Passive Sampling of Pesticides and Polychlorinated Biphenyls Along the Quequén Grande River Watershed, Argentina

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Abstract: Water monitoring is of great importance, especially for water bodies 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 that provides an average concentration of contaminants representative of its deployment period. Thus, the current contamination by organochlorine pesticides, polychlorinated biphenyls (PCBs), and some currently used pesticides was assessed along the Quequén Grande River watershed (Argentina) using the integrative silicone rubber passive sampling technique in a year-long study. Silicone rubber samplers were deployed at 6 sampling sites selected according to different land uses (agricultural–livestock production, agricultural and urban activities) during 3 periods in 2014 and 2015. The organochlorine pesticides 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). Compared with previous reports, no reductions in endosulfan levels were observed at the Quequén Grande River watershed. These results would suggest the illegal use of remaining stocks because water sampling was carried out after endosulfan was banned 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 compared with previous reports from 2007. Levels of PCBs were very low, indicating that probably only minor diffuse sources were still available along the Quequén Grande River watershed. Environ Toxicol Chem 2019;38:340–349. © 2018 SETAC

Keywords: Passive sampler; Watershed analysis; Pesticides; Polychlorinated biphenyls; Argentina

INTRODUCTION

Water quality in agricultural watersheds is of great concern because residues of legacy and currently used pesticides are usually found in the aquatic environment (Reilly et al. 2012; Bonansea et al. 2013; Gonzalez et al. 2013). Organochlorine pesticides had been widely used for different crops in Argentina until they were progressively banned, endosulfan being the last prohibited in 2013 (Servicio Nacional de Sanidad y Calidad Agroalimentaria 2011). This group of compounds is characterized by high hydrophobicity, persistence, toxicity, and capacity for long-range transport (Tolosa et al. 1995). Currently used pesticides 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). In addition, when watersheds are associated with urbanized areas, they are also often contaminated from domestic and industrial sources. Polychlorinated biphenyls (PCBs) represent an important class of industrial compounds that were used as dielectric and coolant fluids in electrical devices and lighting ballasts, as additives in paints, plastics, hydraulic oils, and adhesives, and in other industrial applications. Polychlorinated biphenyls and organochlorine pesticides share many physicochemical properties (e.g., hydrophobicity, persistence, toxicity) and are listed as banned persistent organic pollutants (POPs) by the Stockholm Convention (United Nations Environmental Programme 2017). They are known to cause adverse effects on reproduction (Gross et al. 2002), immunological function (Dunier and Siwicki 1993), the endocrine system (Vutukuru et al. 2016), and behavior (Sledge et al. 2011) of aquatic biota. Humans are also exposed to this contamination.
through consumption of foods such as vegetables and different kinds of meat and fish. Thus, considering the potential effects on biota and humans, the contamination of water bodies by pesticides and PCBs should be adequately addressed.

Sample collection is the first step toward providing water quality information, and obtaining representative samples is a critical part of any monitoring program. Although grab 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 2 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). The silicone rubber 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, its robust performance was demonstrated when the International Council for the Exploration of the Sea organized a passive sampling survey during 2006 to 2007 in coastal waters of 11 countries using silicone rubber passive samplers at 30 sites (Smedes et al. 2007). The samplers are cheap and reusable and have low transport resistance for uptake of chemicals due to the high diffusion of compounds in the material (Rusina et al. 2010a). They are also characterized by their ability to absorb compounds over a wide octanol/water partition coefficient ($K_{OW}$) 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 km²) in the Argentine Pampas region. Previous studies carried out in the Quequén Grande River watershed showed the presence of organochlorine pesticides 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 study was to investigate the contamination by legacy pesticides, PCBs, and some currently used pesticides along the Quequén Grande River watershed using the integrative silicone rubber passive sampling technique in a year-long study. Considering that all organochlorine pesticides and PCBs have been phased out in Argentina, we expected to find relatively lower levels than those reported previously in the area. The present study provides new information on the levels and distribution of these pollutants, data that are scarce for most South American countries.

