

PAPER

## Organic pollutant levels in an agricultural watershed: the importance of analyzing multiple matrices for assessing streamwater pollution

Cite this: *Environ. Sci.: Processes Impacts*, 2013, **15**, 739

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This study is aimed at analyzing the occurrence and transport of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the Quequén Grande river basin, as representative of a catchment under diffuse pollution sources. Pollutant levels in soils, river bottom sediments (RBS), streamwater (Sw), suspended particle materials (SPMs), macrophytes and muscle of silverside were determined by GC-ECD. Soil  $K_d$  values for the current-used insecticides, endosulfans and cypermethrin, were established. Total levels ( $\text{ng g}^{-1}$  dry weight) in soil ranged between 0.07–0.9 for OCPs, 0.03–0.37 for PCBs and 0.01–0.05 for PBDEs. Endosulfan insecticide ( $\alpha$ - +  $\beta$ - + sulfate metabolite) represented up to 72.5% of OCPs. The low soil retention for  $\alpha$ -endosulfan ( $K_d$ : 77) and endosulfan sulfate ( $K_d$ : 100) allows their transport to Sw, SPM and RBS. Levels of endosulfan in Sw in some cases exceeded the value postulated by international guidelines for aquatic biota protection ( $3 \text{ ng L}^{-1}$ ). PCB and PBDE pollution was related to harbour, dumping sites and pile tire burning. Tri and hexa PCB congeners predominated in all matrices and exceeded the quality guideline value of  $0.04 \text{ ng L}^{-1}$  in Sw. Considering levels in silverside muscle, none of the oral reference doses were exceeded, however, PCBs accounted for 18.6% of the total daily allowed ingest for a 70 kg individual. Although the levels of PCBs and OCPs in soil and RBS were low and did not go beyond quality guidelines, these compounds could still represent a risk to aquatic biota and human beings, and thus actions towards preventing this situation should be undertaken.

Received 3rd November 2012

Accepted 8th January 2013

DOI: 10.1039/c3em30882k

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### Environmental impact

Persistent organic pollutants such as OCPs, PCBs and PBDEs are compounds of environmental concern due to their recalcitrant properties and toxicological effects. Analysis of OCPs, PCBs, and PBDEs in six matrices at a watershed scale reveals that although soil and sediments were less polluted, unsafe levels of PCBs and endosulfans were observed in streamwater. Results warn about the risk to aquatic biota and human beings by diffuse PCB pollution and the relevance of streamwater residue analysis. The study of PCB and PBDE pollution in non-industrialized areas should be considered when assessing streamwater quality at a catchment scale. Water, soil and sediment quality guidelines for PBDEs are necessary for the accurate assessment of environmental and human risk.

### Introduction

Inland aquatic environments like rivers and lakes as well as the marine environment are final receptors of land based source

contaminant loads. Water quality standards are designed to set limits on pollution in order to protect goods and services such as aquatic life, swimming and fishing. Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) represent contaminants of concern. Due to their physicochemical characteristics they are highly toxic and widely distributed in environmental compartments. Most countries phase out their use and production and most of these compounds are included in the list of persistent organic pollutants (POPs) regulated by the Stockholm Convention.<sup>1</sup> However, their residues could still constitute a hazard years after their last application or delivery into the environment.

In Argentina, OCP use has been dependent on the productive system, which varies across geographical areas. The Pampean plain is a large flat area occupying about

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1 500 000 km<sup>2</sup> in the East of Argentina. Waterbodies of this region are characterized by shallow lakes and rivers with watersheds draining extensive areas. Inland regions are depicted by small villages and mainly subject to agricultural production, while developed and more industrialized cities are often settled in the coastal environment. About 80% of the total cultivable land of the country is concentrated in the Pampean region, therefore OCPs have been intensively used there. Transgenic soybean culture was introduced in the region in 1997, with increasing harvested areas.<sup>2</sup> Nowadays, the prevalence of the extensive soybean–wheat–sunflower productions is characterized by the use of the pyrethroid  $\alpha$ -cypermethrin and the last OCPs in use, technical endosulfan. Severe soil damage due to water erosion during heavy rainfalls, which are more frequent during the main pesticide application period, November–March,<sup>3</sup> leads to an increasing risk of streamwater pollution. Technical endosulfan levels in streamwater above the maximum allowed for aquatic biota protection were reported in the Quequén Grande River, Southern Pampa.<sup>4</sup> Thus, it is necessary to assess soil–pesticide interactions (adsorption–desorption) mainly for current-used pesticides.

Although PCB pollution is often linked to industrial or urban activities like dumping sites or harbour settlements,<sup>5</sup> significant residues of PCBs were found in sediments and biota of small ponds and streams from the southeastern region of Argentina as a result of diffuse pollution.<sup>6,7</sup> The similarity of the flame retardants PBDE and PCB structures warns about a similar environmental behavior. PBDEs are not chemically bound to the product so they can be released into the environment during the use, production and disposal of PBDE-containing products.<sup>8</sup> Penta- and octa-BDE mixtures are included in the POPs list.<sup>1</sup> Despite scarce data about PBDE levels in Argentina, few recent works reported the occurrence and accumulation of BDE 47 and 99 in fish.<sup>9</sup> Moreover, open landfill dumping areas, where illegal burning of waste occurs, were recognized as a local source of BDEs to the atmosphere in the Pampean region<sup>10</sup> but no information about soil levels is available.

In order to protect water resources, data about the fate, distribution and current state of OCPs, PCBs and PBDEs are required to accurately assess actions toward their control, monitoring or elimination on a catchment scale. This work evaluates the occurrence and distribution of OCPs, PCBs and PBDEs in the Quequén Grande River (QGR) watershed to assess water pollution in a representative agricultural watershed of the Pampean region of Argentina. Transference from the terrestrial to the aquatic environment and further transport were established by studying contaminant levels in soils, streamwater, river bottom sediments, suspended particle materials and macrophytes (*Ludwigia peploides*) from the QGR watershed, while human risk from resource consumption was assessed by studying residues in the muscle of silverside (*Odonthestes bonaerensis*). In addition, studies about adsorption onto soil of the current-used pesticides endosulfans and  $\alpha$ -cypermethrin were conducted to assess their potential transport to the aquatic environment.

## Materials and methods

### Regional setting

The watershed of the QGR, located in the south of Buenos Aires province of Argentina, has a total area of 9990 km<sup>2</sup>. It drains into the Atlantic Ocean in an estuary where the Necochea-Quequén harbour is located (Fig. 1). The average flow rate of the QGR is in the order of 12 m<sup>3</sup> s<sup>-1</sup>, reaching peak values up to 300 m<sup>3</sup> s<sup>-1</sup>. Recharge in the catchment is due to precipitation infiltration, which is in the order of 150 mm per year.<sup>11</sup> Discharge is mainly towards streams, but a considerable proportion probably discharges directly into the sea. Streams are mainly gaining rivers all along the catchment.<sup>12</sup> The average annual temperature is 14 °C.

Soils are an association of typical Argiudols and Udifluent with textures that range from sandy loam to clay loam and relatively high content of organic matter, which makes them suitable for crops. Land use is characterized by agricultural activities in the middle region and livestock production in the northern area. Urban and industrial activities are concentrated on the mouth of the estuary, while streamwater is mainly used for recreational activities.

### Sampling of agricultural soils, river bottom sediments, streamwater and biota

Samples were collected from different sites that were grouped according to their location at the middle (La Dulce: Ld, Center: Ce and Loberia: Lo, Puente Blanco: Pu), lower (Lower Quequén: Lq) and estuary (Harbour: H) zones of the watershed (Fig. 1).

Soil profiles were obtained from a soybean field at three points from the Ld (Ld<sub>1</sub>, Ld<sub>3</sub> and Ld<sub>4</sub>) site during a post-pesticide application period (July 2007) using steel core samplers of 10 cm diameter and 40 cm length. Three equidistant cores were taken at each point, transported to the laboratory, opened to characterize the profile and subsampled into 0–4, 4–10, 10–20 and 20–30 cm from top to bottom. Subsamples were placed in aluminum boxes covered with aluminum foil (in order to avoid

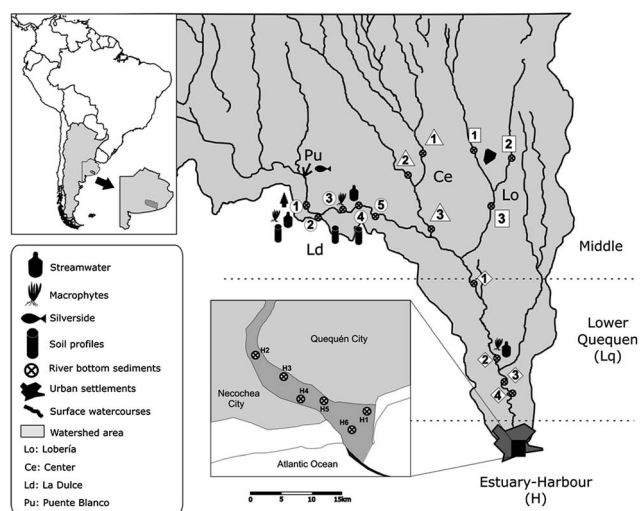


Fig. 1 Study area and sampling points.

contamination) and kept at room temperature until they reached constant weight. Air dried samples were wrapped in aluminum foil and kept at  $-20\text{ }^{\circ}\text{C}$  until analysis.

