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Occurrence and fate of pesticides in the Argentine stretch of the Paraguay-Paraná basin

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Abstract The Argentine stretch of the del Plata basin crosses regions devoted to extensive and intensive agriculture mostly with chemical pest control. The utilization of pesticides in the region has increased 900% in the last two decades associated with the introduction of biotech crops and direct-seeding techniques. Our objective was to study the occurrence, concentration, and fate of pesticides in surface water and bottom sediments of the principal tributaries and main watercourse of the Paraguay-Paraná River. We sampled 22 sites in the distal positions of the main affluents and main watercourse of the Paraná and report here results from two monitoring campaigns (2010–2012). Surface water and bottom sediments were analyzed according to standardized methods by matrix-solid-phase dispersion and liquid-liquid extraction, respectively. Twenty-three pesticide compounds were analyzed by gas chromatography. The results from both campaigns indicated a generalized but variable distribution in the concentrations detected throughout the basin. The ranges of total measured pesticide concentrations in water and sediments were, respectively, 0.004–6.62 μg/l and 0.16–221.3 μg/kg dry weight. Endosulfans, cypermethrin, and chlorpyrifos were ubiquitous compounds in both environmental compartments and quantitatively the most relevant. All concentrations detected in water were over the recommended guidelines for the protection of aquatic biota. The partitioning indicated a higher affinity for the sediments. Agricultural activity is the source of pesticide-pollution loads, transported by tributaries that reach the main watercourse and alter the quality of the aquatic ecosystem.

Keywords GC-μECD · Pesticide fate · Environmental partitioning · Water/sediment

Introduction

In the 1980s, and most intensively in the last decade, a series of changes occurred that altered the dynamic of agricultural production (Bisang 2004). Since then, the new production model of agriculture has become associated with novel achievements in genetic engineering (Morales and Schaper 2004) and mostly based on using synthetic pesticides for the control of pests (Brechelt 2004). As a consequence of the increase in pesticide use, residues have been detected in different environmental compartments worldwide (Li et al. 2014). Accordingly—and within the international context—profound changes have occurred in the country side of

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Argentina, consolidating an intensified production model towards industrialized continuous agriculture (Leguizamón 2013). Direct seeding of soybean displaced traditional methods and crops, as did cattle rearing. Pesticide consumption has increased 900% during the last 23 years, while the cultivated area by only 70% along with an increment in yield of only 50% (CASAFE 2015). The physicochemical properties of pesticides such as volatility, water solubility, sorption, and persistence together with characteristic environmental conditions and spraying techniques determine the transport and fate of those compounds (Loewy 2011). Pesticides can potentially enter surface water by several routes and be partitioned in bottom sediments even when appropriately used in accordance with good agricultural practices. Spray drift, surface runoff, and field drainage are relevant routes of exposure plus contamination may occur via groundwater infiltration (Katagi 2006). Furthermore, many pesticides can persist for long periods within an ecosystem. Organochlorine insecticides, for instance, were still detectable in surface waters 20 years after their use had been banned (Arias Estévez et al. 2007). Research on the occurrence of pesticides in water bodies of the Pampean region, one of the most significant agricultural areas of Argentina, is scarce, and the existing compounds are mainly present within the core production sector (Rovedatti et al. 2001; Peruzzo et al. 2003; Jergentz et al. 2005; Marino and Ronco 2005; Ronco et al. 2008, 2011, 2016 Di Marzio et al. 2010; Mugni et al. 2011; Demetrio 2012; González et al. 2012; Bonansea et al. 2013; Ballesteros et al. 2014; De Gerónimo et al. 2014; Hunt et al. 2016). In view of the extent and magnitude of this issue, a knowledge concerning the concentration levels of pesticides in representative ecosystems of the region and the occurrence of the diverse chemical families in environmental compartments resulting from both intensive and extensive agriculture is highly relevant.

The del Plata basin which is the second largest in South America on the basis of its drainage area of 3,200,000 km^2 represents for Argentina a strategic resource in itself since that watershed holds the main fluvial and rainfall richness and contains, along the Paraná River, most of the population of the country (Ronco et al. 2011; Peluso et al. 2013). That water accordingly is being used for human consumption, recreation, fishing, and navigation. The main-point sources of pollution are the untreated domestic or industrial effluents or those along with diffuse inputs from agriculture runoff, livestock, resource extraction, and urban landfill that leach a heterogeneous load of pollutants directly into the system (PIT-AP 2010).

The new agricultural-production model involving synthetic pesticide use has become thoroughly established in the region. Furthermore, information on the environmental impact of pesticides is scarce, and knowledge of the tributary inputs into the Argentine stretch of the main course of the Paraná is fragmentary. Hence, the objective of this investigation was to determine the occurrence, concentration, and fate of pesticides in surface water and bottom sediments of the principal tributaries and main course of the Paraguay-Paraná River.

