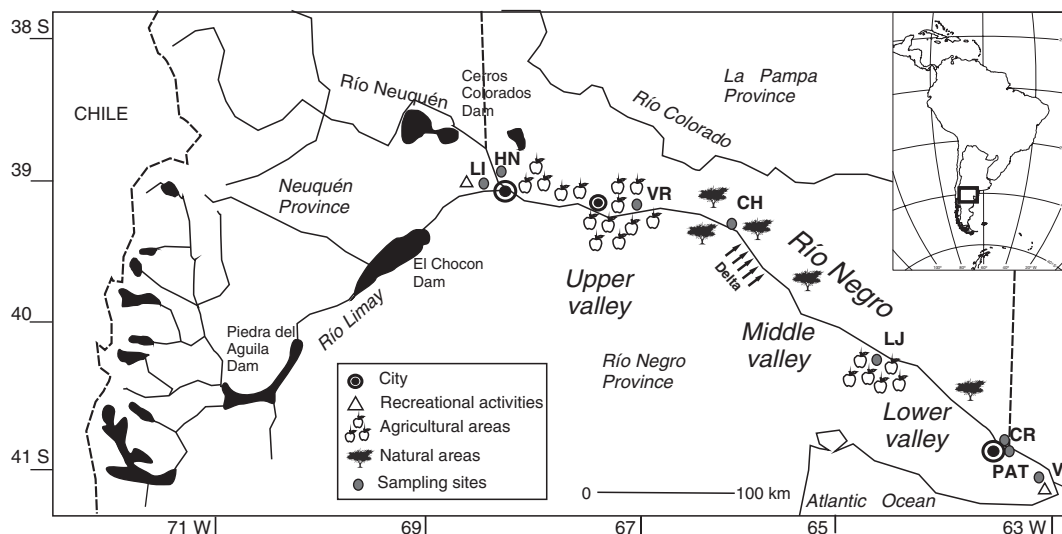


Fig. 1. Study area showing sampling stations of soils, sediments, macrophytes and streamwater (Modified from Isla et al., 2011). Hidronor (HN), Villa Regina (VR) and La Josefa (LJ) = agricultural areas; Villarino (VI) and Limay (LI) = recreational activities; and Chelforo (CH) and Criadero (CR) = natural areas.

### 2.2.2. River bottom sediments (BS) and macrophytes

Bottom sediment samples (N = 5 from each point) were taken from LI, HN, VR, CH, LJ and CR points (Fig. 1) using steel core samplers of 6 cm of diameter and 10 cm of length. Samples were air-dried at room temperature and thoroughly mixed and disaggregated with a mortar and pestle before sieved (250- $\mu$ m) to obtain a homogeneous matrix. Bulrush (*Schoenoplectus californicus*) was collected from LI, HN, VR, LJ and CR using a 20  $\times$  20 cm square sampler with mobile sides. Five sets of six individuals and the sediments associated to their roots were collected in each station. Samples were separated into roots (R), stems (S) and near root sediments (NRS), defined as the sediments that did not fall from bulrush root after collection and need to be separated manually. Samples were air-dried at room temperature and stored at  $-20^{\circ}\text{C}$  until analysis.

### 2.2.3. Streamwater

Subsurface water samples were obtained in MV and LV in order to monitor the transport of pollutants to the estuary. Samples were collected in 1 L amber glass bottles (N = 6 each site) at 30 cm depth, and transported to the laboratory, stored at  $4^{\circ}\text{C}$  and analyzed within four days after sampling. Suspended particulate matter was obtained by filtering water samples through a 0.45  $\mu$ m membrane. SPM was air dried at room temperature until they reached constant weight and kept wrapped in aluminum foil at  $-20^{\circ}\text{C}$  until analysis. Measurements of river water quality (temperature, pH, conductivity and dissolved oxygen) were performed with a Hanna 968i device.

## 2.3. Analytical methods

### 2.3.1. Physicochemical analyses

Soil and sediment subsamples were used to determine total organic carbon (TOC) and particle size distribution (clay, silt and sand content). TOC was determined by wet-oxidation method (Walkley and Black, 1965). Particle size distribution was determined by sieving and the pipette method combined (Galehouse, 1971); obtaining the weight percentages of the three main grain size categories: clay (<0.002 mm); silt (0.002–0.062 mm) and sand (>0.062 mm). Water content was quantified by constant-weight drying in an oven at  $110^{\circ}\text{C}$ .

### 2.3.2. Contaminant analyses

All solvents were residue analysis grade and other reagents were obtained from Merck Co. (Darmstadt, Germany).

## 2.4. Extraction procedure

### 2.4.1. Soils, BS, SPM and macrophytes

OCPs, PCBs and PBDEs were extracted according to Metcalfe and Metcalfe (1997), with the modifications introduced by Miglioranza et al. (2003a, 2003b). Soil and sediment 10 g subsamples, whole filters with SPM and 3 g of roots or stems were homogenized with sodium sulfate, spiked with 20 ng of PCB #103 as internal standard, Soxhlet extracted (8 h) and then concentrated down to 3 ml under vacuum and nitrogen flow. Lipid content from macrophyte extracts was determined gravimetrically after gel permeation chromatography using Bio-Beads S-X3 (200–400 mesh). Further interfering substances were removed with activated silica (24 h at  $200^{\circ}\text{C}$ ). Sulfur compounds were removed with activated copper. Extracts were concentrated down to ca. 1 mL with  $\text{N}_2$  flow and kept at  $-20^{\circ}\text{C}$  in sealed vials until GC analyses.

### 2.4.2. Water

OCPs, PCBs and PBDEs were extracted following the procedure developed by Gonzalez et al. (2012) consisting in spiking 1 L of water with 20 ng of PCB103, vigorous shaken of 500 mL spiked samples during 2 h in a clean amber bottle with 300 mL of hexane-dichloromethane, sample conservation at  $4^{\circ}\text{C}$  during 12 h. Then the organic layer was collected and evaporated down to 2 mL before further clean up using

activated silica. Extracts were concentrated to 1 mL and kept at  $-20^{\circ}\text{C}$  in sealed vials prior to GC analyses. Samples were analyzed in triplicate.

## 2.5. Analytical procedure

OCPs and PCBs were identified and quantified using a Gas Chromatograph, Shimadzu 17-A gas equipped with a  $^{63}\text{Ni}$  Electron Capture Detector (GC-ECD) and a SPB-5 [(5%phenyl)-methyl polysiloxane, 30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness; Supelco Inc.] capillary column. Samples (1  $\mu$ L) were injected on splitless mode. The injector was kept at  $275^{\circ}\text{C}$ , while the detector was at  $290^{\circ}\text{C}$ . The following temperature program was applied: start at  $100^{\circ}\text{C}$  and held for 1 min, followed by an increase of  $5^{\circ}\text{C}/\text{min}$  up to  $150^{\circ}\text{C}$ , held for 1 min, then  $1.5^{\circ}\text{C}/\text{min}$  up to  $240^{\circ}\text{C}$ , and then  $10^{\circ}\text{C}/\text{min}$  up to  $300^{\circ}\text{C}$  for 10 min. Helium was used as carrier (1.5 mL/min) and nitrogen as make-up gas (Miglioranza et al., 2003a).