### 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 (U), middle (M), and lower (L) Quequén Grande River watershed as representative of areas predominantly under the influence of agricultural–livestock production, and agricultural and urban activities, respectively (Figure 1 and Supplemental Data, Table S1).

#### Passive sampling

Silicone rubber sheets (AlteSil™, 600 × 600 mm, 0.5 mm thick, translucent) were purchased from Altec. Prior to deployment, sheets were cut into 10- × 6-cm pieces and Soxhlet pre-extracted using ethyl acetate for at least 100 h to remove sheets oligomers that may interfere with the chemical analysis. 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 $p,p'$-dichlorodiphenyldichloroethane (DDD) and 0.5 μg of $p$-hexachlorocyclohexane (HCH). In the Quequén Grande River watershed these compounds were known to be absent or at such low levels that they would not bias PRC release measurement. Then 130 silicone rubber sheets were added, and the bottle was shaken under stepwise addition of water over a 1-wk period, to obtain 50% v/v methanol solution. The silicone rubber sheets were wrapped in aluminum foil and stored in a freezer (–20 °C) until deployment.

The passive sampling device assembly is shown in the Supplemental Data, Figure S1. Six silicone rubber sheets were attached to the holders (2 sheets made one sample, i.e., $n \equiv 3$). Replicates were all deployed in the same cage. Devices were secured in the water column at approximately 1 m below the surface. Silicone rubber samplers were deployed for 3 periods of 4 to 6 wk between July 2014 and July 2015 (Supplemental Data, Table S1). At the end of the deployment period, the silicone rubber samplers were retrieved and rinsed with local water, and then biofilm was removed with a damp paper tissue. The cleaned silicone rubber sheets were wrapped in aluminum foil, and stored at –20 °C until analysis.

#### Extraction and clean-up

Compounds were cold-extracted from the silicone rubber sheets according to the procedure described by Smedes and Booij (2012) with modifications as described below. Briefly, sheets were transferred to a 250-mL wide-mouth bottle and spiked with 20 ng of PCB 103 (surrogate standard; Sigma Chemical). Hexane (75 mL, analytical grade; Dorwil) 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 chromatograph equipped with an electron capture detector (ECD). Aliquots of 1 μL were injected in splitless mode (275 °C) onto an SPB-5 capillary column (30 m, 0.25 mm i.d., 0.25-μm film thickness; Supelco). The ECD was kept at 310 °C. The oven temperature program was started at 100 °C, held for 1 min, followed by an increase of 5 °C/min up to 150 °C, held for 1 min, increased by 1.5 °C/min up to 240 °C, and then by 10 °C/min up to 300 °C, and 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’-dichlorodiphenyltrichloroethane (DDT), p,p’-(dichlorodiphenyldichloroethylene (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, 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/sampler. For the compounds found in blanks, method detection limits (MDLs) were calculated as 3 times the standard deviation of the blanks plus 3 standard deviations. For those analytes that were not detected in the blanks, the 1/2 instrumental detection limit (IDL) value was used for MDL calculations. The 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/sampler (Supplemental Data, Table S2). The recoveries of surrogate standards were 90 ± 15%.

**Calculation of the chemical concentration in water**

The mass of each analyte accumulated in silicone rubber samplers (N) can be transformed into aqueous concentration (C) using the sampling rate (R) and silicone rubber/water partition coefficients (Kpw; listed in the Supplemental Data, Table S3) following Smedes and Booij (2012):

\[
C = \frac{N}{K_{pw}m \left(1 - \exp\left(-\frac{R_s t}{K_{pw}m}\right)\right)}
\]

where m and t are the mass of the sampler and the deployment time, respectively. The R value is the unknown in Equation 1 and is governed by diffusion through the water boundary layer, whose thickness is determined by flow and turbulence conditions during deployment. The R value slightly decreases with increasing molecular size (lower diffusion). Consequently, R can 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. 2010b):

\[
R_s = \frac{B}{M^{0.47}}
\]

Release and uptake follow the same process and, consequently, R can be estimated from the PRC release.