River bottom sediment (RBS) samples were taken at 24 points from all the sites (Ld, Ce, Lo, Lq, and H<sub>2</sub>, Fig. 1). Samples from middle and lower zones consisted of the upper 0–5 cm of bottom sediments collected with steel core samplers of 4 cm diameter and 10 cm length from the riverbank. Sediment samples from H were collected by dredge from 6 different points and corresponded to a mixture of up to 30 cm depth of bottom sediments. Sampling was performed concomitantly with soil sampling. Samples were air dried as described for soils, and subsamples were wrapped in aluminum foil and kept at  $-20\text{ }^{\circ}\text{C}$  until analysis. A total of 9 cores or 3 dredges were obtained at each site. The core samples were grouped in order to get three samples per site. The values reported here are the mean of three independent analyses of a composite of 3 cores or 3 individual dredges.

Streamwater (Sw) was directly collected in 1 L hexane pre-cleaned glass bottles with Teflon lined caps from Ld<sub>1</sub>, Ld<sub>4</sub>, and Lq<sub>2</sub> points from a 15 cm depth during January (pesticide application period, 2008) and July (post-pesticide application period, 2007–2009), and from Pu during January 2008 and July 2009. A total of 6 L per point and period was taken and kept at  $4\text{ }^{\circ}\text{C}$  and processed within the 4 days after collection. From each Sw sample, suspended particle materials (SPMs) were obtained by passing the water sample through a  $0.45\text{ }\mu\text{m}$  cellulose nitrate membrane filter (Sartorius Stedium Biotech) under vacuum. SPMs were air dried at room temperature until they reached a constant weight and kept wrapped in aluminum foil at  $-20\text{ }^{\circ}\text{C}$  until analysis.

Samples of *Ludwigia peploides* were collected from Ld<sub>1</sub>, Ld<sub>4</sub> and Lq<sub>2</sub> sites during summer (January 2008). Plants were divided into roots and aerial parts (stems and leaves) and kept wrapped in aluminum foil at  $-20\text{ }^{\circ}\text{C}$  until analysis.

Adults (8) of silverside (*Odontheistes bonaerensis*) were caught from Pu during post-application period. Fish were obtained from local fishermen and were frozen immediately. Sex and maturation stage were macroscopically determined resulting in 4 adult males and 4 adult females in the maturation stage. Total weight (male  $160.3 \pm 27.3\text{ g}$ ; female  $169.5 \pm 19.2\text{ g}$ ) and length (male  $27.2 \pm 1.5\text{ cm}$ ; female  $27.5 \pm 1.5\text{ cm}$ ) were determined before dissection and muscle was wrapped in aluminum foil and kept at  $-20\text{ }^{\circ}\text{C}$  until analysis.

### Adsorption isotherms and kinetic assays for current-used pesticides

Adsorption of  $\alpha$ -endosulfan, its main metabolite (endosulfan sulfate<sup>13</sup>) and  $\alpha$ -cypermethrin in surface soil (0–5 cm) from Ld<sub>1</sub> site was measured using batch experiments. 20 mL of aqueous solution containing  $\alpha$ -cypermethrin and endosulfan sulfate from 0.1 to 4 mg L<sup>-1</sup> and  $\alpha$ -endosulfan between 0.5 and 6 mg L<sup>-1</sup> were mixed with 5 g of soil in 50 mL glass centrifuge tubes and shaken end over end at  $20\text{ }^{\circ}\text{C}$  for 24 h. Kinetic assays were performed incubating 5 g of soil with 20 mL of 1 mg L<sup>-1</sup> pesticide solution in the 50 mL centrifuge tubes and incubating

the mixtures from 15 min to 24 h. All assays were run per duplicate (two tubes of soil and solution per concentration or incubation time) and control tubes without soil were used to account for possible pesticide degradation during incubation periods. After incubation, tubes were centrifuged at 3000 rpm and  $18\text{ }^{\circ}\text{C}$  for 15 min (Eppendorf 5810R) and the supernatant was analyzed for pesticide residues. The difference between initial and equilibrium pesticide concentrations was attributed to sorption by soil. Data were adjusted to the Freundlich equation,  $\log C_s = \log K_f + 1/n \log C_e$ , where  $C_s$  ( $\mu\text{g g}^{-1}$ ) is the adsorbed pesticide,  $C_e$  is the pesticide concentration ( $\mu\text{g mL}^{-1}$ ) at equilibrium in solution, and  $K_f$  and  $1/n$  are the affinity and non-linearity Freundlich coefficients, respectively. Sorption equilibrium partition coefficients,  $K_d$  ( $\text{mL g}^{-1}$ ), were calculated for a single concentration as  $K_d = C_s/C_e$ .

### Analysis of RBS and soil physicochemical properties

Water content was determined by constant-weight drying in an oven at  $110\text{ }^{\circ}\text{C}$ . Total organic carbon was determined by the wet-oxidation method.<sup>14</sup> Particle size distribution was determined by the pipette method.<sup>15</sup>

### OCPs, PCBs and PBDEs extraction and clean up

All samples were handled on a glass or aluminum material pre-washed with an hexane : dichloromethane mixture (50 : 50). Compounds were extracted from Sw and isotherm supernatants by the liquid–liquid method.<sup>4</sup> Briefly, one L of water was spiked with 20 ng of PCB #103 as an internal standard and 500 mL of spiked water was shaken with 300 mL of hexane : dichloromethane for 2 h in a Teflon-lined cap glass amber bottle. Clean-up was performed by chromatography on activated ( $200\text{ }^{\circ}\text{C}$ , 24 h) silica gel. Elution was carried out with hexane and hexane : dichloromethane (50 : 50) mixtures, fractions were joined, concentrated under vacuum and kept in sealed vials at  $-20\text{ }^{\circ}\text{C}$ . For isotherm and kinetics assays 5 mL of supernatant were analyzed and extraction volumes were modified to that volume of solution.

For soil, RBS, SPM, macrophytes, and fish, subsamples of 3–10 g were homogenized with sodium sulfate and spiked with 20 ng of PCB #103 as an internal standard and Soxhlet extracted (8 h) with a 50 : 50 mixture of hexane–dichloromethane.<sup>16,17</sup> Extracts were concentrated under vacuum and nitrogen flow to 2 mL. Filters containing the SPM were directly introduced into the Soxhlet extractor. Biological extracts included a lipid separation step by gel permeation chromatography (GPC) in Bio Beads S-X3 (200–400 mesh, Bio-Rads Laboratory, Hercules, CA, USA) followed by lipid percentage calculation. All samples were purified by activated silica gel chromatography as previously described for aqueous samples; extracts were concentrated and kept at  $-20\text{ }^{\circ}\text{C}$  until analysis. Sulfurs were eliminated from sediment extracts by reaction with pre-activated copper particles.

### Gas chromatographic (GC) determination of OCPs, PCBs and PBDEs

All compounds were identified and quantified using a gas chromatograph with an electron capture detector (GC-ECD),

Shimadzu 17-A) using a SPB-5 (Supelco, Bellefonte, PA, USA) capillary column.<sup>17</sup> A pesticide mixture from Ultra Scientific North Kingstown, RI, USA, PCB mixture and BDE-LMS (Bromodiphenyl Ethers Lake Michigan Study) from Accustandard Absolute Standards, INC, CT, USA were used for identification and quantification of single compounds.