PBDEs were identified and quantified using a Gas Chromatography–Mass Spectrometry Perkin-Elmer Clarus 500 MS (GC-MS) equipped with DB-5 MS [(5%phenyl)-methyl polysiloxane, 30 m  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu$ m film thickness ELITE 5MS] capillary column, operated under electron impact mode with the selecting ion and full ion scanning mode (Ondarza et al., 2011). Each PBDE was identified and confirmed by their relative retention time against PCB #103 and 3 monitored ions (1 for quantification and 2 for confirmation) considering a  $\pm 10\%$  deviation of standard proportion.

### 2.5.1. Quality control and assurance

Laboratory and sampling glassware were washed with appropriate solvents to avoid interferences. The quality assurance and quality control (QA/QC) included regular analysis of matrix blank, duplicated samples and instrumental and procedural blanks. Recoveries on spiked matrices were >90%. Detection limits (DL) were calculated according to Keith et al. (1983) and ranged between 0.03 and 0.05 ng/mL for HCHs ( $\alpha$ -,  $\beta$ -,  $\gamma$ -isomers) and between 0.08 and 0.33 ng/mL for the rest of chlorinated compounds [Chlordanes ( $\alpha$ - and  $\gamma$ -isomers and trans-nonachlor), DDTs (*pp'*-DDE, *pp'*-DDD and *pp'*-DDT), endosulfans ( $\alpha$ - and  $\beta$ -isomers and endosulfan sulfate) and PCBs (IUPAC #s 8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 105, 138, 126, 187, 128, 167, 156, 157, 180, 169, 170, 189, 195, 206, 209)]. DL ranged between 0.2 and 1.1 ng/mL for BDEs (IUPAC #s 28, 49, 47, 66, 100, 99, 154, 153, 183). The standard solutions used for identification and quantification of single compounds were obtained from Ultra Scientific – USA (PCB #103), Absolute Standards Inc. – USA (OCPs and PCBs) and Bromodiphenyl Ethers Lake Michigan Study (PBDEs) of AccuStandard Inc. – USA.

## 2.6. Statistics and data expression

Significant differences in OCP levels among different matrices were tested with a one way ANOVA followed by Tukeytest or Mann–Whitney *U* test. When parametric requirements were not fulfilled as well as for comparing OCP levels throughout soil profile, non-parametric comparisons were used (Kruskal–Wallis test followed by a *t*-paired test) for dependent samples. Pearson correlation test was used to determine whether soil concentration correlated with soil TOC. The significance level was set at  $\alpha = 0.05$ , unless otherwise specified. OCPs, PCBs and PBDEs were reported as ng/g dry weight for soils, sediments, SPM and macrophytes, while water samples were expressed in ng/L.

## 3. Results and discussion

### 3.1. Surface soils

The highest total concentrations of contaminants (50 ng/g dry weight) were found in HN sampling point where an intensive apple



culture is developed being in some areas the main activity. A good correlation between pesticide levels and TOC content ( $r = 0.81$ , Table 1) was observed. Both, pesticides and TOC, were higher than soils from MV and LV stations (ANOVA, Tukey test  $p = <0.0001$ ), where pesticide concentrations were higher than the levels set for “clean soils” (5 ng/g dry weight, Department of Soil Protection, 1994). However, levels found in HN station were much lower than those found in VR (1330 ng/g dry weight), where peach is cultivated (Gonzalez et al., 2010). VR represents the typical agricultural soil of fruit production from the upper floodplains of the basin with both current and historical use of pesticides. The difference in concentrations was mainly due to DDT levels (99% *pp'*-DDE, ANOVA, Tukey test  $p = <0.0001$ , Table 3).

HN and VR soils presented the OCP distribution pattern of DDTs > endosulfans and HCHs (ANOVA, Tukey test  $p = 0.005$  for endosulfans, and  $p = 0.004$  for DDTs). *pp'*-DDE predominated in soils from upper and middle valleys with a hot spot at VR. The *pp'*-DDT/*pp'*-DDE ratios < 1 suggest an intense use of *pp'*-DDT in the past.

Miranda-Filho et al. (2007) have suggested that South America is a hot spot for organochlorine compounds on the basis of DDT levels found in elephant seals from Antarctica.

Both, detection frequency and concentration of *pp'*-DDE in soils from UV and MV were higher than other pesticides. This was assigned to the extended use in the past and to the further metabolism of the pesticide with a consequent long half-life. It was reported that for *pp'*-DDE the half-life would be of 11 years depending on the volatilization in the tilled soil in the southern United States (Bidleman et al., 2006; Kurt-Karakus et al., 2006; Scholtz and Bidleman, 2006). Similar results about predominance of *pp'*-DDE, have also been detected in soil samples of Shanghai, Taihu area, Haining, and Shaoxing in Zhejiang province (China) where an intensive use of *pp'*-DDT was reported (Haruhiko et al., 2005).

Endosulfan residues in the agricultural soils of VR, HN (UV) and LJ (LV) were dominated by the sulfate metabolite due to the sampling conducted during February, at the end of the application period of technical endosulfan (Aizen et al., 2009). Thus, the half-life of the parental compounds of 3–4 months, assumes a high metabolism rate.

Composition differences of HCH isomers in the environment could indicate different contamination sources. HCHs were present in almost all sampling sites, with the predominance of  $\gamma$ -isomer (higher 90%) which indicates the use of lindane in the area. The  $\gamma$ -HCH insecticide has been widely used in Argentina to kill lice and its use was reported for Cordoba (Pesce and Wunderlin, 2000). Technical HCH constituted by  $\alpha$ -HCH (60–70%),  $\beta$  (5–12%),  $\gamma$ -HCH (10–15%) and  $\delta$ -HCH (6–10%) has been used as broad spectrum pesticides for agricultural purposes, but has been banned in Argentina since 1990.

The cyclodienes, represented by heptachlor,  $\gamma$ - and  $\alpha$ -chlordanes, presented a similar pattern. Concentrations were below 1 ng/g dry weight, denoting no recent contamination.

Among non-agricultural pollutants, PCBs constituted the second group highlighted in the basin, with the higher levels in soils from LI station. The surrounding area is mainly covered by open dumping sites. Moreover, dams upstream would represent a potential source of PCBs due to the persistence of these compounds used in electric transformers and as refrigerant until its ban in 2005. In addition a chlor-alkali factory settled upstream of Neuquen River (affluent of Negro River) would be another possible source of PCBs to the environment (Arribère et al., 2003).

The predominance of penta- and hexa-CB at all stations reflects the use of Aroclor 1248 and 1254 mixture in the region as previously reported by Ondarza et al. (2012). Flooding events that occur during dams' management may be responsible for the input of such compounds to the soil. In the rest of stations, the levels of PCBs in soil were below 1.5 ng/g dry weight, representing a very low concern to the environment.

Regarding PBDEs, residues were detected in all samples at levels below 1 ng/g dw. A predominance of BDE 47 followed by BDE 99 and BDE 100 was found. The highest PBDE levels were detected in soils from LI station (0.8 ng/g dry weight), probably related to the presence of dumping sites. Particularly, LI station was settled very close (200 m) to a large area used as illegal dumping where unwanted wastes from domestic use including plastics and electronic wastes were disposed. Eguchi et al. (2013) and Kwan et al. (in press) reported PBDEs as the dominant contaminants in the dumping sites in Asian developing countries.