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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.
PRC fraction \( (f_m) \) is given by:

\[
f_m = \exp\left(-\frac{R_s t}{K_{pw} m}\right)
\]  

(3)

and after Equations 3 and 2 are combined, \( f_m \) is expressed as a function of \( B \):

\[
f_m = \exp\left(-\frac{\beta t}{M_0^{0.47} K_{pw} m}\right)
\]  

(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 3 parallel samplers to increase the number of data points. This is justifiable because parallel samplers deployed in the same cage were showing equal \( R_s \) (Smedes 2007). In addition, the \( p,p' \)-DDD used as the PRC contained 7% \( p,p' \)-DDT, providing an extra PRC. By including the \( p,p' \)-DDT as the PRC and combining the results from triplicates, a better estimate for \( B \) could be obtained (Supplemental Data, Figure S2). The \( B \) obtained from fitting was then used to calculate \( R_s \) (Equation 2), which was subsequently applied to calculate \( C_w \) (Equation 1) from the average uptake of all 3 replicate samplers.

Clearly, the PRC selection was not ideal and, in hindsight, more PRCs covering a larger hydrophobicity range would have been better. Nevertheless, uncertainties in \( R_s \) only affect the results for compounds with \( \log K_{pw} > 5 \) because other compounds attained equilibrium and the exponent in Equation 2 = 0 (Smedes and Booij 2012).

**RESULTS AND DISCUSSION**

The distribution of organochlorine pesticides, PCBs, chlorpyrifos, and trifluralin along the Quequén Grande River watershed is shown in Figure 2. Most of the total contaminants analyzed were organochlorine pesticides (22–95%), and endosulfans accounted for >80% of the total organochlorine pesticides. Technically, endosulfan consists of \( \alpha \)- and \( \beta \)-isomers in a ratio of 7:3, with endosulfan sulfate being the main metabolite in aquatic systems (Navarro et al. 2000). In the present study, endosulfan sulfate accounted for 62 to 97% of the total endosulfans (sum of \( \alpha \)- and \( \beta \)-endosulfan and endosulfan sulfate; Figure 3 and Table 1) in the freely dissolved phase. The highest endosulfan levels in the Quequén Grande River were

![Figure 2](image-url)
registered at site 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 because sampling coincided with the pesticide application period. These highest results could possibly be explained by the illegal use of remaining stocks, because water sampling in the present study (2014–2015) was carried out after endosulfan was banned in Argentina (by July 2013; Servicio Nacional de Sanidad y Calidad Agroalimentaria 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), which favors an increase of surface runoff (Leonard et al. 2000; Jergentz et al. 2004; Gonzalez et al. 2009a, 2009b). Heavy rainfall 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 the shallow Mar Chiquita Lake (Córdoba, Argentina), the highest endosulfan concentrations were found in rainy seasons and just after, coinciding with application and postapplication periods of pesticides (Ballesteros et al. 2014). Future studies in the area should 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).

**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.

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TABLE 1: Average (± standard deviation) concentration (pg/L) of pesticides detected in water along the Quequén Grande River watershed

| Compound               | Site          | 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  |
| a-Endosulfan           | 15.6 ± 4.5    | 1086 ± 1600| 9.3 ± 5.2  | 10.3 ± 5.2 | 29.5 ± 1.7 | 9 ± 5.3    |
| b-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  |

*aAll concentrations correspond to average values over the 3 deployments periods.
<dl = below detection limit; U = upper, M = middle and L = lower areas; γ-HCH = γ-hexachlorocyclohexane; p,p’-DDE = p,p’-dichlorodiphenyldichloroethylene.

2018), and fish (Silva-Barni et al. 2014). These 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 (below the detection limit to 22.2 ng/L; Ballesteros et al. 2014), and the Negro River, Argentine Patagonia (3.2 ng/L; Ondarza et al. 2012). However, significantly higher levels have been reported in contaminated areas worldwide, such as the Ganga River in India (739 ng/L; Leena et al. 2012), where endosulfan is currently used even though the Indian Supreme Court has banned it.

Only at L2 (period 2) was endosulfan (α + β-endosulfan = 6.6 ng/L) 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; Instituto Nacional del Agua 2004a) and surpassed international standards (3 ng/L; Canadian Council of Ministers of the Environment 1999). Levels exceeding the guideline limits were previously registered in stream water of Quequén Grande River during a 2007 postapplication period (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 the Quequén Grande River watershed may potentially cause adverse effects to the aquatic organisms.

