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Increasing levels of persistent organic pollutants in rainbow trout (*Oncorhynchus mykiss*) following a mega-flooding episode in the Negro River basin, Argentinean Patagonia

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ABSTRACT

In 2006, a severe flooding episode in the Negro River basin, Argentinean Patagonia, occurred and mainly affected the middle valley where lands are devoted to agriculture and soils known to be polluted with persistent organic pollutants. The aim of this study was to estimate the effects of this event on polybrominated diphenyl ethers (PBDEs), endosulfans (α-, β-, sulfate), DDTs (*p,p*′-DDD, *p,p*′-DDE, *p,p*′-DDT) and polychlorinated biphenyls (PCBs) levels in rainbow trout (*Oncorhynchus mykiss*) tissues. Post-event fish showed higher contaminants levels than pre-event at expenses of all groups. DDTs presented the highest concentrations in all tissues followed by PCBs, endosulfans and PBDEs. The metabolite *p,p*′-DDE represented about 80% of total DDTs, while PCBs were dominated by penta- and hexa-chlorobiphenyls congeners. BDE-47 was the predominant congener among PBDEs. Endosulfan showed the maximum differences between post- and pre-flood fish (up to 43-fold) with a α-/β- ratio >1, suggesting exposure to fresh technical mixture. Contaminant profiles observed in rainbow trout tissues from both periods (pre- and post-event) were consistent with previous results from water, suspended particle matter and soils, showing that this species is a good biomonitor of aquatic pollution of Negro River basin. The presence of the pesticides in the Negro River system resulted from past and current agricultural practices and it was modified and enhanced by the flooding. Additionally, PCBs and PBDEs occurrence in the aquatic environment deserve more attention, and monitoring programs are recommended in order to diminish their incorporation to aquatic ecosystem.

1. Introduction

The transport of contaminated topsoil into aquatic system after a flooding event increases pollutants concentration and bioavailability, and results in a higher exposure to aquatic biota (Ludwig et al., 1993). However, the potential of short-term episodic events to modify pollutant concentrations in aquatic biota is scarcely known (Steward et al., 2003).

Organochlorine pesticides (OCPs), such as the insecticides DDT and endosulfan, polychlorinated biphenyls (PCBs), and penta- and octa-mixtures of polybrominated diphenyl ethers (PBDEs) belong to Persistent Organic Pollutants (POPs) (Stockholm Convention, 2011). They share characteristics such as hydrophobicity, ubiquity, environmental persistence, and endocrine disruption capacity.

Particularly, DDT was extensively applied in Argentina to control insects until its ban in 1998 (Gonzalez et al., 2010). However, it is still used for controlling malaria vectors in many countries (Binelli and Provini, 2003; Mishra and Sharma, 2011). On the other hand, endosulfan represents the last OCP of unrestricted use in Argentina (INTA, 2004), despite it has been recently included (April of 2011) into the POPs list regulated under the Stockholm Convention. Both pesticides are very toxic to aquatic biota, mainly to invertebrates and fish. The PCBs were widely used in electrical transformers, paints, and as pesticide coadjuvants, but their use have been prohibited in Argentina since 2005 (Ondarza et al., 2010). PBDEs are flame retardants used in plastic, textile and electronic materials. A rapid and increasing global dispersion on environmental levels of PBDEs was observed in the last decades (Ikonomou et al., 2011). The use of penta- and octa-PBDEs mixtures has been prohibited in United State since 2005, whereas deca-PBDEs are currently used (BSEF, 2011). The use of PBDEs in Argentina is still unrestricted.

All of these pollutants can reach surface water from diffuse or local sources by means of runoff, atmospheric deposition and leaching (Miglioranza et al., 2004). Once in the aquatic environments, due to their hydrophobicity, these contaminants are adsorbed mainly onto bottom or suspended sediments and, to a minor proportion, remain dissolved in the water column, affecting also non-target organisms

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(Miglioranza et al., 2003a). Fish are frequently used as biomonitors to assess environmental contamination, since they are able to uptake of contaminants via food, gills and, to a lesser extent, skin (Blocksom et al., 2010).

The Negro River is one of the main watercourses in the Argentinean Patagonia which provides water for human consumption and irrigation for the main fruit production area of Argentina. Higher levels of OCPs, particularly DDTs and endosulfan was reported by Gonzalez et al. (2010) and Isla et al. (2010) for soils and sediments from the basin denoting a high potential for aquatic biota contamination. The flow of Negro River is regulated by numerous dams in its headwater, which generate 50% of the electricity consumed in Argentina. Dams lead to changes in the level and dynamic of the river flow. In winter of 2006, a large flooding episode affected the Middle Valley of Negro River basin with economic, social and environmental consequences. Dam discharges were on average 180% higher than previous years (www.aic.gov.ar) and this overflow reached the surrounding soils producing runoff, dragging and washing agricultural soils. Thus, in order to evaluate the effect of such flood on the aquatic contaminant levels, OCPs, PCBs and PBDEs were analyzed in different tissues of rainbow trout collected before (February of 2006) and after (February of 2007) the flood event.