In the case of VR where total PBDE levels were similar to LI station, it could be related to impurities in pesticide plastic containers as well as the input from surrounding urban settlements. In addition, these soils are irrigated with streamwater and fertilization practices are frequently carried out using sewage sludge. Wu et al., 2012 reported the presence of PBDEs, at levels slightly higher than background soils in agricultural soils fertilized with sewage sludge. Other PBDE source for these soils could be related to the input of these compounds from the apple and peartrees, when leaves fall down or by rain wash-out. The “forest filter effect”, where forest canopies are seen as cumulative compartments was previously reported by Nizzetto et al. (2006). However, PBDE values were lower than the mean values of soils from Southeast Asia: Bantar Gebang (Indonesia; 0.11–255 ng/g dry weight), Phnom Phen (Cambodia; 0.55–91 ng/g dry weight), Hanoi (Vietnam; 1.2–429 ng/g dry weight) and Chennai (India; 0.82–19 ng/g dry weight; Eguchi et al., 2009). Hassanin et al. (2004) observed PBDEs in rural surface soils of UK exhibiting congener patterns similar to the penta-BDE product, with values ranging from less than 1 to 12 ng/g.

**Table 1**  
Particle size distribution (%), TOC (%) and texture of soils (surface and profile when corresponding) along the Río Negro basin. a = distance from the coast, S = sandy, SL = sandy loam, CL = clay loam, SiL = silty loam, L = loam.

Valley	km (a)	Sampling station		Particle size distribution (%)				Total organic carbon (%TOC)	Texture
				Sand	Coarse silt	Fine silt	Clay		
Upper	542	HN	0–5 cm	28.96	40.39	0.36	30.29	5.13	CL
			5–10 cm	28.58	41.31	3.36	26.75	3.84	L
			15–20 cm	28.29	42.37	4.05	25.27	1.65	L
	451	VR <sup>a</sup>	0–5 cm	25.62	46.23	4.18	23.97	4.70	L
0–12 cm			52.5	11.21	31.08	5.2	3.90	SL	
Middle	366	CH	12–31 cm	45.31	28	0.93	25.76	1.98	SL
			0–5 cm	34.60	23.60	28.00	13.70	2.66	L
Lower	273	LJ	0–5 cm	66.41	13.00	3.30	17.29	1.60	SL
			0–5 cm	3.90	12.50	48.50	35.20	3.18	SiL
	1.5	VI	0–4 cm	9.8	10.2	41	39.1	1.10	SiL
			4–9 cm	7.6	9.1	41	42.3	1.40	CL
			14–23 cm	92.6	0.2	2.6	4.5	0.60	S

<sup>a</sup> Gonzalez et al. (2010).

Moreover, Matscheko et al. (2002) reported PBDEs in Swedish agricultural soils with a mean value of 0.23 ng/g dry weight. These results indicate widespread occurrence of these compounds in the environment and denote the role of dumping sites and agricultural soil as punctual and secondary sources of PBDEs, respectively, to the environment.

### 3.2. Soil profiles

Two soils were selected, HN and VI, as agricultural and recreational representative soils, with the purpose to understand pesticide dynamics and historical use in the region. Moreover, these results were compared to VR profile previously reported by Gonzalez et al. (2010). HN represents small-case agricultural activity while VR has been historically used for fruit cultures, such as apples, pears, among others, with intensive pesticide application, while VI station is an area close to the estuary with recreational land use. Similar to VR, pesticide distribution pattern in HN was DDTs  $\gg$  endosulfans  $>$  HCHs  $>$  the rest of OCPs for the upper 20 cm, although the total concentrations were lower. Conversely, in VI soil profile, the pattern of each surface layer was DDTs  $>$  HCHs  $>$  endosulfans  $>$  the rest of OCPs, being the concentrations much lower than the other two profiles. Thus, the total concentration pattern VR  $>$  HN  $>$  VI would be in relation with the different land uses and in the case of VR and HN with the intensity of soil use, since DDT was the main group of pesticides in all soil samples and technical endosulfan is currently in use, only these two groups will be further discussed (Fig. 2).

#### 3.2.1. DDTs

At all depths the *pp'*-DDE/*pp'*-DDT relation was  $>1$ , indicating a non-recent use of *pp'*-DDT in the region. When comparing pesticide distribution through profiles a different behavior among soils can be seen. Conversely to that observed on VR soil, where higher DDT levels were found in surface layers decreasing through the profile, in HN a slightly *pp'*-DDE enrichment in deeper layers was observed. In addition, DDT levels on 0–20 cm of HN profile were one half of those on 22–30 cm from VR. DDT leaching was coupled with the increase of fine particles (clay) through the soil profile (Table 2). Mobility alone is not a good indicator of the deep leaching potential of a pesticide, but rather the combination of mobility and persistence. Similar DDT behavior was found in soil profiles from Pampean Region (Miglioranza et al., 2003a) with an enrichment of pesticides in deeper layers. DDT is highly insoluble in water and does not readily leach through the soil profile. Its great molecular stability, with residence time in soils of at least 10 years and the time elapsed since the last application would allow it to reach deeper levels by translocation with colloids (Harris et al., 2000).

As observed in VR, DDT levels in HN exceeded the values for DDTs in soils considered “clean” at the global scale (5 ng/g dry weight, Department of Soil Protection, 1994). Considering DDT sources, the use of the acaricide dicofol in the area, which contains DDT impurities (0.1–10%), could mean a fresh *pp'*-DDT input. However, the amounts applied at recommended field concentration of 48 mg/L on fruit trees (INTA, 2004), are negligible in comparison with *pp'*-DDE levels in these agricultural soils.

