Original Article

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Running head: Passive sampling of pesticides and PCBs in water

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ABSTRACT

Water monitoring is of great importance, especially for waterbodies in agricultural or industrial areas. Grab sampling is a widely used technique for aquatic monitoring but represents only a snapshot of the contaminant levels at a specific point in time. Passive sampling, on the other hand, is an integrative technique which provides an average concentration of contaminants representative for its deployment period. Thus, the current contamination by organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs) and some currently used pesticides (CUPs) was assessed along the Quequén Grande River watershed using the integrative silicone rubber (SR) passive sampling technique in a year-long study. SR samplers were deployed at six sampling sites selected according to different land uses (agricultural-livestock production, agricultural and urban activities) during three periods in 2014 and 2015. OCPs were dominated by endosulfan (sum of α-, β-endosulfan, endosulfan sulfate = 0.15-23.4 ng/L). The highest endosulfan levels were registered during the pesticide application period (December–March), exceeding the international water quality guidelines for protecting freshwater biota (3 ng/L). Comparing with previous reports, no reduction in endosulfan levels were observed at the Quequén Grande River watershed. These results would suggest the illegal use of remaining stocks since water sampling was carried out after endosulfan ban in Argentina. Chlorpyrifos was the second major pesticide found in water (0.02-4.3 ng/L), associated with its widespread usage on soybean crops. A reduction in levels of legacy pesticides (heptachlors, DDTs, dieldrin and chlordanes) was evident when compared with previous reports from 2007. PCBs levels were very low indicating that probably only minor diffuse sources were still available along the Quequén Grande River watershed. This article is protected by copyright. All rights reserved

KEYWORDS: Passive sampler, watershed analysis, pesticides, polychlorinated biphenyls (PCBs), Argentina

3

INTRODUCTION

Water quality in agricultural watersheds is of great concern since residues of legacy and currently used pesticides (CUPs) are usually found in the aquatic environment (Reilly et al. 2012; Bonansea et al. 2013; Gonzalez et al. 2013). Organochlorine pesticides (OCPs) had been widely used for different crops in Argentina until progressively banned, being endosulfan the last prohibited in 2013 (SENASA 2011). This group of compounds is characterized by high hydrophobicity, persistence, toxicity and capacity for long-range transport (Tolosa et al. 1995). CUPs are a diverse group of herbicides, insecticides and fungicides that are considered relatively less persistent and, in many cases, more toxic than legacy pesticides (Kannan et al. 2006). On the other hand, watersheds are also often subjected to contaminants from domestic and industrial sources whenever associated with urbanized areas. Polychlorinated biphenyls (PCBs) represent an important class of industrial compounds that was used as dielectric and coolant fluids in electrical apparatus and lighting ballasts, additives in paints, plastics, hydraulic oils, adhesives and other industrial applications. PCBs and OCPs share many physico-chemical properties (eg. hydrophobicity, persistence, toxicity) and are listed as persistent organic pollutants (POPs) for banning by the Stockholm Convention (UNEP 2017). They are known to cause adverse effects on reproduction (Gross et al. 2002), immunological function (Dunier and Siwicki 1993), endocrine system (Vutukuru et al. 2016) and behavior (Sledge et al. 2011) of aquatic biota. Humans are also exposed to this contamination through food consumption, such as vegetables and different kind of meat including fish. Thus, considering the potential effects on biota and humans, the contamination of water bodies by pesticides and PCBs should be adequately addressed.

The collection of samples is the first step towards providing water quality information and obtaining representative samples are critical parts of any monitoring program. Although grab

4

sampling is the cheapest and most commonly used method, this technique provides only a

snapshot overview of the contaminant levels in a water body at a specific sampling time,

possibly missing short-term concentration variations (Vrana et al. 2005). Passive sampling is

an integrative technique that provides an average concentration of contaminants during the

deployment period. In the last two decades, many passive sampling devices have been

developed to sample different target contaminants in water, including metals (Allan et al.

2007), and hydrophilic (Alvarez et al. 2004) as well as hydrophobic organic chemicals

(Huckins et al. 1990; Adams et al. 2007). Silicone rubber (SR) passive sampler is a device for

monitoring hydrophobic organic chemicals. Different studies have utilized this sampler in field

deployment (Heltsley et al. 2005; Bragg et al. 2006; Smedes 2007). In particular, the robust

performance was demonstrated in the International Council for the Exploration of the Sea

(ICES) organized a passive sampling survey during 2006-2007 in coastal waters of 11

countries using SR passive samplers at 30 sites (Smedes et al. 2007). They are cheap, reusable

and have low transport resistance for uptake of chemicals due to the high diffusion of

compounds in the material (Rusina et al. 2010). They are also characterized by absorbing

compounds in a wide K_{ow} range (Booij et al. 2002; Rusina et al. 2007; Smedes et al. 2010),

providing a reliable method for aquatic monitoring of hydrophobic and also some hydrophilic

contaminants (Ahrens et al. 2015).