Rainbow trout (*Oncorhynchus mykiss*) (Walbaum, 1792) was selected as the bioindicator species based on its abundance, non-migratory behavior, and omnivorous diet, including insect larvae, decapods *Aegla* sp. and fish (Alvear et al., 2007). Females spawn mainly in the headwater and middle valley of Negro River during the winter, usually from May to July, with clear, cold water (11 °C) and gravel-bottomed sediments. Growth rates are highly variable but rainbow trout usually mature at 330 mm in length and at about 2 years old (Huaquín and Marchant, 2002). This species is highly prized by sport fishermen and consumed by local population. Moreover, its worldwide distribution and use on pollution assessment allows for comparisons with other studies. However, several biological factors such as lipids, sex, reproductive stage, body size, age influence on the bioaccumulation of POPs in organisms (Borga et al., 2004). Thus, with the purpose to reduce this variability, only female in repose stage, with similar length and weight were considered.

2. Materials and methods

2.1. Study area

The Negro River has a drainage basin of about 140,000 km^2 and runs for 720 km across the Northern Patagonian region, with an average flow of approximately 1000 m^3/s (Arribére et al., 2003). Its basin represents the main fruit production area (apple, peach, pears and plums) of Argentina.

2.2. Sampling, preparation and storage

Rainbow trout were collected from middle valley of Negro River (39°16´S 64°14´W) in February of 2006 and 2007 (summer), representing pre- and post-flood conditions, respectively. All fish were caught following standard fishing procedures with multifilament gillnet and transported to the laboratory under frozen conditions (−20 °C). Total length (mm), total weight (g) and sex were recorded for each individual before dissection. Muscle, liver, gonads and stomach content for each fish were wrapped in pre-cleaned aluminum foil and kept frozen (−20 °C). A total of twenty four (24) samples from pre-flood period and sixty (60) samples during post-flood period, were analyzed. All analyses were performed in triplicate. Condition (KI), hepatic (HI) and gonadosomatic (GI) indexes were calculated as follow: $KI = \text{total weight} \times 100/\text{total length}^3$, $HI = \text{liver weight} \times 100/\text{total weight}$ and $GI = \text{gonad weight} \times 100/\text{total weight}$.

Additionally, in order to characterize pollutants distribution in the aquatic environment, subsurface streamwater samples were collected during spring, summer, autumn and winter of 2008, when the river reach its normal flow regimen . Samples (6 L in each season) were taken using pre-cleaned amber glass bottles, transported to the laboratory (4 °C) and filtered (0.45 μm) to obtain suspended particulate matter (SPM). Filters were air dried and kept at −20 °C, until analysis. Both matrixes were analyzed in triplicate.

2.3. Analytical procedures

2.3.1. Standard materials and reagents

Identification and quantification of organochlorine compounds were performed using external standard solutions from Absolute Standards (USA), whereas BDEs-LMS, Bromodiphenyl Ethers-Lake Michigan Study from AccuStandard Inc. (USA) was used for PBDEs. PCB #103 (Ultra Scientific, USA) was used as internal standard. High purity n-hexane and dichloromethane (residue analysis grade) were used as solvents for the analytical procedure. Anhydrous sodium sulfate and silica gel were purchased from Merck Inc. (Germany).

2.3.2. Extraction procedure

2.3.2.1. Water. The extraction and clean up was according to Gonzalez et al. (2011). Thus, 12 samples of 500 mL each one was taken by each season. Then, they were spiked with PCB #103, followed by liquid–liquid extraction using 300 mL of n-hexane:dichlorometane (1:2 v/v), shaken during 2 h. Therefore, a total of 48 samples of water along the year were extracted. The organic layer was concentrated until 2 mL for additional clean-up with silica gel chromatography, previously activated at 200 °C during 24 h. It was eluded with 150 mL of n-hexane:dichlorometane (2:1 v/v). The eluate was concentrated to 1 mL and kept at −20 °C until gas chromatographic analyses.

2.3.2.2. Fish tissues and SPM filters. Analytes were extracted according to Metcalfe and Metcalfe (1997) with modifications of Miglioranza et al. (2003b). Subsamples of muscle (5 g), liver, gonads and stomach content (3 g) were homogenized with anhydrous sodium sulfate, Soxhlet extracted with 110 mL of n-hexane:dichlorometane (1:1 v/v) during 8 h and, then, concentrated until 3 mL. Lipid content was removed by gel permeation chromatography, with Bio-Beads S-X3 (200–400 mesh), and gravimetrically determined. The contaminant fraction was further purified with silica gel chromatography. The eluate was concentrated (1 mL) and kept at −20 °C until gas chromatographic analyses. Filters were Soxhlet extracted during 8 h and purified with silica gel chromatography, as was previously described for fish tissues.