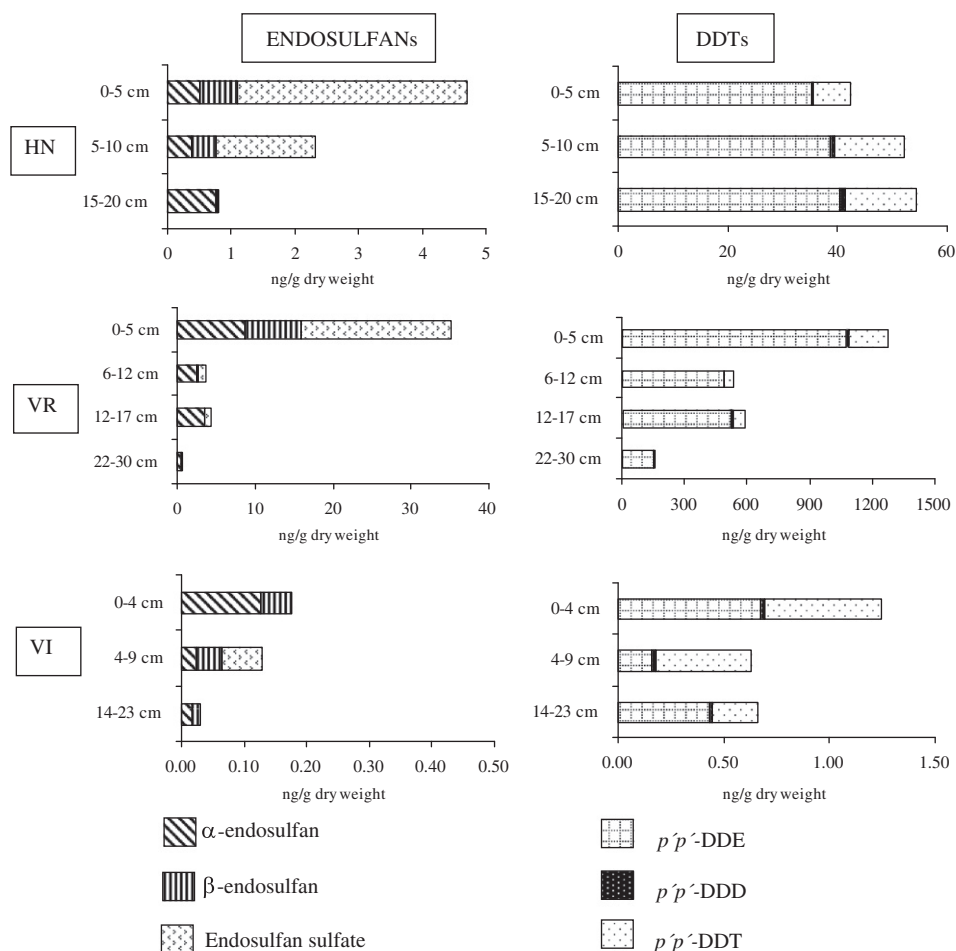


Fig. 2. DDT and endosulfan concentrations, expressed as ng/g dry weight in soil profile from VR, HN and VI sampling stations of the Rio Negro basin.

**Table 2**  
Particle size distribution (%), TOC (%), texture and pH of surface sediments from Río Negro basin. a = distance to the coast, SL = sandy loam, CL = clay loam.

km (a)	Sampling station	Particle size distribution (%)				Total organic carbon (%TOC)	Texture	pH
		Sand	Fine silt	Coarse silt	Clay			
542	HN	87.66	0.68	0.28	11.18	0.7	SL	7.7
545	LI	83.64	0.44	3.85	12.06	0.3	SL	7.2
451	VR	52.00	14.00	25.00	9.00	0.3	SL	7.1
366	CH	59.50	2.82	23.67	15.00	0.8	SL	7.4
273	LJ	46.15	0.77	30.32	22.76	1.2	SL	7.5
15	CR	30.02	0.93	40.20	28.86	1.6	CL	7.5

VI soils showed the lowest DDT level on surface, as well as in deeper layers, considering that it is a natural soil with recreational use. The  $pp'$ -DDT/ $pp'$ -DDE ratios were variable depending on depth, probably by differences on degradation such as biological metabolism. Therefore, these results would be a consequence of background soils mainly polluted from atmospheric inputs. It is known that nearby agricultural soils may act as a source of "aged" OCPs and a fraction of them may get volatilized and dispersed, making them reservoirs of these pollutants and a risk to non-impacted soils (Pereira et al., 2010).

### 3.2.2. Endosulfans

HN and VR soils showed a similar endosulfan distribution pattern, with a predominance of E sulfate in the 0–5 cm level. It can be explained by the fact that the high organic matter content and probably a high microbial activity would lead to enhanced metabolism of parent compounds into its more persistent and toxic sulfate metabolite (Weber et al., 2010). These findings are in concordance with the widespread use of endosulfan in the area as well as the time elapsed since its application, considering that the average life-time of the  $\alpha$ - and  $\beta$ -isomers is less than three months. The predominance of  $\alpha$ -isomer in the deeper layers of both agricultural soils demonstrates its higher leaching potential as a consequence of the relative high hydrophilicity ( $K_{ow}$  3.83; Sabljic et al., 1995) with respect to the other isomer and a low metabolic activity in the deeper layer. Conversely in VI soil,  $\alpha$ - and  $\beta$ -isomers were dominant on surface layer (0–5 cm) with decreasing levels through the profile. Sulfate metabolite was detected on subsurface soil (4–9 cm) which presents the highest levels of TOC and clay content and consequently a greater retention capacity. This different behavior is the result of different sources and soil characteristics. In VI, endosulfans arrive by diffuse or atmospheric sources from application areas which are reflected on the isomers relation  $\alpha/\beta > 1$  of surface layer, similar to technical endosulfan mixture. Besides, soil structure and microorganism density at sub-root depth, where oxygen, water content and nutrients availability would be optimums, represent a good scenario for  $\alpha$ -endosulfan metabolism to endosulfan sulfate.

It is important to emphasize the opposite behavior of DDT and endosulfan groups: while the first increase or kept constant with depth (past use), endosulfans show the highest levels at surface soils (recent use) in all soils.

### 3.3. River bottom sediments (BS)

Physicochemical characteristics of BS varied along the Río Negro with high sand levels in the UV, and increasing TOC levels in the fine fraction toward the outlet. There was no relationship between sediment TOC content and total pollutant concentrations indicating other factors involved in pollutant retention, such as punctual sources and/or differential partition of pollutants between BS and SPM. Particularly, there was an increase in SPM loads from 46 mg/l (MV) to 145 mg/L (LV). Results indicate that residue levels reflect pollutant application history and dissipation rates more than an air–soil equilibrium, as has been reported in agricultural soils of Alabama (Harner et al., 1999) and from Georgia and South Carolina (Kannan et al., 2003). The

dominance of sand along the Río Negro diminishing toward the outlet agrees with the pollutant behavior despite worldwide research stated a non relationship between sand content and organochlorine levels. However, Drake et al. (2002) reported a good relation between sand and  $pp'$ -DDE levels in sediments supporting our results. Generally, organochlorine compounds tended to accumulate in the fine grain-size fractions, rich in organic matter, except  $pp'$ -DDE, which concentrates basically in the coarse grain-size fractions. The highest concentrations of OCPs, PCBs and PBDEs along the Río Negro basin were detected in upstream sediments (UV, 18.5 ng/g dry weight), decreasing gradually toward the coast (LV, 3.1 ng/g dry weight) (Table 3). The OCP/PCB or PBDE ratio was  $> 1$  in all sampling stations denoting the predominance of agriculture over industry and urban pollution sources following the same behavior of soil. The assessment of DDT levels in sediments was directly related to soil concentrations. Thus, higher DDT levels were found at HN and VR stations according to the agricultural land use (Kruskal–Wallis  $p = 0.006$ ). Particularly, the high  $pp'$ -DDT levels found in HN station (16.3 ng/g dry weight) surpassed the maximum limit of "Lowest Effect Levels" (LOEL) for protection and management of aquatic sediment quality in Ontario, Canada (13 ng/g dry weight, CCME, 2001). In order to identify possible sources of DDTs, the  $pp'$ -DDT/( $pp'$ -DDT +  $pp'$ -DDE) ratio was calculated. LI and HN presented mean ratios of 0.65, while VR 0.33 and CH 0.5. After the delta riparian zone, 300 km downstream from VR, in LJ station the ratio was 0.22. These results would indicate a non-recent use of  $pp'$ -DDT although differences among stations were observed according to the intensive agrochemicals use in the past. Moreover, the widely used acaricide dicofol, as was previously mentioned for soils, represents other contemporary source of DDTs into the environment. Surprisingly, in CR station the ratio was 0.9, despite being a zone of scarce agricultural activities. The presence of  $pp'$ -DDT in the coastal zone suggests the entering of fresh inputs of  $pp'$ -DDT, either from local use or long-range transport.