Material and methods

Study area and sampling

The water and sediments were sampled during two monitoring campaigns on October through November 2010 and June through July 2012 conducted on the scientific vessel Luis F. Leloir from the Prefectura Naval Argentina within a survey program that started in 2004 (SAyDS-PNA-UNLP 2007). The sampling was done at 22 sites along the Paraguay-Paraná River and tributaries (Fig. 1). Twenty of the samples were taken at the confluence of the principal tributaries within the Paraguay or Paraná rivers and the rest within the main Paraná watercourse. At each site, a 150-ml water sample was extracted from the first 50 cm of the water column along with 500 g of bottom sediment by means of an Eckman-type dredge. The transportation, conservation, and storage followed the technical recommendations of APHA (1998) and Kennedy et al. (1998).

Pesticides studied

The list of compounds analyzed comprised 23 pesticides, suggested by both the Argentine National Committee for Research on Agrochemicals along with the persistent organic pollutants derived from the Stockholm Agreement (SC 2008). These compounds are grouped as the organochlorine pesticides and their metabolites (OCls, $n = 16$) aldrin, endosulfans (the I and II isomers), the dichloro-diphenyl-trichloroethane (DDT) residues (pp′-DDD, pp′, DDT, op′-DDT, op′-DDE, and pp′-DDE), dieldrin, endrin, heptachlor, heptachlor

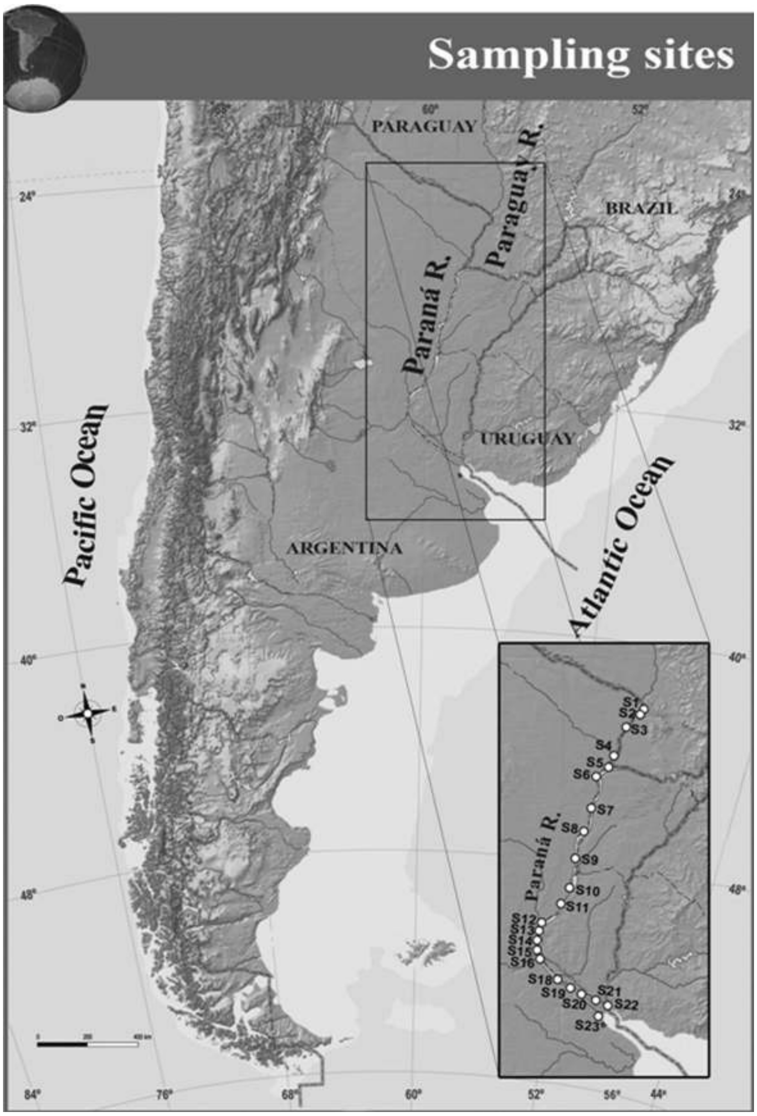

Fig. 1 Study area with the location of the 22 sampling sites in distal positions from the tributaries and the main Paraná River watercourse. *S1* Pilcomayo River, *S2* Paraguay River (border), *S3* Monte Lindo Stream, *S4* Bermejo River, *S5* Paraguay River (mouth), *S6* Negro River, *S7* Santa Lucia River, *S8* Paraná River (main course), *S9* Corrientes River, *S10* Guayquiraró River, *S11* Feliciano River, *S12* Salado River, *S13* Coronda River, *S14* Carcarañá River, *S15* San Lorenzo River, *S16* Saladillo River, *S17* Paraná River (main water course, Rosario), not studied in the present campaigns, *S18* Pavón Stream, *S19* Ramallo River, *S20* Arrecifes River, *S21* Areco River, *S22* Paraná River (main course), *S23* Luján River

epoxide, the α, ß, and γ isomers of hexachlorocyclohexane (HCH), and methoxychlor; the organophosphorus pesticides (OPs, $n = 3$) diazinon, chlorpyrifos, and methyl parathion; and the pyrethroids (PYRs, $n = 4$) lambda cyhalothrin, cypermethrin, tetramethrin, and permethrin.