The prevalence of endosulfan sulfate in all water samples has also been observed in similar studies carried out in other regions of Argentina, such as Córdoba (Ro Suquía), where endosulfan sulfate levels (below the detection limit to 106.7 ng/L) were significantly higher than endosulfan isomers (below the detection limit to 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, meaning that it will eventually enter surface waters. In addition, the half-life times for endosulfan parent isomers in water are relatively short. Jonsson and Toledo (1993) reported half-lives of 22 to 27 h for α- and β-endosulfan, and Leonard et al. (2000) noted half-lives of 3 to 7 d for endosulfan isomers and several weeks for endosulfan sulfate. Considering its short half-life in water, it is likely that the higher levels are associated with fresh inputs of endosulfan from 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 and Supplemental Data, Table S4). 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 yr 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 below the detection limit to 0.004 ng/L (Table 1 and Supplemental Data, Table S4), whereas the parent compound (heptachlor) was below the detection limit for all samples. Higher concentrations of heptachlor were reported in 2007 (below the detection limit to 1.5 ng/L; Gonzalez et al. 2012) and 2012 (below the detection limit to 0.2 ng/L; Lupi et al. 2016) in the Quequén Grande River watershed, indicating a decrease in levels from 2007 to 2014/2015. This insecticide was heavily used, mainly on potatoes crops, in the south of Buenos Aires Province until it was banned in 1998.

Levels of γ-HCH ranged between below the detection limit and 1 ng/L, whereas the α- and β-isomers were not detected in any samples (Table 1 and Supplemental Data, Table S4). Gonzalez et al. (2012) found HCH levels in the range of below the detection limit to 1.5 ng/L in surface water of the Quequén Grande River watershed. Although the HCH technical mixture was banned in Argentina in 1998 for agricultural uses, the use of lindane (>99% γ-HCH) was allowed for the treatment of head lice infestations (health care) until 2011 (Della Ceca 2012).

In terms of the DDTs, only the metabolite p,p’-DDE was detected in the range of below the detection limit and 0.004 ng/L (Table 1 and Supplemental Data, Table S4). Higher levels of DDTs were previously detected in water samples of the Quequén Grande River watershed in 2007 (below the detection limit to 1.5 ng/L; Gonzalez et al. 2012), indicating a decrease in inputs of DDTs to the environment. Previous studies have registered residues of p,p’-DDT in soil samples from the...

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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 \( \gamma\)-chlordane were found at relatively low concentrations (below the detection limit to 0.02 ng/L; Table 1 and Supplemental Data, Table S4), indicating their past use in the watershed. The presence of these pesticides in surface water might also be explained by factors such as release from sediments, soil erosion, and atmospheric transport. Gonzalez et al. (2012) found relatively higher levels of chlordanes (below the detection limit to 2 ng/L) and dieldrin (below the detection limit to 0.8 ng/L) in 2007 at the Quequén Grande River watershed, also indicating a reduction in levels of these legacy pesticides from 2007 to 2014/2015.

Chlorpyrifos was the second most abundant pesticide found in water, accounting for 1.5 to 50% of total pesticide levels (Figure 2, Table 1, and Supplemental Data, Table S4). 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) had much higher levels of chlorpyrifos (4.3 ng/L) than any other site studied (0.02–0.4 ng/L). This is a recreational area called Las Cascadas, where aquatic sports and fishing are the main activities. Even though this site is located at the lower watershed, which was classified as “urban,” extensive agricultural activities take place in the vicinity. In aquatic systems, chlorpyrifos is rapidly removed from the water column through hydrolysis, photolysis, and biological degradation, with 3, 5, 6-trichloropyridinol being 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–March), reflecting the use of chlorpyrifos in the lower Quequén Grande River watershed. In addition, soil/sediment 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 so-called funnel effect, involving 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; Instituto Nacional del Agua 2005). In perspective, levels were similar to those observed at Suquía River, Córdoba, Argentina (below the detection limit to 5.6 ng/L; Bonanse et al. 2013), but were significantly lower than those previously found at the Brown (450 ng/L; Jergentz et al. 2005) and Arrecifes Rivers (10 800 ng/L; Marino and Ronco 2005). These 2 rivers are located in northern Buenos Aires Province, which is the core soybean-producing area; thus we have an indication of how the massive use of pesticides impacts water quality in agricultural areas.