Studies on OCP levels in fishes along the Río Negro also reported the predominance of DDT group, being  $pp'$ -DDE the main compound with mean concentrations of 0.15 and 2.3 ng/g wet weight for the muscle and liver, respectively, in LV (Ondarza et al., 2010) and, 6.4 and 69.0 ng/g wet weight for the muscle and liver, in MV (Ondarza et al., 2012).

VR and LI stations showed the highest concentrations of endosulfans (mean range 1.1–1.96 ng/g dry weight) being significantly different from the rest of the stations, with a mean value of 0.5 ng/g dry weight (Kruskal–Wallis  $p = 0.04$  Table 3). It is clear that despite the high use of technical endosulfan in the region, soils and sediments accumulate the pesticide at relatively low rates, even comparing to DDT levels. The physicochemical characteristics of endosulfans lead to be more available for soil erosion and less subject to adsorption by bed sediments than DDTs (Miglioranza et al., 2003b). All stations, except CR, showed a predominance of  $\beta$ -isomer followed by  $\alpha$ -isomer (Table 3). Beta-endosulfan appears to be mainly associated to sediments in freshwater systems. Thus, Peterson and Batley (1993) conducted studies about partitioning and aquatic fate of endosulfans and demonstrated that a major proportion is associated to sediment over time, reflecting the relatively high  $K_{oc}$  values ( $\log K_{oc\alpha}$  3.6;  $K_{oc\beta}$  4.3), with a relatively higher enrichment of the  $\beta$ -isomer. Similar results were reported by Zhang et al. (2003), Menone et al. (2004) and Miglioranza et al. (2004) showing that the  $\alpha$ -isomer has a greater potential for aquatic transport being more available to degradation. Remobilization experiments indicated that  $\alpha$ -endosulfan was more readily desorbed from sediments than the  $\beta$ -isomer (Peterson and Batley, 1993). Particularly in CR station the relation  $\alpha/\beta$  was  $> 1$  (Table 4). Thus, the ratio of the two isomers reflected technical endosulfan and was probably related to a recent use of the pesticide in close areas, rather than sediment–water partitioning over a longer term. Higher concentrations of  $\alpha$ -isomer related to  $\beta$ -isomer were also found in sediments from several Jamaican rivers and it was also related directly with recent technical endosulfan use (Mansingh et al., 2000).

**Table 3**

Distribution pattern of OCPs, PCBs and PBDEs, expressed as ng/g dry weight for surface soils, bottom sediments and suspended particulate matter, and as ng/L for water, from the Río Negro basin. END = sum of  $\alpha$ ,  $\beta$  endosulfan and endosulfan sulfate; HCHs: sum of  $\alpha$ -,  $\beta$ -,  $\gamma$ - and  $\delta$ -isomers; DDTs: sum of *p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD; Other OCPs = sum of dieldrin, heptachlor, heptachlor epoxide,  $\alpha$ - and  $\gamma$ -chlordanes and transnonachlor; PCBs: sum of IUPAC #s 8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 105, 138, 126, 187, 128, 167, 156, 157, 180, 169, 170, 189, 195, 206, 209; PBDEs: sum of IUPAC #s 28, 49, 47, 66, 100, 99, 154, 153, 183; NA = not available. \*Gonzalez et al. (2010).

		UPPER VALLEY (450-550 km from coast)			MEDIUM VALLEY (200-450 km from coast)		DELTA RIPARIAN ZONE (200 km from coast)			LOWER VALLEY (0-200 km from coast)								
		SOILS						SOILS										
Stations	Analyte	LI	HN	VR*	CH		LJ	CR		VI								
	HCHs		2.3 ± 0.6	4.2 ± 4.4	1.9 ± 1.0		1.2 ± 0.1	1.0 ± 0.1		1.5 ± 1.4								
	END	0.8	4.7 ± 1.5	35.2 ± 53.1	0.3 ± 0.1		1.1 ± 0.8	0.3 ± 0.1		0.2 ± 0.1								
	DDTs	6.0	42.5 ± 8.5	1275.0 ± 1215.0	3.2 ± 2.1		1.6 ± 1.4	1.1 ± 0.3		1.2 ± 0.8								
	Other OCPs	0.5	0.4 ± 0.2	0.6 ± 0.5	0.7 ± 0.5		0.5 ± 0.3	0.4 ± 0.2		0.4 ± 0.2								
	PCBs	15.1	0.6 ± 0.6	0.3 ± 0.3	1.1 ± 0.4		0.9 ± 0.6	0.6 ± 0.4		1.2 ± 1.8								
	PBDEs	0.8	0.1 ± 0.1	0.8 ± 0.1	0.5 ± 0.1		0.2 ± 0.1	0.1 ± 0.1		0.3 ± 0.1								
		SEDIMENTS						SEDIMENTS										
Stations	Analyte	LI	HN	VR	CH		LJ	CR		VI								
	HCHs	0.4 ± 0.1	0.4 ± 0.2	0.3 ± 0.1	1.3 ± 0.7		1.0 ± 0.5	0.4 ± 0.2		NA								
	END	1.1 ± 1.2	0.4 ± 0.1	1.9 ± 1.4	0.7 ± 0.6		0.2 ± 0.2	0.6 ± 0.6		NA								
	DDTs	0.9 ± 0.5	16.3 ± 15.7	1.7 ± 0.1	2.1 ± 1.5		0.8 ± 0.3	0.5 ± 0.1		NA								
	Other OCPs	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1	0.6 ± 0.7		0.2 ± 0.1	0.1 ± 0.1		NA								
	PCBs	2.2 ± 1.2	0.9 ± 0.5	0.3 ± 0.3	0.7 ± 0.5		0.6 ± 0.5	1.4 ± 0.1		NA								
	PBDEs	0.3 ± 0.1	0.2 ± 0.2	0.1 ± 0.1	0.1 ± 0.1		0.1 ± 0.1	0.2 ± 0.1		NA								
		SPM - WATER						PAT										
Stations	Analyte	LI	HN	VR	CH		SPM		WATER		SPM - WATER							
	HCHs	NA	NA	NA	837.8 ± 270.2		2.1 ± 0.2		3.5		5.7 ± 3.0		198.5		3.6 ± 1.3		NA	
	END	NA	NA	NA	708.9 ± 153.3		2.9 ± 1.3		44.5		1.1 ± 0.6		292.1		5.0 ± 2.9		NA	
	DDTs	NA	NA	NA	260.4 ± 58.4		0.8 ± 0.6		113.9		1.9 ± 0.2		64.4		1.9 ± 2.1		NA	
	Other OCPs	NA	NA	NA	101.8 ± 2.3		0.1 ± 0.1		323.8		4.7 ± 2.0		265.3		5.6 ± 3.3		NA	
	PCBs	NA	NA	NA	129.6 ± 19.0		3.3 ± 0.5		765.6		6.2 ± 0.2		558.8		17.8 ± 13.1		NA	
	PBDEs	NA	NA	NA	2.7 ± 2.6		0.2 ± 0.1		39.1		0.5 ± 0.1		65.2		0.8 ± 0.3		NA	

A study conducted on the Namoi River, NSW Australia, revealed endo-sulfan sorption to bottom sediment to be higher on the larger size particle fractions (> 63  $\mu$ m diameter) compared to the finer size fractions (< 24  $\mu$ m). This implies particle-bound transport as well as desorption following sediment re-suspension (Leonard et al., 2001). Therefore in our study, not only the high endosulfans use in the basin, but also the particle size distribution in bottom sediment along the river justifies the endosulfan distribution found.