2.4. Gas chromatographic analysis

Endosulfans, DDTs and PCBs were analyzed with a Shimadzu 17-A gas chromatograph equipped with a ^{63}Ni electron capture detector (GC-ECD). A SPB-5 capillary column was used. The temperature conditions were previously described by Miglioranza et al. (2003b). PBDEs were identified and quantified according to the conditions described by Ondarza et al. (2011) using a Perkin Elmer Clarus 500 gas chromatograph equipped with a mass spectrometer (GC/MS) fitted with an ELITE 5MS capillary column. The data acquisition was done in SIFI (Selected Ion and Full Ion Scanning). The mass spectrometer operated in the electron impact mode (EI) at 70 eV and multiplier at 450 eV. Each PBDE (IUPAC #28, 47, 66, 100, 99, 154, 153 and 183) was identified and confirmed by its relative retention time towards PCB #103 and three main fragmentation ions (one for quantification and two of confirmation) considering a ±10% deviation of standard proportion.

2.5. Quality assurance and Quality Control (QA&QC)

Procedural blanks were analyzed throughout the analyses to check for interference and laboratory contamination. Endosulfans, DDTs, PCBs and PBDEs values were below the detection limit. Recoveries of surrogate standard (PCB #103) were consistently greater than 90%. Detection limits, calculated according to Keith et al. (1983), for tissues and filters ranged from 0.32 to 1.3 ng/g for DDTs (*p,p′*-DDE, *p,p′*-DDD and *p,p′*-DDT), endosulfans (α-, β- and sulfate) and PCBs (IUPAC #8, 18, 28, 52, 44, 66, 101, 110, 149, 118, 153, 138, 126, 187, 128, 167, 156, 157, 180, 169, 189, 195, 206, 209), while for PBDEs (IUPAC #28, 49, 47, 66, 100, 99, 154, 153 and 183) ranged from 0.8 to 4.4 ng/g. In the case of water samples the limits ranged from 0.16 to 0.66 ng/L for DDTs, endosulfans and PCBs, while for PBDEs were 0.4-2.2 ng/L.

2.6. Statistic analyses

The results of fish tissues are expressed as the average ± standard deviation, and reported as ng/g lipid wt., while as ng/L and ng/g dry wt. in water and SPM, respectively. Statistics were performed with STATISTICA 8.0 software. Wilcoxon non-parametric test was used to compare the difference between contamination levels on fish collected before and after the flooding event (independent samples), while differences in contaminant levels among tissues were tested using a Friedman ANOVA analysis for multiple dependent samples. Probability values less than 0.05 ($p<0.05$) were considered as statistically significant.

3. Results and discussion

The contaminant concentrations (ng/g wet weight) were related to lipid content and good correlations were found. So, all concentrations were expressed in ng/g lipid weight. Endosulfans, DDTs, PCBs and PBDEs were found in all rainbow trout samples collected in the Negro River basin (Table 2). A predominance of DDE followed by PCBs and PBDEs was found. Fish collected after the flooding episode had significantly increased levels of contaminants ($p<0.05$, Table 2), reaching values that surpassed the maximum permitted limit for human consumption.

Fish size is known to be a strong covariate with organic contaminants, thus the great overlap in fish size at each time (pre- and post-flood), without significant differences in total length, allowed a more accurate comparison between contaminant levels. In pre-flood fish the range was 341–421 mm while 322–385 mm was found in post-fish (Table 1). Condition (KI) and hepatosomatic indexes (HI) provide simple indication of how well fish are coping with the environment and many change in response to environmental stress (Tricklebank et al., 2002). Rainbow trout presented a good physiological condition with relatively high energetic reserves in liver ($\text{KI}>1$, $0.9<\text{IH}<1.3$), as well as ovaries with a scarce maturation ($0.1<\text{IG}<0.3$) in accordance with the post-spawning stage (Table 1).

Table 1
Biological parameters of rainbow trout (*O. mykiss*) females from Negro River basin (average ± standard deviation).

Sampling	n	TL (mm)	TW (g)	KI (%)	HI (%)	GI (%)
Pre-flood	24	381 ± 56.6 (341–421)	626.4 ± 240.3 (456.5–796.3)	1 ± 0.07 (1.0–1.1)	0.8 ± 0.07 (0.8–0.9)	0.1 ± 0.07 (0.1–0.2)
Post-flood	60	369.4 ± 28.7 (322–397)	572.8 ± 118.5 (385.3–692.3)	1.1 ± 0.04 (1.1–1.2)	0.9 ± 0.3 (0.7–1.3)	0.7 ± 0.5 (0.2–1.4)

Data between brackets show rank values. n: number of samples analyzed. TL: total length. TW: total weight. KI: condition index. HI: hepatosomatic index. GI: gonadosomatic index.

3.1. Contaminant distribution in fish from pre-flood sampling

3.1.1. Organochlorine pesticides: endosulfans and DDTs

Endosulfan patterns in pre-flood fish showed significant differences among tissues. Liver exhibited levels two and four times higher than muscle and gonads, respectively ($p<0.05$, Table 2). Technical endosulfan (α-/β-isomers in a 70:30 composition) application occurs from November to March (summer), when higher temperatures and short and heavy rainfalls are common (INTA, 2004). Alpha-endosulfan predominated over β- and the metabolite endosulfan sulfate in all tissues, suggesting an acute exposure to technical mixture which is widely used in the region.

Endosulfan sulfate results from biological oxidation of the parent isomers and constitutes the major breakdown product under aerobic conditions (Leonard et al., 2001). In relatively low levels, this metabolite was found in all tissues.