### Quality control and assurance

Laboratory and instrumental blanks analyzed throughout the procedure indicate that there were no contaminants or interference on samples during laboratory handling. Recoveries, calculated from spiked matrices, were >90%. Instrumental detection limits<sup>18</sup> ranged between 0.03 and 0.05 ng mL<sup>-1</sup> for HCHs ( $\alpha$ -,  $\beta$ -,  $\gamma$ -, and  $\delta$ -isomers) and between 0.08 and 0.33 ng mL<sup>-1</sup> for the rest of the compounds [chlordanes ( $\alpha$ - and  $\gamma$ -isomers and *trans*-nonachlor), heptachlor and heptachlor epoxide, DDTs (*p,p'*-DDT, *p,p'*-DDE and *p,p'*-DDD), dieldrin, endosulfans ( $\alpha$ -,  $\beta$ -isomers and endosulfan sulfate), PCBs (#18, 44, 52, 66, 101, 87, 110, 118, 153, 138, 180) and PBDEs (#47, 66, 100, 99, 154, 85, 153, 138)]. Method detection limits for soil, RBS, SPM and biota ranged between 0.003 and 0.005 ng g<sup>-1</sup> for HCHs and between 0.008 and 0.033 ng g<sup>-1</sup> for the rest of POPs, while for water samples they varied between 0.015 ng L<sup>-1</sup> and 0.165 ng L<sup>-1</sup>.

### Statistical analyses

A one way ANOVA followed by a Tukey test, *t*-Student's test or Mann-Whitney *U* test was used to test significant differences in contaminant levels among sites. When parametric requirements were not fulfilled a Kruskal Wallis test was used. When comparing contaminant levels throughout the soil profile or within macrophyte tissues a non-parametric ANOVA Friedman test followed by a *t*-paired test for dependent samples was used. Unless otherwise specified, the significance level was set at  $\alpha = 0.05$ . These analyses were performed using an Infostat Software Package (INFOSTAT 2010).<sup>19</sup> To characterize the concentrations of sediment OCPs, PCBs and PBDEs and their relationship with sampling areas a principal component analysis (PCA) was performed after data standard normalization, using the software PRIMER V.6 (developed in Plymouth Marine Laboratory, UK).<sup>20</sup> PCA is a useful tool to reduce the dimensionality of multivariate data (often arranged in tables with rows representing samples and columns representing variables) while retaining most of the variation from the original data. PCA is achieved by transforming raw data to a new set of variables, the principal components (PCs), which are uncorrelated. Often only a few principal components reproduce the majority of the variance and retain most of the information showing patterns that are not immediately obvious from tabular data.<sup>21</sup>

## Results and discussion

### OCPs, PCBs and PBDEs distribution and levels in the soil profile

Total levels (ng g<sup>-1</sup> dry weight) in the soil profile ranged between 0.07–0.9 for OCPs, 0.03–0.37 for PCBs and 0.01–0.05 for PBDEs. The OCP distribution pattern varied through the profile

and among cores (Table 1,  $p < 0.05$ ). PCBs, endosulfans and in some cases DDTs showed higher levels in deeper soil layers ( $p < 0.05$ ). Levels of legacy OCPs are the result of their intensive past use and recalcitrance. Significant differences ( $p < 0.05$ ) were found among cores for the same depth showing the soil matrix heterogeneity. For instance, DDT and PCB values were higher in Ld<sub>4</sub> than in the other cores at 0–4 cm depth, while endosulfans were higher in Ld<sub>1</sub> than Ld<sub>3</sub> and Ld<sub>4</sub> and PBDE levels showed the highest values in Ld<sub>4</sub> and Ld<sub>1</sub> at 20–30 cm. Sampled soils are dedicated to the extensive culture of transgenic soybean and wheat with the subsequent use of technical endosulfan ( $\alpha$ -/ $\beta$ - ratio 70 : 30) to kill pests. However, endosulfan levels were only slightly higher than residues of phased-out pesticides, denoting a relatively lower persistence in soil. Soil OCP levels were low compared to other agricultural soils from the Pampean region (264 ng g<sup>-1</sup> dry weight, 6–8% OC)<sup>22</sup> and similar to soils under organic farming (2.1 ng g<sup>-1</sup> dry weight, 7% OC).<sup>23</sup> Such a result is mainly related to the low OC and high sand content of these soils that promote low retention and high pesticide losses.

The  $\sum$ endosulfan/ $\sum$ OCPs ratio (%) increased with depth confirming the mobility and transport of these compounds in the soil profile ( $p < 0.05$ , Table 2). This transport was previously reported and associated with groundwater pollution by endosulfans in the area.<sup>4,24</sup>

Although endosulfans can be transformed to endosulfan diols, lactona, ether and hydroxy ethers, the biological transformation to endosulfan sulfate is the primary metabolic pathway.<sup>13,25,26</sup> The endosulfan sulfate metabolite represents 100% of endosulfans in the 0–4 cm depth with decreasing values ( $p < 0.05$ ) down to 5% in Ld<sub>1</sub> and Ld<sub>3</sub>, while in Ld<sub>2</sub> it ranges from 80 to 100% (Table 2). These results may be the consequence of the higher metabolism of technical endosulfan in the organic matter-rich and well oxygenated surface soil.

PCBs showed a homogeneous distribution pattern below the 5 or 10 cm depth depending on the core, with lower values on the surface (Table 1). Physicochemical processes and biological activity may cause PCB loss from the surface by volatilization, transformation, metabolism or bioaccumulation.<sup>27–29</sup>

The occurrence of PCBs #18, 44, 66, 101, 118, 153 and 138 agrees with the Arochlors 1254 and 1260 mixtures as the PCB source in the region.<sup>30</sup> PBDE levels were one order of magnitude lower than PCBs with a homogeneous distribution on all profiles (Table 1). BDE 47 was the main congener followed by BDE 153 and 154 + 85 in agreement with the penta-BDE mixture source. PCB and PBDE residues are expected to be negligible in agricultural soils with atmospheric transport being the main source of these pollutants.<sup>27</sup> However, the occurrence of PCBs in this area could be also related to their use in tractor oil, or to their use as adjuvants for pesticide application. Uncontrolled combustion of wastes is related to atmospheric PBDE pollution in non-urban areas<sup>31</sup> and tire pile burning is recognized as another polluting activity, although their role as the source of PCBs is unknown. Refuse or pile tire burning events are frequent in the study area during farmer breaks and could represent a neglected source for PCBs and PBDEs that needs to be further investigated.

**Table 1** Physicochemical characteristics and total levels ( $\text{ng g}^{-1}$  dry weight) of polybrominated diphenyl ethers ( $\Sigma$ PBDEs), polychlorinated biphenyls ( $\Sigma$ PCBs), polychlorinated biphenyls ( $\Sigma$ PCBs), organochlorine pesticide groups (OCPs) in soil profiles from Ld<sub>1</sub>, Ld<sub>3</sub> and Ld<sub>4</sub> sites from the Quequén Grande watershed.  $\Sigma$ PBDEs: #47, 154 + 85, 153;  $\Sigma$ PCBs: #18, 44, 52, 66, 101, 87, 118, 153, 138;  $\gamma$ -HCH:  $\gamma$ -hexachlorocyclohexane;  $\Sigma$ Endosulfans sulfate:  $\Sigma$ Chlordanes:  $\alpha$  +  $\gamma$ -chlordane and transnonachlor;  $\Sigma$ DDTs:  $p,p'$ -DDE +  $p,p'$ -DDD;  $\Sigma$ DDT:  $p,p'$ -DDT +  $p,p'$ -DDD; <dl, below detection limit.