Quequén Grande River is the most important watershed (9900 km^2) in the Argentine Pampas

region. Previous studies carried out in the Quequén Grande River watershed showed the

presence of OCPs and PCBs in surface water (Gonzalez et al. 2012, 2013). However, these

results from grab sampling represent only a snapshot of the contamination. Thus, the aim of the

present work was to investigate the contamination by legacy pesticides, PCBs and some CUPs

along the Quequén Grande River watershed using the integrative SR passive sampling

5

technique in a year-long study. Considering all OCPs and PCBs are currently phased out in Argentina, it was expected to found relatively lower levels than those reported previously in the area. This study provides new information on levels and distribution of these pollutants, which is quite scarce in most countries of South America.

MATERIALS AND METHODS

Sampling sites

The Quequén Grande River watershed is situated in the south of Buenos Aires province of Argentina (37° - 38° S). Agricultural production is the main economic activity, although urban and industrial activities might be sources of contamination within this watershed. Six sites were selected along the upper, middle and lower Quequén Grande River watershed as representatives of areas predominantly under the influence of agricultural-livestock production, agricultural and urban activities, respectively (Figure 1 and Table S1- Supplementary Information).

Passive sampling

SRs sheets (AlteSil^{TM}, 600 x 600 mm, 0.5 mm thick, translucent) were purchased from Altec, United Kingdom. Prior to deployment, sheets were cut into 10 x 6 cm and Soxhlet pre-extracted using ethyl acetate for at least 100 h to remove sheets oligomers that may interfere with the chemical analysis. In order to estimate the in situ sampling rate, the sheets were spiked with performance reference compounds (PRCs), according to Smedes and Booij (2012). Briefly, 390 mL of methanol in a wide-mouth glass bottle was spiked with 0.9 μg of *p,p'*-DDD and 0.5 μg of *δ*-HCH. In the Quequén Grande River watershed these compounds were known to be absent or at that low levels that they would not bias PRC release measurement. Then, 130 SRs sheets were added and the bottle was shaken under stepwise addition of water over a week

6

period, to obtain 50% v/v methanol solution. The SRs sheets were wrapped in aluminum foil and stored in a freezer (-20 °C) until deployment.

The passive sampling device assembly is shown in Figure S1-Supplementary Information. Six SRs sheets were attached to the holders (2 sheets made one sample; i.e. n=3). Replicates were all deployed in the same cage. Devices were secured in the water column at approximately 1 m below the surface. SRs samplers were deployed for three periods of 4 to 6 weeks between July 2014 and July 2015 (See Table S1-Supplementary Information). At the end of the deployment period, the SR samplers were retrieved, rinsed with local water and biofilm was removed with a damp paper tissue. The cleaned SRs were wrapped in aluminum foil, and stored at -20 °C until analysis.

Extraction and clean up

Compounds were cold-extracted from the SRs according to the procedure described by Smedes and Booij (2012) with modifications as describe below. Briefly, sheets were transferred to a 250 mL wide-mouth bottle and spiked with 20 ng of PCB #103 (surrogate standard, Sigma Chemical Ltd., USA). Hexane (75 mL, analytical grade, Dorwil, Buenos Aires, Argentina) was added and the bottle was shaken overnight. Subsequently, the extraction was repeated using fresh solvent for 8 h. The extracts were combined and evaporated to 1 mL, followed by clean-up on activated silica gel (200 °C, 24 h). Extracts were concentrated to 1 mL and kept in sealed vials at -20 °C until instrumental analysis.

Instrumental analysis

Extracts were analyzed in a Shimadzu GC-17A gas chromatographer equipped with an electron capture detector (ECD). Aliquots of 1 µL were injected in splitless mode (275 °C) on a SPB-5 capillary column (30 m, 0.25 mm i.d., 0.25 µm film thickness, Supelco, Bellefonte, PA, USA).

7

The ECD was kept at 310 °C. The oven temperature program started at 100 °C, held for 1 min, followed by an increase of 5 °C/min up to 150 °C, held for 1 min, increase 1.5 °C/min up to 240 °C, and then 10 °C/min up to 300 °C, held for 10 min (Miglioranza et al. 2003). Analyzed compounds included: α-, β-, γ- and δ-HCH, α- and β-endosulfan, endosulfan sulfate, *p,p′*-DDT, *p,p′*-DDE, *p,p′*-DDD, α- and γ-chlordane, trans-nonachlor, aldrin, dieldrin, endrin, heptachlor, heptachlor epoxide, chlorpyrifos, trifluralin, and PCBs #8, 18, 28, 31, 44, 52, 66, 87, 101, 105, 110, 118, 123, 126, 128, 138, 149, 153, 156, 157, 167, 169, 170, 180, 187, 189, 195, 206 and 209.