Endosulfan concentrations in ovaries (0.006 μg/g wet wt.) did not exceed those levels responsible of reproductive damage in fish (10 μg/g wet wt.) (Singh and Singh, 2008). However, Gormley and Teather (2003) found several negative effects over fertilization, growth, behavior and reproductive dysfunction in fish japanese medaka (*Oryzias latipes*), as a result of short-term exposure to sublethal concentrations of endosulfan (0.01 and 0.1 μg/L), close to those values found in streamwater samples from the present study (0.004 μg/L). Levels in muscle were lower than the acceptable daily intake for human consumption according with Food and Agriculture Organization (0.006 mg/k) (FDA/EPA, 2001). In stomach content, there was not significance differences in endosulfan concentrations regard to muscle suggesting a low biomagnification process. Similarly, Kelly et al. (2004) showed that non-volatile and less hydrophobic chemicals, such as endosulfan, would not be able to biomagnify in fish due to their low K_{ow}.

DDTs represented the main pesticide group found in all tissues, constituting more than 80%, 48% and 33% of total contaminants in muscle, liver and gonads, respectively. Levels ranged between 186 ng/g lipid wt. (gonad) and 988 ng/g lipid wt. (muscle) ($p<0.05$, Table 2), whereas liver and stomach content showed DDTs levels close to 400 and 500 ng/g lipid wt., respectively (Table 2). Conversely to endosulfans, muscle showed higher (two fold) DDTs levels than liver, suggesting a chronic exposure to these insecticides, which agree with their ban over more than 12 years ago (Gonzalez et al., 2010) and previous results found in soils in the study area (Miglioranza et al., 2008, 2009a). Moreover, DDTs concentrations in muscle (28.1 ± 0.1 ng/g wet wt.) were above the guideline of 14.4 ng/g wet wt. set by US Environmental Protection Agency (US-EPA, 2000), indicating that its consumption might pose a risk to human health. A clear biomagnification process for these pesticides was observed, with a factor equal to 1.85 ($p<0.05$, Table 2).

The relative distribution of DDT and its metabolites have been used to identify their possible sources as well as their fate in the aquatic environment (Lee et al., 2001). In this study, the DDE + DDD/DDT ratios ranged from 17.6 in gonads to 33.9 in muscle, with significant differences on DDE levels in all tissues ($p<0.05$, Table 2). The observed predominance of DDE over parent compound, suggest a historic source of DDT in the surrounding soils that contribute to the load in the Negro River basin (Gonzalez et al., 2010).

3.1.1.1. PCBs and PBDEs. Significant high levels of PCBs were found in liver and ovaries ($p<0.05$, Table 2). Muscle presented the lowest PCBs levels, however these levels were higher than those recommended by the Italian Government (100 ng/g lipid wt.) for human consumption for fish (Storelli et al., 2003), suggesting a potential risk to human health. PCBs levels were much higher (15-folder) than those reported for brown trout (*Salmo trutta*) from a nearby watershed (Ondarza et al., 2011). These levels were also higher than those found in other matrixes such as soils and sediments from

Table 2
Average values (± standard deviation) of contaminants (ng/g lipid wt.) and lipid content in tissues of rainbow trout (*O. mykiss*) from Northern Patagonia Argentina, sampled in February 2006 (pre-inundation) and February 2007 (post-inundation).