Point	Depth (cm)	Particle size distribution (%)			OC (%)	$\Sigma$ PBDEs	$\Sigma$ PCBs	$\gamma$ -HCH	$\Sigma$ Endosulfans	$\Sigma$ Heptachlors	Dieldrin	$\Sigma$ Chlordanes	$\Sigma$ DDTs
		Sand	Silt	Clay									
Ld <sub>1</sub>	0-4	41.2	50.4	8.3	1.4	<dl	0.04 ± 0.01	0.21 ± 0.03	0.21 ± 0.08	$6 \times 10^{-3} \pm 4 \times 10^{-3}$	0.10 ± 0.02	0.06 ± 0.01	0.06 ± 0.02
	4-10	55.8	27.4	16.8	0.9	0.02 ± $7 \times 10^{-3}$	0.21 ± 0.08	0.13 ± 0.03	0.23 ± 0.04	0.03 ± 0.04	<dl	0.04 ± 0.02	0.10 ± 0.03
	10-20 <sup>a</sup>					0.02 ± $4 \times 10^{-3}$	0.18 ± 0.03	0.03 ± 0.01	0.28 ± 0.02	<dl	<dl	$0.05 \pm 4 \times 10^{-3}$	0.15 ± 0.05
Ld <sub>3</sub>	0-4	45.9	30.8	23.2	0.9	0.02 ± $2 \times 10^{-3}$	0.22 ± 0.07	0.07 ± 0.05	0.44 ± 0.10	<dl	<dl	0.06 ± 0.01	0.13 ± 0.04
	4-10	59.2	21.1	19.6	0.8	0.03 ± $2 \times 10^{-3}$	0.03 ± $2 \times 10^{-4}$	0.19 ± 0.04	0.10 ± 0.01	0.04 ± 0.04	0.09 ± 0.04	0.09 ± $5 \times 10^{-3}$	0.14 ± 0.02
	10-20	55.9	26.9	17.2	1.3	0.02 ± $2 \times 10^{-3}$	0.09 ± 0.08	0.03 ± 0.03	0.21 ± 0.24	<dl	<dl	0.02 ± 0.01	0.02 ± 0.01
Ld <sub>4</sub>	0-4	53.9	32.4	13.7	0.7	0.01 ± $4 \times 10^{-3}$	0.18 ± 0.10	0.04 ± 0.01	0.19 ± 0.35	<dl	<dl	0.02 ± 0.01	0.03 ± 0.02
	4-10	56.2	26.7	17.1	1.0	0.01 ± 0.02	0.06 ± 0.04	0.19 ± 0.03	0.13 ± 0.04	$7 \times 10^{-3} \pm 1 \times 10^{-3}$	0.09 ± 0.05	0.06 ± $3 \times 10^{-3}$	0.13 ± 0.01
	10-20 <sup>a</sup>					0.03 ± 0.02	0.19 ± 0.09	0.08 ± 0.04	0.26 ± 0.10	0.01 ± 0.02	<dl	0.07 ± 0.02	0.47 ± 0.18
	20-30 <sup>a</sup>					0.04 ± 0.02	0.30 ± 0.17	0.06 ± 0.02	0.26 ± 0.08	$2 \times 10^{-3} \pm 4 \times 10^{-3}$	0.03 ± 0.06	0.10 ± 0.05	0.28 ± 0.16
						0.03 ± $4 \times 10^{-3}$	0.37 ± 0.21	0.05 ± 0.02	0.34 ± 0.13	<dl	0.01 ± 0.02	0.08 ± 0.06	0.29 ± 0.14

<sup>a</sup> Particle size distribution is the same as the previous depth profile.

**Table 2**  $\Sigma$ Endosulfan/ $\Sigma$ OCPs and endosulfan sulfate/ $\Sigma$ Endosulfans ratios (%) in soil profiles from Ld<sub>1</sub>, Ld<sub>3</sub> and Ld<sub>4</sub>.  $\Sigma$ Endosulfans =  $\alpha$  +  $\beta$  isomers + endosulfan sulfate,  $\Sigma$ OCPs =  $\gamma$ -hexachlorocyclohexane +  $\alpha$ -endosulfan +  $\beta$ -endosulfan + endosulfan sulfate +  $\alpha$ -chlordane +  $\gamma$ -chlordane + transnonachlor +  $p,p'$ -DDT +  $p,p'$ -DDE +  $p,p'$ -DDD + dieldrin, heptachlor + heptachlor epoxide.

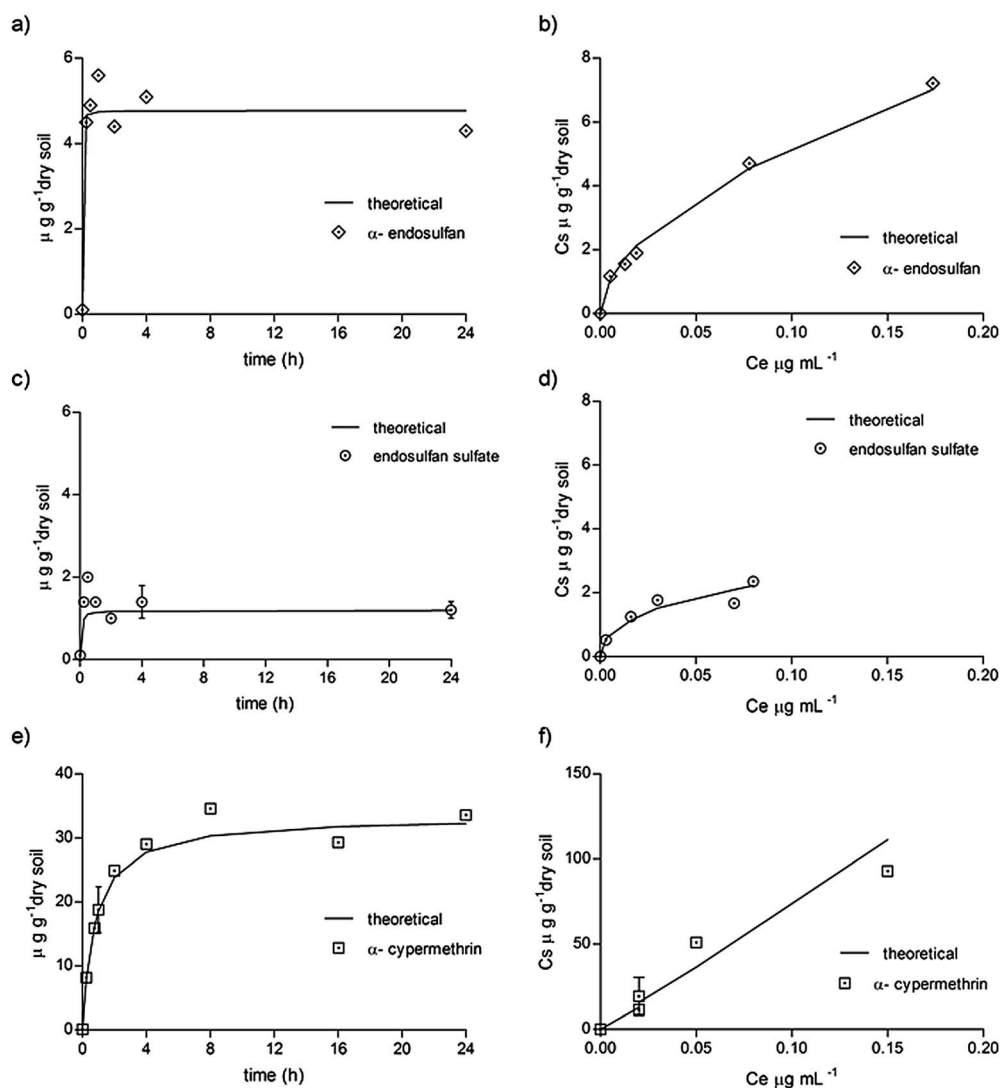
	Depth (cm)	$\Sigma$ Endosulfan/ $\Sigma$ OCPs	E. sulfate/ $\Sigma$ Endosulfans
Ld <sub>1</sub>	0-4	33.1	100.0
	4-10	42.9	19.8
	10-20	54.1	10.3
	20-30	63.4	5.3
Ld <sub>3</sub>	0-4	14.8	100.0
	4-10	16.0	99.7
	10-20	72.5	78.0
	20-30	68.7	88.4
Ld <sub>4</sub>	0-4	21.3	100.0
	4-10	29.2	18.4
	10-20	35.2	14.0
	20-30	44.2	13.3

### Current-used pesticide isotherms and kinetic studies in soil

Sorption exerts a significant effect on the fate of pesticides in soil governing their leaching to surrounding environments. So, the study of current-used pesticide adsorption gives information about the potential impact of authorized agricultural products on water resources. Pesticide adsorption was dependent on pesticide characteristics. For  $\alpha$ -endosulfan ( $K_{ow} = 3.83$  (ref. 32)) and endosulfan sulfate ( $K_{ow} = 3.66$  (ref. 33)) adsorption was fast with equilibrium times lower than 2 h and a maximum adsorption ( $\mu\text{g g}^{-1}$ ) of 5.6 (Fig. 2a) and 2 (Fig. 2c), respectively. Conversely, the more hydrophobic  $\alpha$ -cypermethrin ( $K_{ow} = 6.6$  (ref. 34)) required longer equilibrium time (8 h) and reached a higher maximum adsorption ( $35 \mu\text{g g}^{-1}$ , Fig. 2e). The fitting of the sorption values to the Freundlich model indicates that endosulfans follow a convex isotherm ( $1/n < 1$ ) with a decrease in sorption sites as the adsorptive sites become occupied by the solute (Table 3, Fig. 2b and d). On the other hand  $\alpha$ -cypermethrin displayed a linear isotherm ( $1/n \approx 1$ , Table 3, Fig. 2f). Values of  $K_d$  (Table 3) represent the relative soil retention of the studied pesticides. These results agree with the low concentration of endosulfan sulfate and  $\alpha$ -endosulfan in surface soil and their lixiviation through the profile, particularly during rain events, while for  $\alpha$ -cypermethrin higher retention is expected. The  $K_d$  values for  $\alpha$ -cypermethrin are higher than those reported for a calcareous silty loam soil with slightly lower organic carbon levels ( $K_d$ : 194,  $K_{oc}$ : 17424).<sup>35</sup> Thus, soil composition influences  $\alpha$ -cypermethrin retention parameters.