Quality assurance and quality control

Procedural blanks were analyzed to check for possible contamination. Field blanks were also included, consisting of samplers that were not deployed but were exposed to air during deployment and recovery of exposed samplers. Some compounds were detected in blanks at levels between 0.1 and 0.4 ng per sampler. For the compounds found in blanks, method detection limits (MDLs) were calculated as three times the standard deviation of the blanks plus three standard deviations. For those analytes that were not detected in the blanks, the 1/2 instrumental detection limit (IDL) value was used for MDLs calculation. IDLs, estimated according to Keith et al. (1983) were in the range of 0.05 and 0.1 ng/mL for HCHs (α-, β-, γ- and δ-isomers), and between 0.1 and 0.3 ng/mL for other compounds. Final MDLs ranged between 0.025 and 1.3 ng per sampler (Table S2- Electronic Supplementary Information). The recoveries of surrogate standards were 90±15%.

8

Calculation of the chemical concentration in water

The mass of each analyte accumulated in SRs (N_t) can be transformed into aqueous

concentration (C_w) using the sampling rate (R_s) and SR–water partition coefficients (K_{pw}, listed

in Table S3- Electronic Supplementary Information) following Smedes and Booij (2012):

$$C_w = \frac{N_t}{K_{pw}\, m \left\{ 1 - \exp\left(-\frac{R_s\, t}{K_{pw}\, m} \right) \right\}} \tag{1}$$

Where m and t are the mass of the sampler and the deployment time, respectively. R_s is the

unknown in equation 1 and is governed by diffusion through the water boundary layer, of

which the thickness is determined by flow and turbulence conditions during deployment. The

R_s slightly decreases with increasing molecular size (lower diffusion). Consequently, R_s could

be modeled as a function of the molecular weight (M) and a proportionality factor (B), which

represents the influence of local turbulence conditions and includes unit conversion (Rusina et

al. 2007):

$$R_s = \frac{B}{M^{0.47}} \tag{2}$$

Release and uptake follow the same process and, consequently, R_s can be estimated from the

PRCs release. The modeled retained PRC fraction (f_m) is given by:

$$f_m = \exp\left(-\frac{R_s\, t}{K_{pw}\, m} \right) \tag{3}$$

and after combining equations 3 and 2, f_m is expressed as a function of B:

$$f_m = \exp\left(-\frac{B\,t}{M^{0.47}\,K_{pw}\,m}\right) \qquad (4)$$

The factor B is then estimated by fitting f_m to the measured retained PRC fractions (ratio of PRC amount after and before deployment) by using the nonlinear least squares method (Booij and Smedes 2010).

By applying the above procedure to the data, it was observed that B (and thus R_S) was mainly determined by one PRC (*p,p'*-DDD). Therefore, PRC data were combined for the three parallel samplers to increase the number of data points. This is justifiable as parallel samplers deployed in the same cage were showing equal R_s (Smedes 2007). Additionally, the *p,p'*-DDD used as PRC, was contained 7% *p,p'*-DDT providing an extra PRC. Including the *p,p'*-DDT as PRC and combining the results from triplicates, a better estimate for B could be obtained (see Figure S2 - Supplementary Information). The B obtained from fitting is then used to calculate R_s (equation 2), which is subsequently applied to calculate C_w (equation 1) from the average uptake of all three replicate samplers.

Clearly, the PRC selection was not ideal and, in hindsight, more PRC covering a larger hydrophobicity range would have been better. Nevertheless, uncertainties in R_s only affect the results for compounds with $\log K_{pw} > 5$ as other compounds attained equilibrium and the exponent in equation 2 equals zero (Smedes and Booij 2012).

RESULTS AND DISCUSSION

Distribution of OCPs, PCBs, chlorpyrifos and trifluralin along the Quequén Grande River watershed is shown in Figure 2. OCPs comprised the major percentage (22-95%) of the total analyzed contaminants, while endosulfans accounted for more than 80% of total OCPs. Technical endosulfan consists of α- and β-isomers in a ratio of 7:3, being endosulfan sulfate

10

the main metabolite in aquatic systems (Navarro et al. 2000). In the present study, endosulfan sulfate accounted for 62-97% of total endosulfans (sum of α-, β-endosulfan and endosulfan sulfate; Figure 3; Table 1) in the freely dissolved phase. The highest endosulfan levels at the Quequén Grande River were registered at L2 during period 2 (23.4 ng/L; Figure 3), which might be attributed to fresh inputs of endosulfan in the lower part of the watershed since sampling coincided with the pesticide application period. These highest results could possibly be explained by the illegal use of remaining stocks, since water sampling in the present study (2014-2015) was carried out after the endosulfan ban in Argentina by July 2013 (SENASA 2011). Except for site L2 (period 2), endosulfan levels (0.15 – 7.9 ng/L; Figure 3) were comparable to those reported for the same watershed in 2007 (1.5-7.5 ng/L; Gonzalez et al. 2012).