The highest PBDE value (0.32 ng/g dry weight) was found in sediment collected from LI station (UV, Fig. 3). This site is close to a landfill with disposal of wastes such as wood, paper, demolition materials, garbage, industrial wastes, and dredged sediments and reflects a

specific site supplying pollutants to the river. Particularly, in the LV an increase was denoted with decreasing concentrations towards the coast.

Despite the widespread contamination of PBDEs in a variety of aquatic and terrestrial environments, this study demonstrates that PBDE levels in sediments from the Río Negro basin are low and consistent with worldwide level of a mean PBDE concentration in sediment of 2.5 ng/g dry weight except for BDE-209 (Hites, 2004). Therefore, PBDE levels in sediments from the Río Negro are similar to those found on river sediments from areas non-directly impacted by urban and industrial sources (Song et al., 2004). The PBDE congeners found in the present study were tetra- (BDE 47) and penta-PBDEs (BDEs 99 and

**Table 4**

DDTs and endosulfans in surface soils and bottom sediments along the Río Negro basin.  $\alpha$ -END =  $\alpha$ -endosulfan,  $\beta$ -END =  $\beta$ -endosulfan, END SULF = endosulfan sulfate, <LD = below limit of detection.

Matrix	Compound	LI	HN	VR	CH	LJ	CR
Soils	$\alpha$ -END	0.4	0.5 ± 0.1	8.7 ± 10.0	0.3 ± 0.1	0.2 ± 0.1	0.3 ± 0.1
	$\beta$ -END	0.5	0.6 ± 0.1	7.2 ± 11.9	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1
	END SULF	<LD	3.6 ± 1.4	19.3 ± 31.2	<LD	0.7 ± 0.5	<LD
	<i>p,p'</i> -DDE	3.6	35.2 ± 7.3	1074.0 ± 998.1	2.5 ± 1.9	1.1 ± 0.9	0.6 ± 0.3
	<i>p,p'</i> -DDD	<LD	0.4 ± 0.2	12.8 ± 12.6	0.1 ± 0.1	<LD	<LD
	<i>p,p'</i> -DDT	2.5	6.8 ± 2.4	188.2 ± 204.8	0.7 ± 0.2	0.5 ± 0.4	0.6 ± 0.1
	$\alpha$ -END	0.1 ± 0.1	0.2 ± 0.1	0.6 ± 0.5	0.1 ± 0.1	0.1 ± 0.1	0.6 ± 0.5
Sediments	$\beta$ -END	1.1 ± 1.1	0.2 ± 0.1	1.2 ± 1.2	0.6 ± 0.5	0.1 ± 0.1	0.1 ± 0.1
	END SULF	<LD	0.1 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	<LD
	<i>p,p'</i> -DDE	0.3 ± 0.1	4.2 ± 0.3	1.1 ± 0.2	1.0 ± 0.6	0.7 ± 0.3	0.1 ± 0.1
	<i>p,p'</i> -DDD	<LD	0.1 ± 0.1	<LD	<LD	<LD	<LD
	<i>p,p'</i> -DDT	0.6 ± 0.3	8.6 ± 0.6	0.6 ± 0.1	1.0 ± 1.2	0.2 ± 0.1	0.5 ± 0.1



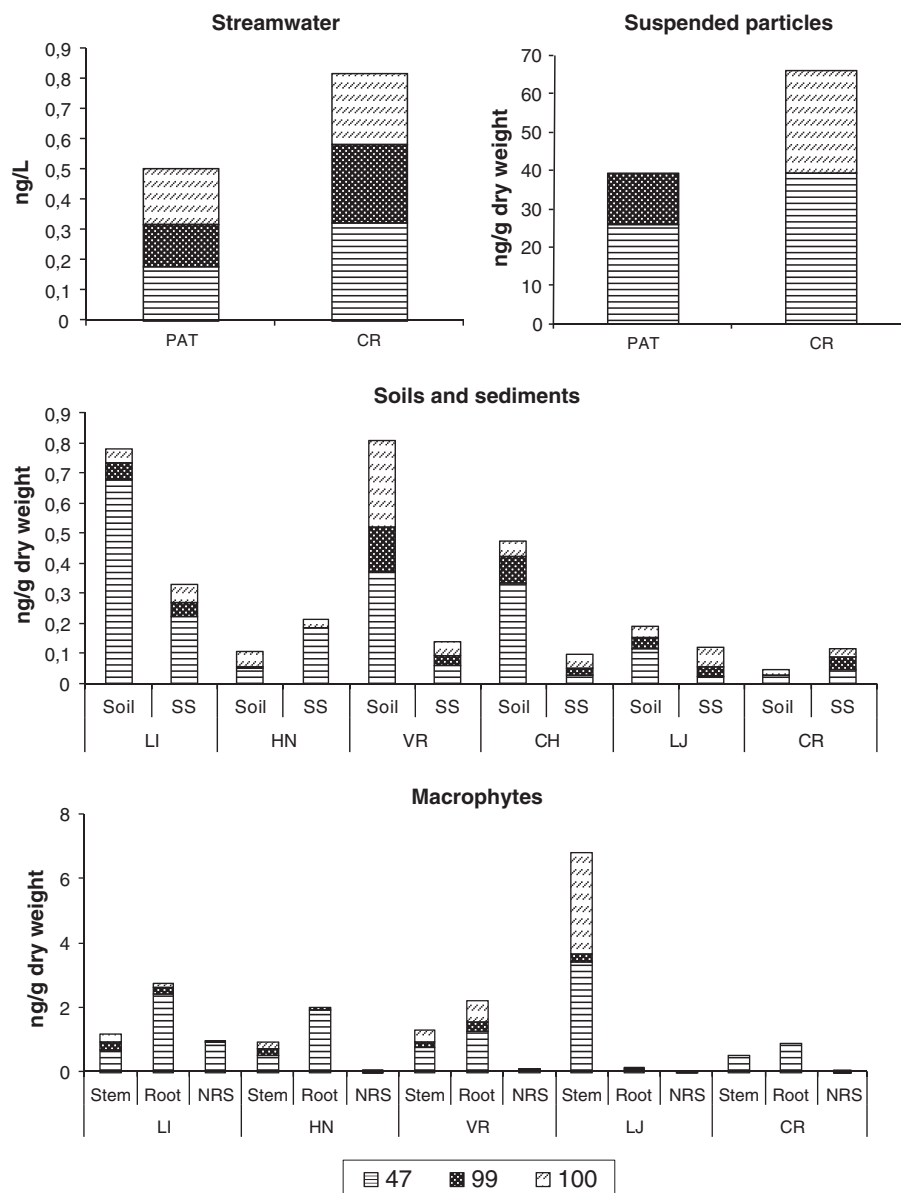


Fig. 3. Concentration of PBDEs in streamwater (ng/L), suspended particles, surface soils, surface sediments and macrophytes (ng/g dry weight) along the Río Negro basin, SS = surface sediment, NRS = near root sediment.