### River bottom sediments (RBS)

Results showed that in most of the sampling sites RBS had a dominant sand content and quite variable silt and clay proportions (Table 4). OCPs, PCBs and PBDEs are known by their tendency to adsorb preferentially onto clays or organic matters, however, in this work, contaminant levels did not correlate well with any of these components (Table 4).



**Fig. 2** Pesticide kinetics and sorption isotherms [amount of pesticide sorbed ( $C_s$ ) vs. concentration of pesticide in solution ( $C_e$ )] of (a and b)  $\alpha$ -endosulfan, (c and d) endosulfan sulfate and (e and f)  $\alpha$ -cypermethrin in 0–5 cm soil from Ld<sub>1</sub>.

**Table 3** Sorption parameters of  $\alpha$ -endosulfan, endosulfan sulfate and  $\alpha$ -cypermethrin in 0–5 cm soil from Ld<sub>1</sub> point

	$K_f^a$	$1/n^a$	$R^{2a}$	$K_d^b$	$K_{oc}^c$
$\alpha$ -Endosulfan	18.01	0.54	0.98	100.8	7202.6
Endosulfan sulfate	6.46	0.42	0.92	77.6	5546.3
$\alpha$ -Cypermethrin	703.23	0.96	0.86	1024.2	73154.8

<sup>a</sup> Obtained from the fitting to the Freundlich equation. <sup>b</sup>  $K_d$  (for a  $C_e = 0.02 \text{ mg L}^{-1}$ ), calculated as  $C_s (\mu\text{g g}^{-1}) = K_d \times C_e (\mu\text{g mL}^{-1})$ . <sup>c</sup>  $K_{oc}$  was calculated as  $K_{oc} = K_d \times 100/\%OC$ .

The distribution pattern of pollutants in RBS was dependent on the zone. OCPs > PCBs  $\approx$  PBDEs was mainly observed in the upper zone, while in the middle zone and estuary, the greater difference between PCBs and PBDEs leads to a OCPs > PCBs > PBDEs pattern. When comparing sites, H > Lq > rest and H = Lo = Ce > Lq > Ld patterns were found for PCBs + PBDEs and OCPs, respectively (Table 4,  $p < 0.05$ ). Principal

component analysis (PCA) was performed on pollutant levels in RBS from all sites in order to visualize in an integral way the behavior of OCPs, PCBs and PBDEs due to combinations of factors and their relationship with land use. From Fig. 3 and Table 4 it can be seen that H sites were enriched in PCBs, PBDEs, endosulfans and chlordanes in relation to the rest of areas. Moreover, variability within RBS from H was mainly due to PCB, PBDE and chlordanes residues. Since H sediments were collected by means of a dredge, differences in depth sampling could exist, and historical deposition patterns might influence the results particularly for phased-out compounds. PCB enrichment was associated with the H zone or the vicinity to urban settlements (Fig. 3a and b). Moreover, an increasing number of congeners was detected (#18, 52, 44, 110, 138, 153, 118 and 180) in H sites. These results and the OCP/PCB ratios allow for the recognition of a hot spot for PCBs in H, related to the industrial activity of the area and to the sink watershed effect. PBDEs represent between 2 and 5%

**Table 4** Physicochemical characteristics and total polybrominated diphenyl ethers ( $\Sigma$ PBDEs), polychlorinated biphenyls ( $\Sigma$ PCBs) and organochlorine pesticides ( $\Sigma$ OCPs) in river bottom sediments from the Quequén Grande River watershed. <dl: below detection limit, OC: organic carbon.  $\Sigma$ PBDEs: #47, 100, 99, 153, 154 + 85;  $\Sigma$ PCBs: #18, 44, 52, 66, 101, 110, 153, 118, 138, 180;  $\Sigma$ OCPs =  $\gamma$ -hexachlorocyclohexane +  $\alpha$ -endosulfan +  $\beta$ -endosulfan + endosulfan sulfate +  $\alpha$ -chlordane +  $\gamma$ -chlordane + transnonachlor +  $p,p'$ -DDT +  $p,p'$ -DDE +  $p,p'$ -DDD + dieldrin

Zone	Site	Point	Physicochemical characteristics (%)				Organic compounds (ng g <sup>-1</sup> dry weight)		
			Sand	Silt	Clay	OC	$\Sigma$ PBDEs	$\Sigma$ PCBs	$\Sigma$ OCPs
Upper	Center (Ce)	Ce <sub>1</sub>	52.5	35.0	12.5	0.4	0.07 ± 0.05	0.22 ± 0.10	1.34 ± 0.54
		Ce <sub>2</sub>	34.4	38.5	27.1	2.0	<dl	0.25 ± 0.05	1.72 ± 0.50
		Ce <sub>3</sub>	40.0	35.0	25.0	2.9	0.11 ± 0.01	<dl	2.85 ± 0.40
	Lobería (Lo)	Lo <sub>1</sub>	37.5	42.5	20.0	1.9	0.14 ± 0.10	0.10 ± 0.06	1.99 ± 1.01
		Lo <sub>2</sub>	65.2	24.5	9.5	0.9	0.15 ± 0.04	0.96 ± 0.50	3.02 ± 1.66
		Lo <sub>3</sub>	87.5	2.5	10.0	0.4	0.05 ± 0.02	0.05 ± 0.01	2.77 ± 0.71
		Lo <sub>4</sub>	57.5	30.1	12.5	0.4	0.05 ± 0.03	0.04 ± 0.06	2.38 ± 0.80
	La Dulce (Ld)	Ld <sub>1</sub>	45.4	32.1	22.5	1.7	<dl	0.06 ± 0.03	0.88 ± 0.31
		Ld <sub>2</sub>	66.1	21.6	12.4	1.0	<dl	0.15 ± 0.11	1.58 ± 0.21
		Ld <sub>3</sub>	59.4	7.2	33.5	1.2	<dl	0.10 ± 0.05	1.12 ± 0.6
Ld <sub>4</sub>		44.3	45.1	10.7	1.4	0.06 ± 0.08	0.20 ± 0.04	1.37 ± 0.39	
Ld <sub>5</sub>		49.0	38.6	12.5	1.6	0.03 ± 0.02	0.05 ± 0.02	1.23 ± 0.08	
Middle	Lower Quequén (Lq)	Lq <sub>1</sub>	60.0	27.5	12.5	1.0	0.07 ± 0.03	0.33 ± 0.08	1.13 ± 0.10
		Lq <sub>2</sub>	60.0	25.0	15.0	0.7	<dl	0.11 ± 0.04	1.31 ± 0.51
		Lq <sub>3</sub>	56.9	16.8	26.4	1.4	0.04 ± 0.01	0.43 ± 0.05	1.14 ± 0.39
		Lq <sub>4</sub>	60.0	27.5	12.5	0.6	0.09 ± 0.03	0.58 ± 0.13	1.36 ± 0.18
Estuary	Harbour (H)	H <sub>1</sub>	87.5	2.5	10.0	0.03	0.06 ± 0.03	0.74 ± 0.50	0.56 ± 0.03
		H <sub>2</sub>	42.5	30.1	27.5	2.0	0.15 ± 0.06	0.49 ± 0.03	3.47 ± 0.18
		H <sub>3</sub>	85.0	5.0	10.0	1.8	0.16 ± 3 × 10 <sup>-3</sup>	1.18 ± 0.14	4.35 ± 0.39
		H <sub>4</sub>	56.1	32.4	11.5	1.1	0.16 ± 0.05	1.67 ± 0.40	3.61 ± 0.50
		H <sub>5</sub>	85.0	2.5	12.5	2.6	0.28 ± 0.08	1.06 ± 0.70	3.19 ± 0.11
		H <sub>6</sub>	51.2	30.6	18.2	1.4	0.20 ± 0.2	1.62 ± 1.00	2.62 ± 0.45