Silva-Barni et al. (2018) reported the presence of endosulfan in air samples from the Quequén Grande River watershed, with higher levels also overlapping the application period (December–March, summer in South Hemisphere). A possible explanation for the occurrence of this insecticide in water samples could be the spray drift during aerial application of pesticides on soybean crops, which is a common practice in the study area. Additionally, surface runoff from contaminated soils into Quequén Grande River surface water is also a potential input pathway of endosulfan. The rainy season in the study area coincides with the pesticide application period (December to March), which favors an increase of surface runoff (Leonard et al. 2000; Jergentz et al. 2004; Gonzalez et al. 2009a, 2009b). Heavy rainfalls events were observed over the Quequén Grande River watershed immediately after period 2 (675 mm during February 2015) which might increase endosulfan levels in water. In Mar Chiquita shallow lake (Córdoba, Argentina), the highest endosulfan concentrations were found in rainy and post-rainy season, coinciding with application and post-application periods of

11

pesticides (Ballesteros et al. 2014). Future studies in the area must focus on better assessing the effect of meteorological conditions on pesticide levels.

Occurrence of endosulfan in this watershed has also been reported in soils (Gonzalez et al. 2010; Lupi et al. 2016), sediments, stream water, groundwater (Gonzalez et al. 2012, 2013), macrophytes (Gonzalez et al. 2013), air (Silva-Barni et al. 2018), and fish (Silva-Barni et al. 2014). This data indicate a wide distribution of endosulfan in different compartments as a consequence of its use in the region. Similar levels of endosulfans were reported in water samples from other regions in Argentina, such as Mar Chiquita lake, Córdoba province (<dl-22.2 ng/L; Ballesteros et al. 2014) and Negro River, Argentine Patagonia (3.2 ng/L; Ondarza et al. 2012). Nevertheless, significantly higher levels have been reported in contaminated areas worldwide, such as Ganga River, India (739 ng/L; Leena et al. 2012), where endosulfan is currently used despite the Supreme Court of India has banned it.

Only at L2 (period 2), endosulfan (α- + β- = 6.6 ng/L) was close to the threshold levels established by the Argentine water quality guidelines for protecting freshwater biota (7 ng/L for the sum of α- + β-endosulfan; INA 2004) and surpassed international standards (3 ng/L; CCME 1999). Levels exceeding the guideline limits were previously registered in stream water of Quequén Grande River during a post-application period of 2007 (Gonzalez et al. 2012). Adverse effects of endosulfan have been reported in fish, including histological (Ballesteros et al. 2007; Silva-Barni et al. 2016), biochemical (Ballesteros et al. 2009) and behavioral alterations (Rehman 2006). Therefore, the level of endosulfan found at the lower area of Quequén Grande River watershed may potentially cause adverse effects to the aquatic organisms.

The prevalence of endosulfan sulfate in all water samples is also observed in similar studies carried out in other regions of Argentina, such as Córdoba (Río Suquía), where endosulfan

12

sulfate levels (<ld - 106.7 ng/L) were significantly higher than endosulfan isomers (<ld - 9.2 ng/L; Bonansea et al. 2013). Leonard et al. (2001) suggested that the prevalence of endosulfan sulfate in water bodies could be due to the persistence of this metabolite in soils after spraying, which, eventually, will enter surface waters. Additionally, the half-life times for endosulfan parent isomers in water are relatively short. Jonsson and Toledo (1993) reported half-lives of 22-27 h for α- and β-endosulfan, while Leonard et al. (2000) described half-lives of 3-7 days for endosulfan isomers and several weeks for endosulfan sulfate. Considering its short half-life in water, it is likely that the higher levels seen are associated with fresh inputs of endosulfan due to its illegal use in the area.

Concentrations of heptachlors, HCHs, DDTs, dieldrin and chlordanes were very low and/or below the detection limit in most samples (Table 1; Table S4 - Electronic Supplementary Information). For all these pesticides, no spatial or temporal pattern was noticeable, possibly because of their past use in the watershed, considering that they were banned more than 15 years ago in Argentina. The residues found indicate possible inputs from diffuse sources, such as atmospheric transport or remobilization and runoff of soils where they might have been trapped.