	Muscle		Liver		Gonad		Stomach content	
	Pre-	Post-	Pre-	Post-	Pre-	Post-	Pre-	Post-
% lipids content %	3.2 ± 0.7	1.3 ± 0.5	3.3 ± 0.4	1.7 ± 1.1	23.8 ± 13.4	0.9 ± 0.6	6.9 ± 2.8	1.1 ± 0.6
α-endosulfan	14.9 ± 9.5	127.7 ± 32.8	54.7 ± 40.3	1367.8 ± 1121.3	25.2 ± 6.6	542.3 ± 161.2	16.5 ± 5.2	916.7 ± 470.5
β-endosulfan	6.3 ± 3.7	61.6 ± 39.9	31.1 ± 23.1	354.9 ± 302.0	15.7 ± 5.2	237.5 ± 106.8	9.8 ± 5.5	346.5 ± 2.3
Eendosulfan sulfate	2.6 ± 1.6	21.2 ± 7.6	7.7 ± 5.7	32.5 ± 7.2	1.2 ± 1.3	66.9 ± 14.9	3.3 ± 0.5	<dl
Σ endosulfan	23.8 ± 4.1	210.6 ± 16.9	93.6 ± 17.3	1755.2 ± 577.3	42.1 ± 2.7	846.6 ± 73.9	29.6 ± 2.8	1263.2 ± 270.9
Pp,p´-DDE	923.3 ± 165.6	2370.6 ± 781.4	381.0 ± 165.9	1388.5 ± 708.5	172.9 ± 61.9	2199.1 ± 1322.9	500.0 ± 89.0	3652.0 ± 1461.2
Pp,p´-DDD	36.4 ± 7.4	37.8 ± 27.4	6.0 ± 2.6	27.1 ± 13.4	3.1 ± 1.0	52.5 ± 22.2	11.8 ± 3.9	<dl
Pp,p´-DDT	28.3 ± 13.4	196.9 ± 79.3	16.4 ± 7.0	272.5 ± 101.6	10.0 ± 6.2	533.5 ± 278.6	22.0 ± 7.8	490.1 ± 199.4
Σ DDTs	973.1 ± 86.0	2570.7 ± 425.9	403.4 ± 93.1	1688.0 ± 378.3	186.0 ± 33.7	2785.2 ± 688.9	533.8 ± 48.1	4508.6 ± 792.4
#52	<dl	<dl	5.2[a]	7.7[a]	<dl	<dl	<dl	<dl
#44	4.4 ± 3.6	24.4 ± 11.6	11.2 ± 8.1	17.2[a]	8.3 ± 2.8	37 ± 9.8	4.3 ± 2.0	<dl
#66	13.3 ± 9.8	54.4 ± 10.6	10.0 ± 7.4	51.5[a]	10.5 ± 2.6	41.3 ± 28.3	6.3 ± 1.8	<dl
#101	13.4 ± 9.7	25.9 ± 13.1	10.1 ± 3.4	197.5 ± 31.9	11.4 ± 2.5	90 ± 26.0	11.5 ± 2.6	138.7[a]
#110	23.0 ± 11.1	130.1 ± 30.4	53.5 ± 25.9	195.7 ± 137.8	35.2 ± 11.7	123.9 ± 43.4	25.4 ± 5.5	331.9 ± 93.2
#149	10.0 ± 7.3	101.2 ± 37.4	24.6 ± 20.6	59.8 ± 69.3	15.9 ± 3.0	205.3 ± 104.1	15.3 ± 4.4	518.4 ± 100.9
#118	27.2 ± 21.6	139.6 ± 45.6	28.4 ± 11.4	183.6 ± 175.9	26.7 ± 5.2	332.2 ± 157.2	28.8 ± 10.2	627.1 ± 111.5
#153	38.1 ± 30.1	222.0 ± 94.4	59.0 ± 28.8	232.8 ± 95.7	57.6 ± 17.2	382.0 ± 240.9	57.2 ± 19.5	491.3 ± 77.6
#138	38.3 ± 27.2	177.4 ± 63.9	47.5 ± 30.6	234.9 ± 148.7	47.0 ± 16.4	334.9 ± 160.0	43.9 ± 15.4	514.8 ± 182.8
Σ PCBs	167.6 ± 9.9	876.0 ± 29.9	249.4 ± 10.7	1180.7 ± 94.9	212.4 ± 6.4	1546.5 ± 83.3	192.6 ± 6.7	2622.2 ± 40.8
#47	45.5 ± 9.1	62.6 ± 27.1	51.2 ± 1 0.9	262.3 ± 193.5	88.0 ± 39.2	158.4 ± 156.6	57.1 ± 24.6	153.3 ± 119.1
#100	6.8 ± 1.4	16.0 ± 6.4	16.4 ± 9.4	20.3 ± 9.8	18.4 ± 6.0	22.8 ± 5.8	20.5 ± 16.0	<dl
#99	6.0 ± 1.3	14.4 ± 5.9	24.4 ± 8.9	24.3 ± 11.3	25.0 ± 8.4	27.6 ± 11.2	19.3 ± 15.6	31.0[a]
Σ PBDEs	58.3 ± 4.5	93.1 ± 12.1	92.0 ± 1.1	306.9 ± 105.6	131.5 ± 18.5	208.8 ± 85.5	96.9 ± 5.1	184.3 ± 39.7

pre-: pre-inundation. post-: post-inundation. Σ endosulfans = Σ (α-, β-, endosulfan sulfate); Σ DDTs = Σ (*p,p´*-DDE, *p,p´*-DDD, *p,p´*-DDT); Σ PCBs = Σ (#52, 44, 66, 101, 110, 149, 118, 153, 138). Σ PBDEs = Σ (#47, 99, 100). <dl: below the detection limit.

[a] Since only one data was available no standard error could be calculated.

Negro River (Miglioranza et al., 2008, 2009a; Isla et al., 2010). The settlement of numerous dams together with an important industrial development and dumping sites in Negro River headwaters could represent the potential source of PCBs. The congener patterns in all tissues were dominated by hexa- and penta-chlorobiphenyls. The highly persistent PCB-153 and PCB-138 accounted for more than 43% of ΣPCBs, while PCB-110 and PCB-118 reached 30% of $\sum$PCBs ($p<0.05$, Table 2). The results suggest that the majority of PCBs in rainbow trout tissues could have stemmed from historical usage of Arochlor 1254 and 1260 in Argentina. These mixtures have an enrichment composition in congeners with five and six chlorines as was reported by Schulz et al. (1989). The same pattern was reported for several fish species of Argentina, such as common carp (*Common carp*), striped weakfish (*Cynoscion guatucupa*) and brown trout (*Salmo trutta*) (Lanfranchi et al., 2006; Ondarza et al., 2010, 2011). In addition, PCB pattern would suggest a slightly metabolic degradation from the heavily chlorinated congeners in rainbow trout, and it could be due to a steric effects resulting from the *p,p´*-substitution, such as in PCB-138 (Kammann et al., 1993).