100, Fig. 3). Penta-BDEs are the predominant congeners found in several technical flame-retardant mixtures, including DE-71 and Bromkal 70-5 DE (La Guardia et al., 2006), and their presence can also be indicative of the breakdown of larger PBDE congeners, including deca-BDE (Rahman et al., 2001). A similar distribution pattern was found in UV and MV being BDE 47 > 100 > 99. However, in LV the pattern was different with a predominance of hexa-BDE. Although these values are not indicative of high impacted sediments, they represent a source of PBDEs for aquatic biota as was reported by Ondarza et al. (2012) for fishes.

### 3.4. SPM and streamwater

The total levels of OCPs, PCBs and PBDEs in SPM were one to ten orders of magnitude higher than in BS in all sampling sites (Table 3). These results agree with the fact that SPM traps more efficiently hydrophobic contaminants than BS (Liu et al., 2008). SPM significantly influences contaminant transport to the aquatic environment. Hydrophobic pollutants are removed from the water column, adsorbed onto SPM due to their high organic matter content, transported along the river

and further accumulated in bottom sediments. The resuspension of BS represents a secondary contamination source to overlying water.

The total pollutant levels in SPM from MV presented the highest concentration with a mean value of 2604.5 ng/g dry weight. HCHs, endosulfans and PCBs represented the main groups being 80% of total pollutants (Table 3). Relationships  $\alpha$ -HCH/ $\gamma$ -HCH (4:1),  $\alpha$ -endosulfan: $\beta$ -endosulfan:endosulfan sulfate (7:2:1), and *pp'*-DDT:*pp'*-DDE:*pp'*-DDD (2:2:1) were found. The relation between HCH isomers denotes the higher partition of  $\gamma$ -HCH in the water column as dissolved form. Regarding endosulfans the isomer ratio clearly indicates a recent use of this insecticide in the surrounding area. The DDT group relation reflects the impact of UV soils on aquatic pollution. After the delta, in LV the total pollutant concentrations in SPM decreased 50% (PAT station) which can be attributed to the role of macrophytes, both floating and rooted, on pollutant trapping.

The impact of urban areas at LV was reflected in the distribution groups in CR station, PCBs > cyclodienes > DDTs, due to proximity to sewage and rainfall outlet. Even though the delta riparian zone was effective in pesticide retention clearly observed in the decrease of these pollutants in CR station, the increase in PBDE levels could be

due to the presence of a dumping site in Viedma city (main urban settlement of the basin) settled close to the sampling station. Particularly, CR station is affected by flooding episodes in the river side soils, during exceptional tide phenomena. As a consequence, these soils stay flooded during high tide hours, and pollutant residues are transported to the main stream when low tide takes place. Leachates from landfills have been identified as one of the possible sources of PBDEs in the environment. Kwan et al. (in press) demonstrated that leachates of PBDEs from dumping sites were predominantly found in the adsorbed phase. Therefore the impact of tidal onto dumping site of Viedma could lead to more available PBDEs in the Río Negro, associated mainly to SPM. (Isla et al., 2011).

The proportion of PBDE congeners in CR station would indicate a relatively recent use of penta-BDE mixtures because of the similarity between BDE-47 and BDE-100 proportions, resembling the technical mixture (Fig. 3). The BDE-100 is characterized by a high persistence while BDE-47 despite being the main congener of penta-BDE mixture also constitutes the most ubiquitous BDE as a result of atmospheric transport.

Pollutant levels in streamwater ranged between 9.7 and 34 ng/L, with the highest levels at CR station (Table 3). A similar distribution pattern between SPM and water was found for all studied groups indicating a clear relationship between both matrices where equilibrium partition would be the main factor for pollutant distribution. Thus, in MV endosulfans (2.9 ng/L) and HCHs (2.1 ng/L) predominated, while in LV pollutants were mainly represented by PCBs, HCHs, endosulfans and cyclodienes. As is noted, the DDT group levels were low in water solution, while BS and SPM from the same stations showed high DDT levels, favored by its hydrophobicity and preferential adsorption on organic matter and sand, particularly in the case of *pp'*-DDE. Endosulfan concentrations ( $\alpha$ -/ $\beta$ - > 1) were below the maximum allowable levels for surface waters (7 ng/L National Argentinean Water Council) but they were quite similar to that from the international guidelines (3 ng/L, CCME, 2001), for biota protection, surpassing this value in CR station (5 ng/L). Considering total concentrations of pollutant groups, the river outflow would be of 196 g/day for HCHs, 260 g/day for endosulfans, 99 g/day for DDTs, 290 g/day for the other OCPs, 920 g/day for PCBs and 41 g/day for PBDEs.

### 3.5. Macrophytes (*S. californicus*, *bulrush*)

Aquatic macrophytes that colonize littoral zones have two characteristics which make them good indicators of water pollution. Firstly, they react slowly and progressively to changes in nutrient conditions,

in contrast to bacteria and microalgae. Macrophytes, therefore, act as integrators of environmental conditions and thus can be used as long-term indicators with high spatial resolution. Secondly, the coastal zone may experience patterns of pollutant concentrations (Dave, 1992; Drake and Heaney, 1987), caused by natural or artificial inflows as well as by non-point sources.

As a measure of absorption capacity of pollutants by macrophytes, lipid contents were determined with mean values of 1.3 in stem and 0.5 in roots and non-significant differences were observed among stations. Table 5 shows OCP, PCB and PBDE concentrations expressed as ng/g dry weight in roots and stems of *S. californicus*, and in near root sediments (NRS) collected along the Río Negro basin.

Bulrush accumulated significant amounts of OCPs, PCBs and PBDEs. The contaminant sequestration may occur across many interfaces, as sediments, water and air. In stems there was no relationship between lipid content and pollutant concentration expressed in ng/g dry weight (Table 5). It can be speculated that other non-lipid cellular components like lignin contribute substantially to chemical partitioning (Trapp et al., 2001). Roots presented higher contaminant levels than stem in UV, indicating closely the distribution pattern of contaminants found in soils. Thus roots from VR showed the highest total levels (62 ng/g dry weight) with 70% being represented by DDTs (*pp'*-DDE). Stems from HN and VR showed higher levels of endosulfan (Kruskal–Wallis  $p = 0.04$ ) as a consequence of its higher water–sediment partition coefficient, being more available to uptake from water.