Heptachlor epoxide concentrations were in the range of <dl-0.004 ng/L (Table 1; Table S4 - Electronic Supplementary Information), while the parent compound (heptachlor) was below the detection limit for all samples. Higher concentrations of heptachlor were reported in 2007 (<dl-1.5 ng/L; Gonzalez et al. 2012) and 2012 (<dl-0.2 ng/L; Lupi et al. 2016) at the Quequén Grande River watershed, indicating a decrease in levels from 2007 to 2014-15. This insecticide was heavily used, mainly on potatoes crops, in the south of Buenos Aires province until forbidden in 1998.

13

γ-HCH levels ranged between <dl and 1 ng/L, while α- and β-isomers were not detected in any samples (Table 1; Table S4 - Electronic Supplementary Information). Gonzalez et al. (2012) found HCHs levels in the range of <dl-1.5 ng/L in surface water of Quequén Grande River watershed. Although the HCH technical mixture was banned in Argentina in 1998 for agriculture uses, the use of lindane (>99% γ-HCH) was allowed for the treatment of head lice infestations (health care) until 2011 (Della Ceca 2012).

Regarding DDTs, only the metabolite *p,p'*-DDE was detected in the range of <dl-0.004 ng/L (Table 1; Table S4 - Electronic Supplementary Information). Higher levels of DDTs were previously detected in water samples of Quequén Grande River watershed in 2007 (<ld-1.5 ng/L; Gonzalez et al. 2012), indicating a decrease in the inputs of DDTs to the environment. Previous studies have registered residues of *p,p'*-DDT in soil samples from the Quequén Grande River watershed (Lupi et al. 2016). This might be associated with the use of the acaricide Dicofol, which contains traces of DDT (Qiu et al. 2005). Aerobic metabolism of *p,p'*-DDT and consequent runoff from soils/sediments might explain the occurrence of *p,p'*-DDE in surface water of the Quequén Grande River.

Dieldrin and γ-chlordane were found at relatively low concentrations (<dl-0.02 ng/L; Table 1; Table S4 - Electronic Supplementary Information), indicating their past use in the watershed. The presence of these pesticides in surface water might be also consequence of different processes such as release from sediments, soil erosion and atmospheric transport. Gonzalez et al. (2012) found relatively higher levels of chlordanes (<dl-2 ng/L) and dieldrin (<dl-0.8 ng/L) in 2007 at the Quequén Grande River watershed, indicating also a reduction in levels of these legacy pesticides from 2007 to 2014-15.

Chlorpyrifos was the second most abundant pesticide found in water, accounting for 1.5-50% of total pesticide levels (Figure 2; Table 1; Table S4 - Electronic Supplementary Information).

14

Chlorpyrifos is one of the most-used insecticides in Argentina, mainly on soybean crops (Álvarez et al. 2013). As seen for endosulfan, site L2 (period 2) showed much higher levels of chlorpyrifos (4.3 ng/L) than any other studied site (0.02-0.4 ng/L). This is a recreational area called "Las Cascadas", where aquatic sports and fishing are the main activities. Despite this site is located at the lower watershed, which was classified as "urban", extensive agricultural activities are developed in the vicinity of this area. In aquatic systems, chlorpyrifos is rapidly removed from the water column through hydrolysis, photolysis and biological degradation, being 3, 5, 6-trichloropyridinol (TCP) the main metabolite (Racke 1993). Nevertheless, the sampling period when the highest levels were found (December 2014-January 2015) corresponds to the pesticide application period in the region (November to March), reflecting chlorpyrifos use at the lower Quequén Grande River watershed. In addition, soils/sediments runoff might also contribute to the occurrence of pesticides in the aquatic environment. The relatively high levels of both chlorpyrifos and endosulfan at the lower watershed might be attributed to a "funnel effect" of the watershed. This process involves the transport and concentration of contaminants from the headwaters to the mouth, resulting in higher concentrations in the lower watershed. In any case, the levels of chlorpyrifos (0.02-4.3 ng/L) detected at the Quequén Grande River watershed were below the threshold limits established by the Argentine National Water Institute for protecting freshwater biota (6 ng/L; INA 2005). Putting in perspective, levels were similar to those observed at Suquía River, Córdoba, Argentina (<dl-5.6 ng/L; Bonansea et al. 2013), but significantly lower than previously found at Brown (450 ng/L; Jergentz et al. 2005) and Arrecifes rivers (10800 ng/L; Marino and Ronco 2005). These two rivers are located at the north of Buenos Aires province (Argentina), which is the core soybean-producing zone, warning about how the massive use of pesticides impacts on water quality in agricultural areas.