The present study represents the first record of PBDE contamination in rainbow trout from Negro River basin. Levels ranged from 58.3 ng/g lipid wt. to 131.4 ng/g lipid wt. in ovaries ($p<0.05$), whereas liver had 92 ng/g lipid wt. (Table 2). Similarly to endosulfan and PCBs, muscle showed the lowest PBDEs concentrations ($p<0.05$, Table 1). These values were several times higher in muscles of common carp (*Cyprinus carpio*) from the Danube Delta (14.3 ng/g lipid wt.) (Covaci et al., 2006) and lower than brown trout (*Salmo trutta*) from a nearby watershed (80.7 ng/g lipid wt.) or brown trout from Mjøsa Lake, Norway (21–1215 ng/g lipid wt.) (Ondarza et al., 2011; Mariussen et al., 2008). Total PBDEs in stomach content (96.9 ng/g lipid wt.) indicate that diet is the main accumulation source, as previously reported for this species and common carp (Stapleton et al., 2006).

The most frequently reported brominated congeners in fish are BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154 (Ikonomou et al., 2011). In the present study, the congener BDE-47 showed the highest values ($p<0.05$) followed by BDE-99 and BDE-100 (Table 1). Fish have a widely variable capacity to assimilate and metabolize PBDEs via debromination processes, both in terms of efficiency and metabolite profiles and it is dependent on the species as well as the congener itself (Munschy et al., 2011). These results suggest that local sources, such as final disposal sites and waste incinerators, and also atmosphere deposition would lead to the occurrence of PCBs and PBDEs in the Negro River.

3.2. Contaminants distribution in fish from post-flood sampling

3.2.1. Organochlorine pesticides: endosulfans and DDTs

All contaminants in post-flood fish tissues were markedly increased. A similar situation was documented by Steward et al. (2003) for chlorinated residues in the Red River (USA and Canada).

Endosulfans levels presented the highest differences between post- and pre-flood samples, mainly on ovaries and liver, being two orders of magnitude higher ($p<0.05$, Table 2). However, concentrations in ovaries were one order of magnitude lower than those levels responsible of reproductive damage in fish (10 μg/g wet wt.) (Singh and Singh, 2008). Muscle levels were nine times over those found in pre-flood condition ($p<0.05$). The main difference was found in stomach content being 43-fold higher ($p<0.05$). However, there were not differences in the distribution pattern of isomers and metabolite with respect to pre-flood samples: α- > β- >>> endosulfan sulfate. Total endosulfans increase in post-flood fish was mainly due to an enhanced enrichment in α- and β-isomers.

These results could be a consequence of an enhanced runoff of endosulfan from agricultural soils, facilitated by its relative low soil adsorption and relatively high hydrophilicity (log $K_{ow}<4$) (Sabljic, 2001). Similarly, Jergentz et al. (2005) showed that storm events produced edge-of-field runoff of technical endosulfan applied in soybean fields from Pampa region in Argentina. Moreover, Gonzalez et al. (2010) reported the occurrence of both isomers in surface water at risk levels for aquatic biota showing the availability of these compounds after runoff. Other researches about fish kills related to endosulfan occurrence by runoff from agricultural areas or directly discharged into aquatic environments have been reported (Naqvi and Vaishnavi, 1993; Ondarza et al., 2011). The higher loads of total endosulfans in post-flood fish indicate a higher contaminant exposure may be as an additive effect of current use of technical mixture and flood impact onto nearby soils and subsequently runoff.

As was observed for endosulfans, post-flood fish had higher values of DDTs than pre-flood ($p<0.05$, Table 2), showing ovaries the highest difference followed by liver and muscle. In stomach content, DDTs rises up to 4500 ng/g lipid wt., which increase 8-fold than pre-flood ($p<0.05$, Table 1). The pattern *p,p*´-DDE >> *p,p*´-DDT was also found ($p<0.05$, Table 2). Background DDTs contamination in the Negro River was reported in soils, sediments, macrophytes and pine needles denoting a hot-spot of DDTs in soils, mainly *p,p*´-DDE (1,330 ng/g dry wt.) collected upstream from the sampling site of this study. These levels would be a result of the intensive use of this insecticide during long time on agricultural practices (Miglioranza et al., 2003a, 2003b, 2008, 2009a, 2009b; Isla et al., 2010; Gonzalez et al., 2010). Nevertheless, Qui et al. (2005) suggested that DDT impurities from the Dicofol manufacturing process could be considered as a new source of DDT for the environment. Thus, this common acaricide is used in the Negro River basin, and it could represent a fresh DDT source for the environment. Furthermore, enhanced DDTs solubilization by dissolved organic carbon, and surfactants in water solution was reported for patagonian soils (Gonzalez et al., 2010). Therefore, the occurrence of surfactants in river waters due to urban discharges in addition to increased organic matter content may lead to an enhanced availability of DDTs from soil during flooding event. Despite the regulatory controls of DDTs sales and uses in Argentina, concentrations in the environment are still high and may represent a potential environmental risk.