Bulrush from LI station showed a predominance of PCBs and DDTs, with similar values between them, both in roots and stem (Table 5). This pattern agrees with that found in soil. Conversely to UV sites, bulrush from LJ station showed higher values in stem than roots, with the following pattern: PBDEs > endosulfans > PCBs > DDTs = HCHs. It would be a result of the impact of water and SPM onto stem pollutant levels more than point source from soil erosion, as seen for UV sites. Similar pattern was found for SPM and water in PAT station, where enrichment of PBDE levels in both matrices was observed after the delta zone. The relation among congeners in stems (BDE 47  $\geq$  100 > 99) reveals the use of mainly penta-BDE mixture in the area as was observed for SPM downstream, atmospheric deposition as well as possible debromination process from higher brominated congeners would not be discarded.

Particularly in CR station, endosulfan was the main pesticide group found in roots (11.7 ng/g dry weight), showing a clear accumulation pattern from sediment (BS), where the same pattern was observed.

**Table 5**

Total concentration of OCPs, PCBs and PBDEs, expressed as ng/g dry weight, in roots and stems of *Schoenoplectus californicus*, and near root sediments (NRS) collected along the Río Negro basin. TOC = total organic carbon. END = sum of  $\alpha$ -,  $\beta$  endosulfan and endosulfan sulfate; HCHs: sum of  $\alpha$ -,  $\beta$ ,  $\gamma$ - and  $\delta$ -isomers; DDTs: sum of *pp'*-DDT, *pp'*-DDE and *pp'*-DDD; Other OCPs = Sum of dieldrin, heptachlor, heptachlor epoxide,  $\alpha$ - and  $\gamma$ -chlordanes and transnonachlor; PCBs: sum of IUPAC #s 8, 18, 28, 52, 44, 66, 101, 87, 110, 149, 118, 153, 105, 138, 126, 187, 128, 167, 156, 157, 180, 169, 170, 189, 195, 206, 209; PBDEs: sum of IUPAC #s 28, 49, 47, 66, 100, 99, 154, 153, 183; <LD = below limit of detection.

Sampling site	Sample type	% lipid-TOC	HCHs	END	DDTs	Other OCPs	PCBs	PBDEs
LI	Stem	1.4	1.3 ± 1.2	2.1 ± 1.2	3.2 ± 0.5	1.0 ± 0.6	4.9 ± 2.2	1.2 ± 0.1
	Root	0.6	1.8 ± 1.1	4.4 ± 2.3	7.5 ± 3.2	1.6 ± 1.3	7.7 ± 6.5	2.8 ± 0.2
	NRS	1.7	1.4 ± 0.3	0.3 ± 0.1	1.8 ± 0.6	0.4 ± 0.1	1.7 ± 3.8	0.3 ± 0.1
HN	Stem	1.1	1.6 ± 0.1	4.7 ± 2.1	2.7 ± 1.0	1.0 ± 0.3	3.8 ± 0.4	1.0 ± 0.5
	Root	0.3	3.5 ± 2.9	5.9 ± 3.5	19.6 ± 6.4	1.0 ± 1.3	3.5 ± 4.1	2.6 ± 1.3
	NRS	0.5	0.1 ± 0.1	0.3 ± 0.2	1.2 ± 0.3	<LD	0.4 ± 0.4	0.1 ± 0.1
VR	Stem	1.3	1.8 ± 0.9	7.9 ± 2.5	4.7 ± 0.8	1.3 ± 0.8	3.8 ± 2.1	1.3 ± 0.7
	Root	0.7	2.1 ± 2.6	9.8 ± 10.7	44.5 ± 49.3	1.5 ± 1.4	6.1 ± 5.6	2.2 ± 1.4
	NRS	0.3	0.2 ± 0.1	0.4 ± 0.1	1.3 ± 0.1	0.4 ± 0.1	1.7 ± 0.8	0.1 ± 0.1
LJ	Stem	1.0	2.2 ± 0.6	4.8 ± 1.0	2.8 ± 1.0	1.7 ± 0.3	3.9 ± 1.1	6.8 ± 5.5
	Root	0.4	0.2 ± 0.3	0.5 ± 0.9	0.7 ± 1.3	0.1 ± 0.2	1.0 ± 1.8	0.2 ± 0.1
	NRS	0.8	0.2 ± 0.2	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.4 ± 0.2	0.1 ± 0.1
CR	Stem	1.5	0.8 ± 0.4	2.0 ± 0.1	3.0 ± 2.7	0.8 ± 0.4	1.6 ± 0.3	0.5 ± 0.1
	Root	0.2	4.6 ± 1.7	11.7 ± 0.9	1.5 ± 0.8	2.0 ± 0.6	2.4 ± 1.5	0.9 ± 0.1
	NRS	1.0	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1

Moreover, it agrees with the high enrichment in endosulfans observed in SPM from CR (292.1 ng/g dry weight) regarding PAT (44.5 ng/g dry weight) station, located 30 km upstream.

Bulrush reflected the environmental profile of pollution since they possess a similar distribution pattern of contaminants (OCPs > PCBs > PBDEs) found in the other matrices (sediments, soils and streamwater). Moreover, the role of riparian vegetation as pollutant filter was significantly observed in this study leading to lower pesticide concentrations in macrophyte tissues and SPM in stations located after the delta riparian zone.

#### 4. Conclusions

This work provided the first systemic data on the contamination status of OCPs, PCBs and PBDEs in soils, sediments, SPM, streamwater and macrophytes along the Rio Negro basin, Patagonia Argentina. Due to historical intense pesticide application, the urban and industrial discharges, the presence of dams, atmospheric transport and the persistence of OCPs, PCBs and PBDEs, residues of these compounds are present in Rio Negro basin, although most of them are phased-out compounds in Argentina. The UV was the most contaminated area along the floodplain of the Rio Negro, where the soil can be considered a hot spot of DDTs in the southern region of South America. The *pp'*-DDE, a persistent metabolite of *pp'*-DDT, was dominant in all samples, indicating input of heavily weathered *pp'*-DDT. The occurrence of endosulfans with a relation  $\alpha$ -/ $\beta$ -isomers > 1 in all matrices denotes the current use in the region. The endosulfan levels in streamwater could represent a risk to the environment since it was found at higher values than the maximum established limits for aquatic biota protection. PCBs were confined mainly to close areas related with hydroelectric power plants and dams located in the UV, and also to urban areas. PBDEs were distributed similarly to PCBs as a result of common sources like dumping sites and similar dynamics in the environment. The predominance of BDE-47 in most samples denotes the use of penta-BDE mixture in the region; atmospheric deposition and the metabolism of higher brominated congeners are not discarded. Pollutant level in SPM was 1–10 fold higher than bottom sediments, with a similar distribution pattern of pollutants, showing the high OCP, PCB and PBDE loads transported by streamwater. Macrophytes along the basin reflected efficiently soil pollution, being *S. californicus* a good biomonitor for Rio Negro basin. The delta zone, located in the middle of the basin, rich in macrophytes (rooted and free-floating) trapped OCPs, PCBs and PBDEs acting as a natural filter, reducing pollutant levels in all matrices including SPM downstream. Since pesticide use in UV contributed greatly to pesticide loads in the whole basin, especially for DDTs, outreach efforts are needed to carry out a regional program on soil monitoring and promote better policy-maker control. It should be focused to identify and classify critical points of past contamination and to prevent both soil erosion and pesticide releases.

#### Conflict of Interest

All the authors have no conflicts of interest.

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