Levels of trifluralin were very low, ranging from <dl-0.03 ng/L (Table 1; Table S4 - Electronic Supplementary Information). Higher levels have been reported in water samples from Beijing Guanting reservoir (3.4-5.1 ng/L; Xue et al. 2005) and streams and ponds near farms in three geographic areas across the United States of America (maximum value 2.1 ng/L; Reilly et al. 2012). Since trifluralin (a dinitroaniline herbicide) has relatively low water solubility (0.6 mg/L) and high soil affinity, water levels are usually low (Zimmerman et al. 2000). In addition, its agricultural use is not very extensive in Argentina, which also explained the water levels significantly lower than threshold levels established for drinking water (20000 ng/L; OMS 2006) and aquatic biota protection (200 ng/L; CCME 1999).

PCBs levels (Σ29PCBs= <dl-0.01 ng/L, Table 2; Table S5 - Electronic Supplementary Information) were lower than those reported in other regions of Argentina, such as Mar Chiquita lake, Córdoba province (Σ25PCBs= 0.3-7.3 ng/L; Ballesteros et al. 2014) and Negro river basin, Patagonia (Σ24PCBs$_{max}$= 5.9 ng/L; Ondarza et al. 2012). Inputs of PCBs to the environment could be associated with many sources, such as emissions from old transformers and stockpiles, landfills and clandestine dumping grounds and open burning that may still contain PCBs, as well as long-range atmospheric transport (Breivik et al. 2002).

In accordance with their solubility, freely dissolved aqueous PCBs profiles were dominated by #18, 44 and 52 congeners, accounting for 30, 26 and 33% of total PCBs, respectively. For #101, 110 and 118 congeners, lower levels were occasionally detected, representing less than 10% of total PCBs. Additionally, compared to lower molecular weight congeners, higher molecular weight congeners are more strongly associated with organic matter in colloidal or particle phase because of their higher hydrophobicity, reducing their proportion in the freely dissolved phase measured by passive sampling (Peven et al. 1996).

16

PCBs levels were below the national regulatory limits for aquatic biota protection (9 ng/L; INA 2004), posing no relevant risk to aquatic organisms. This threshold is established for unfiltered water samples. Passive sampling only accumulates the freely dissolved phase and higher levels could be present in the suspended particulate matter due to the hydrophobic nature of PCBs (Vilanova et al. 2001). However freely dissolved concentrations are considered a better measure for biota exposure than total concentrations including bound fractions (Smedes 1994; Reichenberg and Mayer 2006).

CONCLUSIONS

Among the analyzed compounds, endosulfan was the main contaminant in the Quequén Grande River watershed despite prohibited in Argentina since 2013, followed by chlorpyrifos, a widely used insecticide. These two pesticides showed the highest concentrations at the lower part of the watershed. No reduction in endosulfan levels was detected after the ban of endosulfan, suggesting that possibly during the present study residual stocks of endosulfan were still being used at the Quequén Grande River watershed. On the other hand, reduction in levels of heptachlors, DDTs, dieldrin and chlordanes from 2007 to 2014-15 was evident. PCBs levels were very low indicating that probably only minor diffuse sources were still available along the Quequén Grande River watershed.

Since SR passive sampling has shown to be a useful technique in determining pesticides and PCBs in the freely dissolved phase of water, it could be adopted by Argentine authorities as a routine tool for water quality monitoring of aquatic systems.

17

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DATA AVAILABILITY

Raw dataset and calculations tools are available from the corresponding author (fsilvabarni@gmail.com).

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24

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Figure 1: The Quequén Grande River watershed, Argentina, indicating the positions of the sampling sites. *U= upper, M= middle, L= lower zones.*

Figure 2: Spatial distribution of organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), chlorpyrifos and trifluralin in water (ng/L). *P1, P2 and P3 correspond to periods 1, 2 and 3, respectively. U= upper; M= middle; L= lower areas. SL= samplers lost during deployment. Note different scales for U2 and L2 graphs.*

Figure 3: Endosulfans (ng/L) at the sampling sites. P1, P2 and P3 correspond to periods 1, 2 and 3, respectively. *Endo =endosulfan; U= upper; M= middle; L= lower areas. SL= samplers lost during deployment. Note different scales for U2 and L2 graphs.*

26

Table 1. Average (±SD) concentration (pg/L) of pesticides detected in water along the Quequén Grande River watershed.