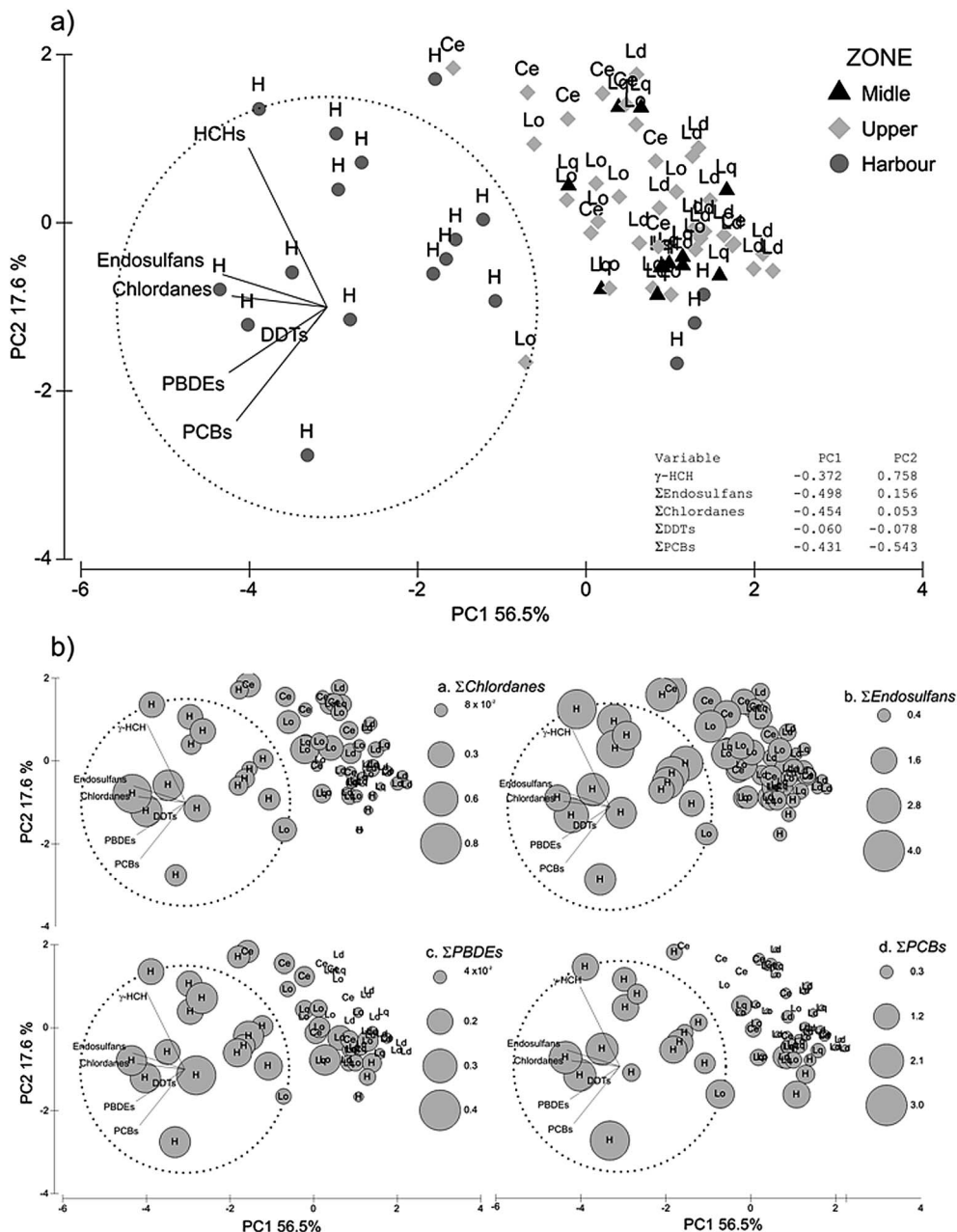
of total POPs in all RBS showing their relatively low relevance in the area but a clear increase in H and Lq sites. BDE-47 and 153 were predominant followed by BDE-100, BDE-99 and BDE-154 + 85, suggesting the penta-BDE mixture as a source of PBDEs. The highest PCB levels in H ranged between 1.1 and 1.7 ng g<sup>-1</sup> dry weight, quite lower than the value given by Sediment Quality Guidelines from the Canadian government (21.5 ng g<sup>-1</sup>, ref. 36). PCB levels in RBS from the Ququén Grande river were much lower than those reported for the central and southern areas (1.9–98.5 ng g<sup>-1</sup>) of the Río de la Plata estuary,<sup>37</sup> which is known as the major source of anthropogenic contaminants in the region,<sup>38</sup> but similar to those reported for the northern area (0.04–1 ng g<sup>-1</sup>). For PBDEs there are no sediment quality guidelines available but levels were low and comparable with those reported by Moon *et al.*<sup>39</sup>

Regarding OCPs, endosulfans were predominant in all RBS samples, followed by chlordanes and  $\gamma$ -HCH or lindane (Fig. 3a). This pattern correlates well with the low soil retention of the current-used endosulfans, and the high persistence of chlordanes and lindane, strongly used in the past. Moreover, endosulfan levels showed a growing gradient in RBS from the middle zone to the estuary ( $p < 0.05$ , Fig. 3b), highly marked for the  $\beta$ -isomer and the sulfate metabolite. This result agrees with the distance to the source and with the relatively higher persistence of these compounds.<sup>40,41</sup> When comparing sites, levels in H, Lo and Ce were similar and higher than in other sampling sites. This distribution pattern responds to a sink effect enhanced by the use of endosulfans and the absence of

vegetative barriers to trap them on their way to the estuary. In Lq points the lower sediment deposition leads to lower pollutant accumulation. Chlordane and lindane pulses in RBS may be related to small urban settlement as Lobería city. The use of lindane as lice killers was responsible for point-source pollution in the Suquia River<sup>42</sup> and a similar situation may be expected for the QGR watershed. DDT levels did not vary among zones or sites showing a diffuse pollution behavior. Values of legacy OCPs in RBS were in agreement with the low levels found in soils. Thus, current-used compounds should be the focus of pollution survey rather than legacy pesticides in the QG estuary. However, none of the OCPs found exceeded sediment quality guidelines.<sup>36</sup>

### Streamwater (Sw) and suspended particle material (SPM)

The pollutant distribution pattern in Sw was dependent on sampling time (Fig. 4a). Higher total pollutant loads were found in post-application samples from 2007 with decreasing values in 2009, except for endosulfan residues with similar values. Endosulfans represented 15–60% of all the compounds with a predominance of  $\alpha$ -endosulfan and endosulfan sulfate ( $p < 0.05$ ). Depletion of levels during application periods was mainly due to endosulfans ( $p < 0.05$ ,  $\alpha$ -isomer and endosulfan sulfate). Deviation from the technical  $\alpha/\beta$  endosulfan ratio (7 : 3) could be used to understand the time passed after application.<sup>13</sup> The observed isomer ratio coincided with that of the technical mixture (data not shown) indicating that technical endosulfan reach Sw immediately after application to