Levels of trifluralin were very low, ranging from below the detection limit to 0.03 ng/L (Table 1 and Supplemental Data, Table S4). Higher levels have been reported in water samples from the Beijing Guanting reservoir in China (3.4–5.1 ng/L; Xue et al. 2005) and streams and ponds near farms in 3 geographic areas across the United States (maximum value 2.1 ng/L; Reilly et al. 2012). Because trifluralin (a dinitroaniline herbicide) has a 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 explains why the water levels were significantly lower than the threshold levels established for drinking water (20 000 ng/L; Organización Mundial de la Salud 2006) and aquatic biota protection (200 ng/L; Canadian Council of Ministers of the Environment 1999).

Levels of PCBs (\( \Sigma 29\)PCBs = below the detection limit to 0.01 ng/L, Table 2 and Supplemental Data, Table S5) were lower than those reported in other regions of Argentina, such as Mar Chiquita Lake, Córdoba Province (\( \Sigma 25\)PCBs = 0.3–7.3 ng/L; Ballesteros et al. 2014), and the Negro River basin, Patagonia (\( \Sigma 24\)PCBmax = 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 <10% of total PCBs. In addition, compared with lower molecular weight congeners, higher molecular weight congeners are more strongly associated with organic matter in the colloid or particle phase because of their higher hydrophobicity, which reduces their proportion in the freely dissolved phase measured by passive sampling (Peven et al. 1996).

Levels of PCBs were below the national regulatory limits for aquatic biota protection (9 ng/L; Instituto Nacional del Agua 2004b), posing no relevant risk to aquatic organisms. This threshold was established for unfiltered water samples. Passive sampling only accumulates the freely dissolved phase, and

**TABLE 2:** Average (± standard deviation) concentration (pg/L) of polychlorinated biphenyls (PCBs) detected in water along the Quequén Grande River watershed

| Compound | Siteb | 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 ± 0.1 | 2.5 ± 0.3 | 1.5 ± 0.5 | 1.3 ± 1.1 |
| 101      |       | <dL | <dL | <dL | 5L | 0.6 ± 0.3 |
| 110      |       | <dL | <dL | 0.3 | <dL | 0.5 ± 0.2 |
| 118      |       | <dL | 1.7 | <dL | 1.6 ± 0.1 | <dL |
| \( \Sigma 29\)PCBs |       | 9.9 ± 4.9 | 4.8 ± 1.7 | 4.9 ± 2.4 | 7 ± 2.3 | 5.5 ± 0.9 |

*All concentrations correspond to average values over the 3 deployment periods.

**b**Polychlorinated biphenyl levels were below detection limit at the L1 site. <dL = below detection limit; U = upper, M = middle, and L = lower areas.

SL = samplers lost during deployment.
higher levels could be present in the suspended particulate matter due to the hydrophobic nature of PCBs (Vilanova et al. 2005). However, freely dissolved concentrations are considered a better measure of 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 even though it has been banned in Argentina since 2013, followed by chlorpyrifos, a widely used insecticide. These 2 pesticides had the highest concentrations at the lower part of the watershed. No reduction in endosulfan levels was detected after the ban took effect, suggesting that during the present study residual stocks of endosulfan might have been used in the Quequén Grande River watershed. In contrast, reductions in levels of heptachlor, DDTs, dieldrin, and chlordane from 2007 to 2014/2015 were evident. Levels of PCBs were very low, indicating that probably only minor diffuse sources were still available along the Quequén Grande River watershed.

Because silicone rubber passive sampling has been shown to be a useful technique in determining levels of 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.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.4325.

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Data Accessibility—The raw dataset and calculations tools are available from the corresponding author (fsilvabarni@gmail.com).

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