Compound	Sites					
	L1	L2	M1	M2	U1	U2
Heptachlor epoxide	<dl	<dl	<dl	3.6	3±0.6	2.2±1.4
γ-HCH	<dl	494±580	7.2±5.6	8.3	<dl	65±12
p,p'-DDE	1±0.1	1.8±1.3	0.3±0.1	0.6±0.4	0.5	0.6±0.4
Dieldrin	2±1.3	10.3±6.7	1.6±0.8	5±3.5	1.3±1.1	5.8±3.7
γ-chlordane	2.±0.4	3.2±2.5	0.3±0.2	0.5±0.3	0.8±0.5	1.6±1.1
α−endosulfan	15.6±4.5	1086±1600	9.3±5.2	10.3±5.2	29.5±1.7	9±5.3
β−endosulfan	60±20	1230±1850	21±28	24±22	26±5.4	56±60
Endosulfan sulfate	780±676	7487±7190	524±670	833±657	470±286	2850±4045
Chlorpyrifos	265±170	1621±1995	48.1±59	206±195	171±182	95±37
Trifluralin	1.9±0.8	13.5±1.1	3.4±2.4	3.1±1.2	3.6±2.1	3.1±1.1

<dl = below detection limit; U = upper, M = middle and L = lower areas; SL = samplers lost during deployment. All concentrations correspond to average values over the three deployments periods.

Table 2. Average (±SD) concentration (pg/L) of PCBs detected in water along the Quequén Grande River watershed.

Compound	Sites[a]				
	L2	M1	M2	U1	U2
#18	4.7±2	1.5±1.1	0.4	3.3±0.3	1.7±0.6
#52	5.2±5.3	0.4±0.2	1.7±1.3	0.6±0.5	1.4±1.4
#44	<dl	1.2±1	2.5±3.1	1.5±0.5	1.3±1.1
#101	<dl	<dl	<dl	SL	0.6±0.3
#110	<dl	<dl	0.3	<dl	0.5±0.2
#118	<dl	1.7	<dl	1.6±0.1	<dl
Σ29PCBs	9.9±4.9	4.8±1.7	4.9±2.4	7±2.3	5.5±0.9

<dl = below detection limit; U = upper, M = middle and L = lower areas; SL = samplers lost during deployment.
[a] PCBs levels were below detection limit at L1 site.
All concentrations correspond to average values over the three deployments periods.
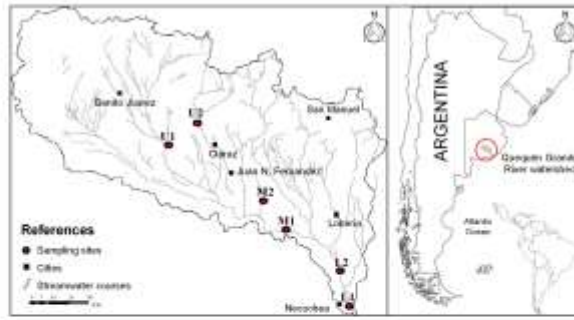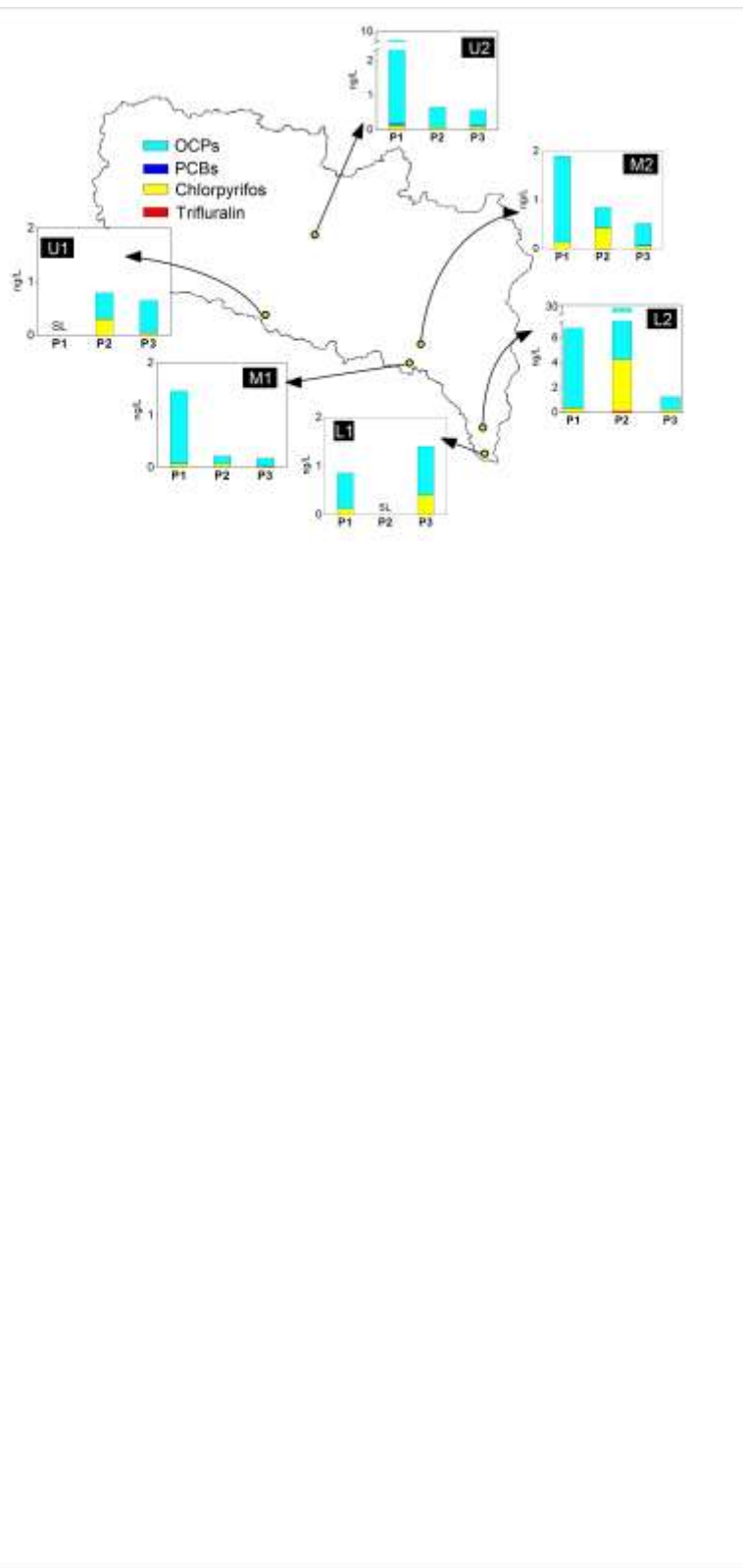
Figure 1