3.2.1.1. PCBs and PBDEs. PCBs levels in post-flood fish were significantly higher than pre-flood samples ($p<0.05$, Table 1). Stomach content showed the highest difference, being 13-fold higher than pre-flood ($p<0.05$, Table 2). Particularly, post-flood tissues were characterized by a considerably large contribution of higher chlorinated PCB congeners ($p<0.05$, Table 2). The sum of penta- and hexa- congeners accounted a fairly constant 95% of total PCBs, including IUPAC #110, 118, 153 and 138, with a relatively similar composition among samples denoting possibly similar sources (Table 2). Previous studies (Zhou et al., 2001) suggested that a heavy-PCB-dominated pattern is an indicator of near source emission of PCBs, while a light-PCB-dominated pattern reflects a more weathered source. In this study, the PCB pattern distribution suggests that local contamination sources would mainly contribute to this finding.

Compared to available literature, the maximum level for PCBs was set at 2 μg/g by FDA/EPA (FDA/EPA, 2001) and a maximum limit of 100 ng/g lipid wt., was stated by the Italian Government for food of animal origins (Storelli et al., 2003). Our results are below FDA/EPA limits but higher than the limit set by the Italian Government.

Levels of PBDEs measured in muscle, ovaries and stomach content of post-flood fish were two times higher than those found in pre-flood collected tissues, while post-flood liver samples were three times higher than pre-flood collected samples ($p<0.05$, Table 2). The highest PBDEs levels were found in ovaries and liver, ($p<0.05$, Table 2), as was observed for endosulfans and PCBs. In addition, BDE-47 was the most abundant congener in all samples ($p<0.05$, Table 2), showing a mean percentage of 71% to the total concentration.

3.3. Contaminants distribution in streamwater and suspended particulate matter (SPM)

The question raises how accurately the observed concentrations in post-flood fish from the Negro River basin, reflect the influence of the flood over those contaminants. Briefly, we present the seasonal distribution of contaminants studied in streamwater and SPM (Table 3), in order to identify changes in potential sources of exposure that may have mediated the increases of pollutant levels in fish.

Contaminant levels in streamwater showed a small seasonal variability, with endosulfans > PCBs > DDTs > PBDEs as the general distribution pattern in each sampling period. The increase during post-pesticide application period may be due to heavy rainfalls which washed out uncovered soil. Similar results were reported in

Table 3
Contaminants levels (average ± standard deviation) in streamwater (ng/L) and suspended particulate matter (ng/g dry weight) in Negro River basin.

	Water streamwater				SPM (suspended particle matter)			
	Summer	Autumn	Winter[a]	Spring	Summer	Autumn	Winter	Spring
α-endosulfan	1.8 ± 0.9	1.1 ± 0.6	1.9[a]	1.5 ± 0.01	435.0 ± 69.2	883.9 ± 328.2	111.8 ± 28.0	622.2 ± 147.5
β-endosulfan	0.4 ± 0.05	1.1 ± 0.7	1.1[a]	1.3 ± 0.5	111.3 ± 16.6	310.3 ± 148.9	57.2 ± 8.4	535.4 ± 74.8
Endosulfan endosulfan sulfate	0.4 ± 0.1	0.5 ± 0.1	1.0[a]	0.7 ± 0.1	37.7 ± 4.6	84.0 ± 33.8	5.2 ± 0.1	12.7 ± 11.6
Σ endosulfan	2.6 ± 0.9	2.7 ± 0.3	4.0[a]	3.6 ± 0.6	577.2 ± 87.9	1224.2 ± 434.5	174.1 ± 36.3	1253.3 ± 250.2
pp pp´-DDE	0.2 ± 0.1	0.9 ± 0.6	1.0[a]	1.4 ± 1.5	82.0 ± 10.0	1008.4 ± 804.1	5.1 ± 2.9	16.2 ± 2.9
pp pp´-DDD	<dl	0.1 [a]	0.7[a]	<dl	<dl	76.4 ± 40.4	5.1 ± 0.3	19.1 ± 5.7
pp pp´-DDT	0.3 ± 0.1	0.7 ± 0.3	0.5[a]	0.5 ± 0.2	66.8 ± 5.2	172.4 ± 42.8	2.4 ± 1.0	2.2 ± 0.1
Σ DDTs	0.5 ± 0.1	1.6 ± 0.7	2.2[a]	1.9 ± 1.3	169.8 ± 40.6	1257.2 ± 887.3	5.5 ± 1.9	39.6 ± 11.7
#52	0.1 ± 0.03	0.4 ± 0.1	1.2[a]	0.8 ± 0.1	20.7 ± 10.3	141.4 ± 84.0	5.8 ± 0.2	2.8 ± 1.2
#44	0.2 ± 0.05	0.7 ± 0.5	1.4[a]	0.9 ± 0.1	42.5 ± 3.8	178.7 ± 116.2	7.2 ± 2.5	10.8 ± 8.6
#66	<dl	<dl	<dl	<dl	<dl	<dl	4.3 ± 6.1	<dl
#101	<dl	<dl	<dl	<dl	47.0 ± 4.8	<dl	3.5 ± 2.1	3.5 ± 1.5
#110	0.4 ± 0.2	1.1 ± 0.8	0.6[a]	0.5 ± 0.01	135.1 ± 15.1	201.5 ± 23.6	6.6 ± 4.4	4.5 ± 1.2
#149	0.1 ± 0.02	0.4 ± 0.3	0.6[a]	0.2 ± 0.03	72.2 ± 4.9	172.6 ± 29.5	2.7 ± 0.7	6.7 ± 3.6
#118	0.1 ± 0.02	0.2 ± 0.1	0.6[a]	0.2 ± 0.05	57.4 ± 7.4	85.1 ± 33.8	2.9 ± 1.4	5.6 ± 3.5
#153	0.2 ± 0.0003	0.5 ± 0.3	0.8[a]	0.3 ± 0.03	99.4 ± 0.7	163.4 ± 82.0	2.4 ± 0.7	15.8 ± 4.7
#138	0.3 ± 0.02	0.6 ± 0.6	0.7[a]	0.4 ± 0.02	60.7 ± 12.7	73.7 ± 16.7	2.5 ± 0.5	6.1 ± 2.2
Σ PCBs	1.5 ± 0.06	3.9 ± 0.2	5.9[a]	3.2 ± 0.06	535.0 ± 4.9	1016.6 ± 38.4	37.8 ± 2.0	55.8 ± 2.5
#47	0.1 ± 0.02	0.1 ± 0.04	0.6[a]	0.1 ± 0.03	23.7 ± 0.1	19.4 ± 5.6	1.1 ± 0.5	3.3 ± 0.5
#100	0.1 ± 0.04	0.1 ± 0.1	0.06[a]	0.1 ± 0.03	9.4 ± 5.1	23.2 ± 7.8	0.8 ± 0.1	4.8 ± 1.9
#99	<dl	0.2 ± 0.03	0.1[a]	<dl	<dl	<dl	<dl	<dl
Σ PBDEs	0.2 ± 0.01	0.4 ± 0.04	0.4[a]	0.2 ± 0.01	33.1 ± 3.6	42.6 ± 1.5	1.9 ± 0.2	8.2 ± 0.9