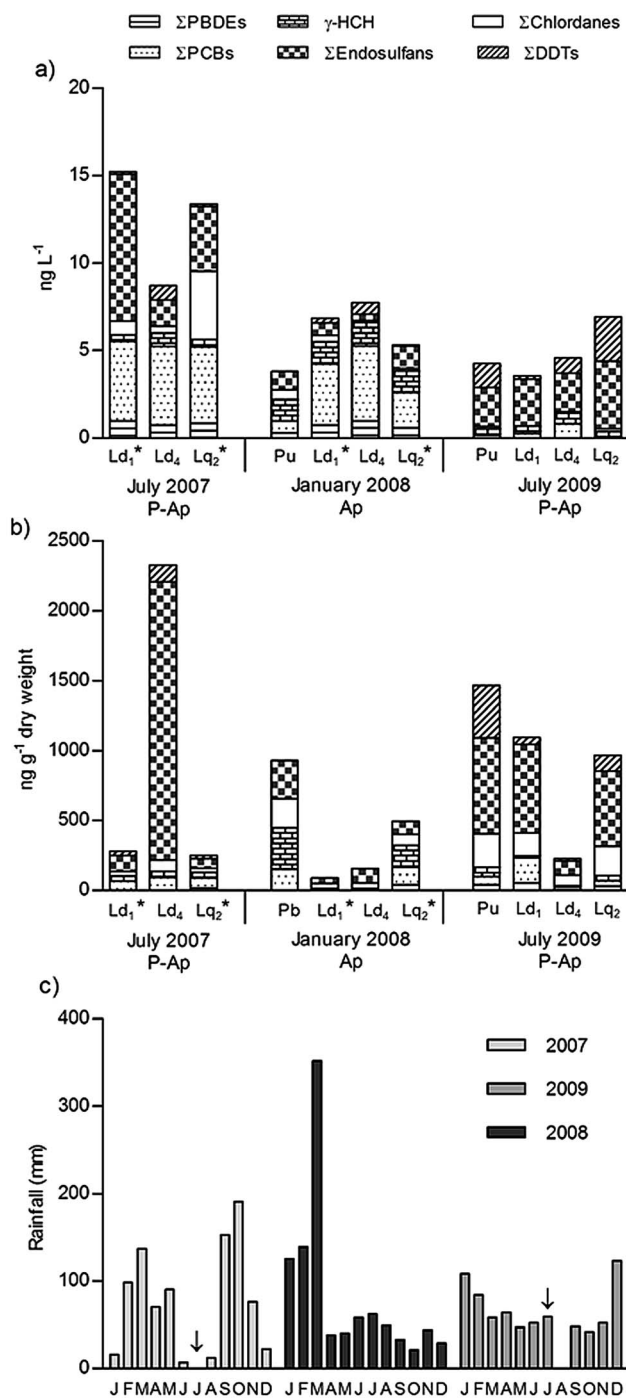


**Fig. 3** (a) Principal Component Analysis (PCA) plot of pollutant levels on river bottom sediments from middle, upper and harbour areas of the Quequén Grande watershed. Correlation of variables and principal component (PC1, PC2) table is included. (b) PCA bubble plots of levels for (1)  $\Sigma$ Chlordanes, (2)  $\Sigma$ Endosulfans, (3)  $\Sigma$ PBDEs and (4)  $\Sigma$ PCBs.  $\gamma$ -HCHs:  $\gamma$ -hexachlorocyclohexane;  $\Sigma$ Endosulfans:  $\alpha$ - +  $\beta$ - + endosulfan sulfate;  $\Sigma$ Chlordanes:  $\alpha$ - +  $\gamma$ -chlordane and transnonachlor;  $\Sigma$ DDTs:  $p,p'$ -DDT +  $p,p'$ -DDE +  $p,p'$ -DDD;  $\Sigma$ PBDEs: #47, 100, 99, 153, 154 + 85;  $\Sigma$ PCBs: #18, 44, 52, 66, 101, 110, 153, 118, 138, 180.

soil during the summer season. Aerial sprays and culture settlements in the edges of the river margins provide an excellent scenario for endosulfans to reach surface waters. The higher concentration of endosulfans in the post-application periods (Fig. 4a) could be explained by their transport from application sites to the river waters by rain events. Additionally, the predominance of the  $\alpha$ -isomer (70%) and endosulfan sulfate metabolite (25–65%), together with the low value of  $\beta$ -endosulfan (0–20%) may indicate the transport of aged technical mixture, because of the transformation of the  $\beta$ - into the  $\alpha$ -isomer<sup>43</sup> and the production of the metabolite mainly from

the  $\alpha$ -isomer.<sup>41</sup> Pesticide differences between the two post-application periods, 2007 and 2009, were related to the precipitation during these years (Fig. 4c). In July 2007 rains registered values of 7 mm while in July 2009 the mean value was 52 mm. Thus, under dry conditions the contaminant content in Sw was higher probably due to the concentration effect caused by the lower water inputs. An exceptional condition occurs for the current-used endosulfans, which would be more available to be transported by soil runoff during rain events helped by the absence of vegetation. Moreover, considering the vapor pressures, the sulfate





**Fig. 4** Organic compounds in streamwater (a) and suspended particle matter (b) from Ld<sub>1</sub>, Ld<sub>4</sub>, Lq<sub>2</sub> and Pu sites in pesticide post-application (P-Ap) and application (Ap) periods, and monthly rainfall distribution in Ld<sub>1</sub> point for the 2007–2009 period (c) in the Quequén Grande River watershed. ΣPBDEs: #47, 100, 154 + 85; ΣPCBs: #118, 153, 138; γ-HCH: γ-hexachlorocyclohexane; ΣEndosulfans: α + β + endosulfan sulfate; ΣChlordanes: α + γ-chlordane and transnonachlor; ΣDDTs: p,p'-DDT + p,p'-DDE + p,p'-DDD. \*OCs levels from Gonzalez *et al.*, 2012.<sup>4</sup>

metabolite (0.0013 Pa<sup>44</sup>) has 4 fold lower values than α- and β-isomers which have similar values (0.0044 and 0.0040 Pa, respectively<sup>45</sup>), but both β-endosulfan and endosulfan sulfate have higher aqueous solubility, therefore being more

susceptible to be scavenged from the atmosphere by rain as well as to be dissolved on streamwater.<sup>44,46</sup> In samples from 2009 (rainy season) endosulfan sulfate accounted for 59–75% of total endosulfans and the α/(α + β) ratio ranged between 0.3 and 0.7, suggesting the effect of precipitation scavenging.<sup>46</sup> Regarding safety levels for aquatic biota, the Argentinean National Water Institute (Spanish acronym, INA) establishes a value of 7 ng L<sup>-1</sup> for the sum of α- and β-isomers. As was previously reported by Gonzalez *et al.*,<sup>4</sup> endosulfan levels in samples from Ld<sub>1</sub> point in the post-application period of 2007 exceeded this limit only on the basis of the α-isomer. Considering international guidelines (3 ng L<sup>-1</sup>, ref. 36), Lq<sub>2</sub> station also went beyond this value in post-application sampling (2007). Although the endosulfan sulfate metabolite is recognized to be more toxic than parent compounds<sup>47</sup> it is not included in water quality guidelines. In this work the endosulfan metabolite accounted for up to 75% of total endosulfans in Sw samples. Thus, endosulfans reached levels in Sw that represent a risk to aquatic biota, but it could be higher since the toxic endosulfan sulfate metabolite is not being considered.

The high PCB levels observed in Sw lead to the pattern endosulfans > PCBs > rest of compounds in most of the sampling points (Fig. 4a, *p* < 0.05). No differences among sites or periods were found for samples from Ld and Lq, indicating a chronic and diffuse pollution pattern by PCBs in the middle and lower areas of the QGR watershed. The occurrence of small urban settlements as well as dumping sites and burning events represents potential sources for these compounds. Moreover, soil washout as well as atmospheric inputs might contribute to the occurrence of PCBs in Sw. PCB levels were above the recommended INA values for aquatic biota protection considering its use for human consumption (0.004 ng L<sup>-1</sup>), but below the limit for biota risk (9 ng L<sup>-1</sup>). PBDE levels in water responded, like PCBs, to a diffuse pollution condition. In RBS BDE-153, 154, 85, 99, 47 and 100 were detected while in Sw only the BDE-47 and 100 were found. For PCBs, enrichment in lower chlorinated congeners (#18, 66, 52 and 44) was observed in Sw related to RBS. These results were in agreement with the higher solubility of lower brominated or chlorinated congeners.<sup>48,49</sup>

Although SPM pollutants distribution pattern resembled that of Sw (Fig. 4b), PBDEs and chlordanes were more abundant in Sw and this could be related to the association of these highly hydrophobic compounds with dissolved organic matter. Endosulfan values in both application periods were in the same range as those previously reported by Gonzalez *et al.*<sup>4</sup> for the Quequén River and by Jergentz *et al.*<sup>3</sup> for the Horqueta stream after a rainfall event of 184 mm day<sup>-1</sup> in a soybean area from the Northern Pampa.

### Macrophytes

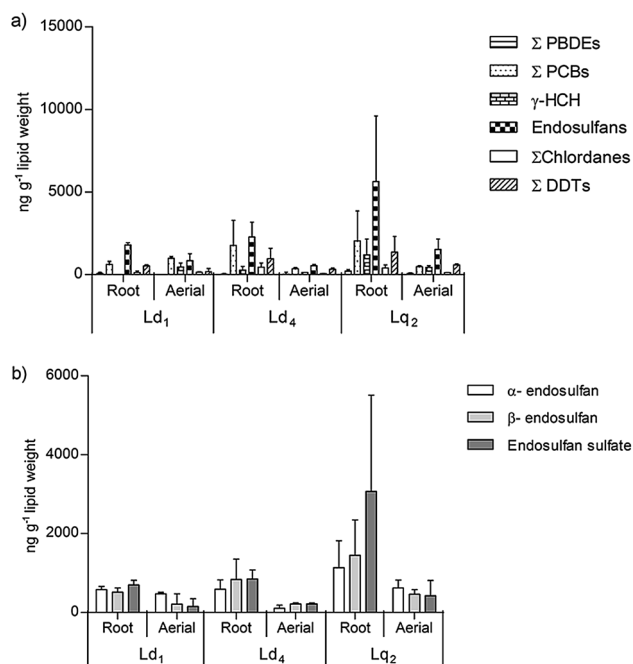
*Ludwigia peploides* samples were available only on application periods. The pollutant distribution pattern in this macrophyte was similar to Sw with the predominance of endosulfans and

PCBs but also DDTs (Fig. 5a). Moreover, the pattern  $\alpha$ -isomer + endosulfan sulfate >  $\beta$ -isomer reflects the technical mixture use and metabolism to endosulfan sulfate within tissues (Fig. 5b).<sup>13,41</sup> Comparing levels from Ld<sub>1</sub> to Lq<sub>2</sub> a contaminant growing gradient was observed with significant differences between Ld<sub>1</sub> and Lq<sub>2</sub> in roots (endosulfan sulfate, chlordanes,  $p < 0.05$ ) and aerials (endosulfan sulfate,  $\alpha$ -endosulfan, PCBs and DDTs,  $p < 0.05$ ). Aerial tissues showed lower levels than

roots, independently of the lipid content that ranged between 0.13–0.2 and 0.07–0.09%, respectively. Roots were mainly enriched in the  $\alpha$ -isomer and endosulfan sulfate in macrophytes from Ld<sub>4</sub> and Lq<sub>2</sub> ( $p < 0.05$  and  $p < 0.1$ , respectively) while only in endosulfan sulfate for Ld<sub>1</sub> ( $p < 0.05$ , Fig. 5b). PBDEs and PCBs represent 1.6 and 23.3% of total compounds respectively in all tissues from all sites. These macrophytes may incorporate pollutants in roots directly from water or by adsorption from suspended particle matter. The PBDE/PCB ratio < 1 in roots reflected the Sw and SPM pattern. The root/aerial ratio showed the role of the water–root uptake in the bioaccumulation of these contaminants. For aerial parts atmospheric deposition as well as translocation from roots should be considered. Thus, differences between roots and aerials are the combined effect of uptake route and plant metabolism.