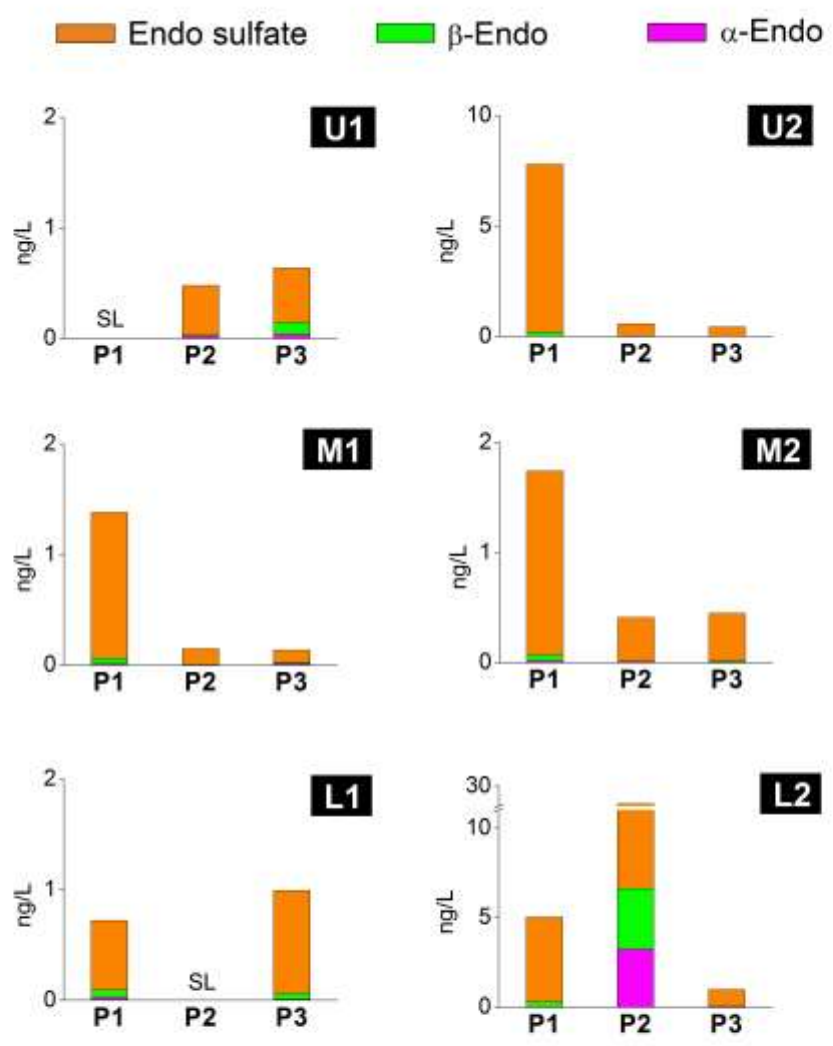**Figure 2**

30

Figure 3