Σ endosulfans = Σ (α-, β-, endosulfan sulfate); Σ DDTs = Σ (*p,p*´-DDE, *p,p*´-DDD, *p,p*´-DDT); Σ PCBs = Σ (#52, 44, 66, 101, 110, 149, 118, 153, 138). Σ PBDEs = Σ (#47, 99, 100). <dl: below the detection limit.

[a] Since only one data was available no standard error could be calculated.

streamwater by Gonzalez et al. (2011) from a soybean culture basin in Argentina.

Total endosulfans levels (3.2 ng/L), were below the limit for freshwater biota protection established by the National Argentinean Water Council (7 ng/L of α- more β-isomer, (www.hidricosargentina.gov.ar/base_niveles_guia.xls), but slightly above international guidelines (3 ng/L) (CCME, 2010). The distribution pattern α->β->endosulfan sulfate is according to the current use of this insecticide. The other pollutant groups such as DDTs, PCBs and PBDEs showed similar distribution pattern that those found in fish being the main compounds, DDE, PCB-153 and BDE-47. Pollutants levels adsorbed on SPM presented seasonal variability, as a consequence of pesticide application period, major rainfall events and dam management, being this last activity mainly affected for thaw events. Thus, two different temporal patterns of pollutants were distinguished. Particularly, endosulfans with the highest values showed two peaks along the year, one in autumn corresponding post-pesticide application period followed by a temporary decrease and a second rise during spring, which could be related to the beginning of application period and thaw.

4. Conclusions

Contaminants levels in rainbow trout showed an increase in post-flood samples suggesting that flood event enhance pollutants runoff from surrounding soils, in addition to contaminant load from upstream urban and industrial areas, with the consequent impact onto aquatic environment. DDTs and PCBs constituted the main compounds in both pre- and post-flood fish, as a result of a chronic exposure and intensive agricultural use of these pollutants in the past, revealing the importance of these soils and surrounding areas as sources of these forbidden compounds. The concentrations in muscle were above the maximum permitted levels for human consumption. The significant increase of PBDEs, DDTs, and PCBs in post-flood fish should be mainly attributed to the entry of particle matter from the runoff. Endosulfans showed the highest increase between both periods, denoting the current use of this insecticide in the area. Thus, the presence of these pesticides in the Negro River system resulted from past and current agricultural practices and it was modified and enhanced by the flooding. As a whole, the flooding event resulted in an enhanced availability of endosulfan, currently used, facilitated by its relative hydrophilicity. This fact was reflected in organs of post-flooding fish with a particular distribution pattern in relation to other POPs. Therefore, these results suggest that the possibility of flooding events should be considered in monitoring program planning, particularly in rivers where flow is mainly managed by dams, like the Negro River of Argentinean Patagonia. The use of natural barriers is recommended in this kind of areas, where soils mainly represent sources of persistent organic contaminants and, by runoff they can reach the aquatic ecosystem. Research is ongoing to more clearly define the potential adverse effects associated with acute and chronic exposure of organisms to complex mixtures of these environmental contaminants.

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