### Silverside muscle tissue

Water resource protection and conservation is a challenge due to the impact and risk related to both environment and human beings. Sport and subsistence fishing are frequent in the study area so, knowing how the residues in abiotic matrices are related to the final levels in fish and particularly in muscle tissue is of concern. Contaminant pattern distribution in fish muscle was endosulfans > PCBs >  $\gamma$ -HCH > DDTs > PBDEs > chlordanes (Table 5). Thus, bioaccumulation of pollutants on silverside muscle responds to the distribution pattern of Sw and RBS. The quantity of pollutant in a 300 g filet was calculated and the total amount that an individual of 70 kg could ingest per day without risk was obtained on the basis of the reference dose (Table 4). PCB values in Sw exceeded limits for human biota consumption and the PCB content in the filet accounts for 18.6% of the daily allowed ingest for a 70 kg person. Although PCB pollution was described as chronic and diffuse, daily fish consumption represents a potential risk for human beings in the QGR watershed.



**Fig. 5** Organic compounds in roots and aerial tissues of *Ludwigia peploides* from Ld<sub>1</sub>, Ld<sub>4</sub> and Lq<sub>2</sub> sites of the Quequén Grande River watershed. (a)  $\Sigma$ PCBs: 18, 44, 87, 110, 118, 153, 138;  $\Sigma$ PBDEs: #47, 153, 100;  $\gamma$ -HCH:  $\gamma$ -hexachlorocyclohexane;  $\Sigma$ Endosulfans:  $\alpha$ -isomer +  $\beta$ -isomer + endosulfan sulfate;  $\Sigma$ Chlordanes:  $\alpha$ - +  $\gamma$ -chlordane and transnonachlor;  $\Sigma$ DDTs:  $p,p'$ -DDT +  $p,p'$ -DDE +  $p,p'$ -DDD, (b) details of  $\alpha$ -endosulfan,  $\beta$ -endosulfan and endosulfan sulfate distribution.

**Table 5** Contaminant levels in muscle of silverside from the Quequén Grande River watershed, burden in a 300 g filet, percentage of allowed ingest, oral reference dose (RfD) values for each contaminant group and total daily allowed ingest for a 70 kg individual. Values represent the mean  $\pm$  standard error of 8 individual (4 males and 4 females) obtained from Puente Blanco point in a post pesticide application period. Lipid percentage was 0.4%.  $\Sigma$ PBDEs: #47, #100;  $\Sigma$ PCBs: #153;  $\gamma$ -HCH:  $\gamma$ -hexachlorocyclohexane isomer;  $\Sigma$ Endosulfans:  $\alpha$ - +  $\beta$ -isomers + endosulfan sulfate;  $\Sigma$ Chlordanes:  $\alpha$ - +  $\gamma$ -isomer + transnonachlor;  $\Sigma$ DDTs:  $p,p'$ -DDT +  $p,p'$ -DDE +  $p,p'$ -DDD

Contaminants <sup>a</sup>	Silverside muscle				
	(ng g <sup>-1</sup> wet weight)	Burden ( $\mu$ g)	% of daily allowed ingest for a 70 kg individual	RfD ( $\mu$ g kg <sup>-1</sup> per day)	$\mu$ g in a 70 kg individual
$\Sigma$ PBDEs <sup>a</sup>	0.22 $\pm$ 0.15	0.07	1	0.1 <sup>c</sup> , 2 <sup>d</sup>	7.0
$\Sigma$ PCBs <sup>b</sup>	0.86 $\pm$ 1.09	0.26	18.6	0.02 <sup>e</sup>	1.4
$\gamma$ -HCH <sup>b</sup>	0.56 $\pm$ 0.30	0.17	0.8	0.3	21.0
$\Sigma$ Endosulfans <sup>b</sup>	10.51 $\pm$ 3.38	3.15	0.75	6.0	420.0
$\Sigma$ Chlordanes	0.06 $\pm$ 0.03	0.02	0.5	0.06 <sup>b</sup>	4.2
Dieldrin <sup>a</sup>	0.15 $\pm$ 0.06	0.04	1.1	0.05	3.5
$\Sigma$ DDTs <sup>b</sup>	0.26 $\pm$ 0.13	0.08	0.2	0.5 <sup>f</sup>	35.0

<sup>a</sup> IRIS epa database (<http://www.epa.gov/IRIS/>, accessed May 2012). <sup>b</sup> ATSDR (<http://www.atsdr.cdc.gov/>, accessed May 2012). <sup>c</sup> BDE-47. <sup>d</sup> Penta BDE. <sup>e</sup> Arochlor 1254/1248. <sup>f</sup>  $p,p'$ -DDT.

## Conclusions

Watershed pollution studies are necessary to assess the quality status of their waters and produces. Geomorphological, edaphic and climatic characteristics of the Pampean region of Argentina allow the development of extensive agricultural production areas and urban settlements leading to specific pollution patterns. In order to analyze the fate and distribution of contaminants in a watershed context two main concepts should be addressed. One is a multi-matrix approach considering the fate of the compounds and analyzing their distribution. While the other one is necessary for an integrated study at the catchment scale in order to understand the processes leading to the mobility of contaminants between these different matrices. Two main conclusions can be drawn in relation to the former concepts. One is related to the fate of the intentionally applied compounds in the soil environment, such as OCPs, and the other one to the compounds originating from urban or industrial activities, like PCBs and PBDEs. It is clear that all the analyzed matrices are affected. However, considering the spatial and temporal scale, results reveal different scenarios, a chronic pollution by legacy OCPs (those whose use was phased-out several years ago) and a current pollution source represented by the insecticide endosulfan. Although some source contamination may be recognized for PCBs and PBDEs (*i.e.* dumping sites, pile tire burning, urban activities, harbour) the pollution pattern may be described as diffuse in the upper and middle regions. Changes in land use together with the QGR dynamics of sediment transport and rain processes influence the spatial distribution of pollutants, showing the harbour as a pollutant sink and as a secondary source of PCBs. Soil characteristics are responsible for insecticide transport to streamwater and macrophytes act as good indicators of endosulfan inputs into the aquatic environment. Transport processes from soil, represented by SPM values, contribute to bringing the levels of some compounds above water quality guidelines. Consequently, endosulfan streamwater levels approach the hazard limits for aquatic biota protection and PCB levels go beyond the limits for protection of food resources and PCB residues in fish may represent a risk for human consumption. Thus, although PCB and OCP levels in sediments and soil are low and did not exceed quality guidelines, the damage of the QGR watershed water quality was mainly based on the transport and partition of pollutants in the aqueous phase, pointing out the relevance of this matrix analyses in a catchment scale study. This is particularly of interest since low soil or sediment pollution is often associated with non-risk scenario. Thus, PCB and PBDE pollution in slightly industrialized areas might also be considered including the study of streamwater residues. Actions towards minimizing pollutant transfer and movement from soil are necessary to reduce the fate of endosulfans and PCBs, while for PBDEs the development of guideline values is compulsory to accurately assess the pollution status of this watershed. Particularly, buffer strip areas along the riverbanks, keeping native vegetation, could be useful for the maintenance of biodiversity and trapping pollutants from runoff or soil erosion. Finally, preservation of macrophytes might contribute to lower pollutant levels in streamwater.

## Acknowledgements

This study was supported with grants from Universidad Nacional de Mar del Plata, ANPCyT (PICT-07/390), CONICET (PIP 5668) and the Spanish Ministry of Science and Innovation (CGL2007-60355) co-funded with European Feder funds. M. Gonzalez stay at CSIC was supported by CONICET and Incentivos de Carácter Científico y Técnico, Junta de Andalucía.

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