Analytical methods

Extraction of OCls, OPs, and PYRs

Whole water was extracted with dichloromethane according to Method 3510C (USEPA 1996), followed by a cleanup with florisil (Method 3620C, USEPA 2014). The extraction and cleanups for the sediment samples were done by matrix solid-phase dispersion (MSPD) following the method described by Lozowicka et al. (2012). A portion of 3 g of homogenized wet sediment was dried at room temperature to constant weight, followed by MSPD. In that procedure, a portion of the dry sediment was dispersed with florisil and the mixture introduced into a glass chromatographic column 10 mm in internal diameter and 40 cm in length, previously loaded with silica gel and anhydrous sodium sulfate. The system was first eluted with a mixture of 4:1 hexane/acetone followed by 1:2:2 hexane/acetone/ethyl acetate. Both water and sediment extracts were concentrated by rotoevaporation (120 rpm, 40 °C, and

100 mmHg) and reduced to dryness under a stream of N_2 at room temperature. The concentrated samples were resuspended in *n*-hexane for further instrumental analysis. The concentrations measured are expressed as micrograms per liter and micrograms per kilogram dry weight for water and sediments, respectively.

Analytical determination

Pesticides were identified and quantified by GC-μECD through the use of an Agilent 6890N chromatograph, equipped with a DB-5 (15 m × 0.53 mm i.d. ×1.5 μm film thickness) column. A volume of 2 μl of sample was injected splitless (injector temperature, 250 °C) with temperature-gradient separation at an oven-temperature range of 80–250 °C and the detector set at 290 °C. Hydrogen was used as the carrier and nitrogen as the make-up gas (Ballesteros et al. 2014). The identification and quantification of compounds were performed by injection of OCl, OP, and PYR standard solutions. The ChemStation software version REV.A.10.02 was used for the system operation. Quantification was done by means of an external calibration curve within the range 0–20 μg/l and through a measurement of the area under the chromatographic peaks, after considering the dilution effected with each of the two matrices and the recovery of each compound.

Chemicals and reagents

The pesticide-residual-grade acetone, dichloromethane, and *n*-hexane used for sample treatments, the HPLC-grade ethyl acetate, the anhydrous granular sodium sulfate used for the MSPD, and the activated florisil (60–100 mesh) were all obtained from J. T. Baker (USA); the concentrated hydrochloric (37%, *w/w*) and nitric (65%, *w/w*) acids, both of analytical grade, from Riedel de Haën (Germany); and the silica gel 60 Å (A 5267) for column chromatography was from AppliChem (Germany).

Quality controls

Procedural and instrumental blanks were analyzed throughout the process to check for interference and laboratory contamination. Recoveries in surface water and sediment samples were calculated from a spiked standard of the following 15 analytes: aldrin, endosulfan isomers I and II, DDT residues (pp′-DDD, pp′, DDT, op′-DDT, op′-DDE, pp′-DDE), dieldrin, endrin, heptachlor, heptachlor epoxide, and HCH (α, ß, and γ isomers). In addition, chorpyrifos and cypermethrin were also spiked for standards as compounds representative of their respective pesticide families. The limits of detection and quantification were evaluated according to the criteria established by the International Conference on Harmonization of Technical Requirements for Registration of Pharmaceuticals for Human Use (ICH 2005). Certified standards of organochlorine, organophosphorus, and pyrethroid pesticides as 10 mg/l standard stock solutions in hexane were obtained from AccuStandard, Inc. (USA).

Statistical analysis

The data obtained were analyzed by means of the Shapiro-Wilk test of data normality; then comparisons were made of the mean values between the results of the two sampling campaigns. The potential relationships between the pesticide measurements and the sampling sites were investigated by means of multivariate statistical considerations through principal component analysis (PCA). This evaluation was done only for sediment samples, those being the more relevant environmental matrix according to the pesticide-concentration levels (cf. Figs. 3 and 6) and the frequency of detection (cf. Fig. 2). The PCAs were done by loading the main variables and using the biplot of factor scores for the sampling sites in order to correlate both types of data. Significant factors were selected on the basis of the Kaiser principle of accepting eigenvalues >1 (Quinn and Keough 2002). Concentrations below the detection limit were replaced with a value of one half of the corresponding limit. Statistical analysis was done by means of the software Statistica (Stat Soft version 7) and XL-STAT software (Addinsoft 2005, version 7.5.3).

Results and discussion

Recovery of analytes

The recoveries of the analytes were satisfactory, as calculated from spiking with a standard mixture of OCls plus chlorpyrifos and cypermethrin, those compounds being representative of their corresponding groups (i.e., the OPs and PYRs, respectively). The average recovery ± standard deviation (SD) for the 15 OCl

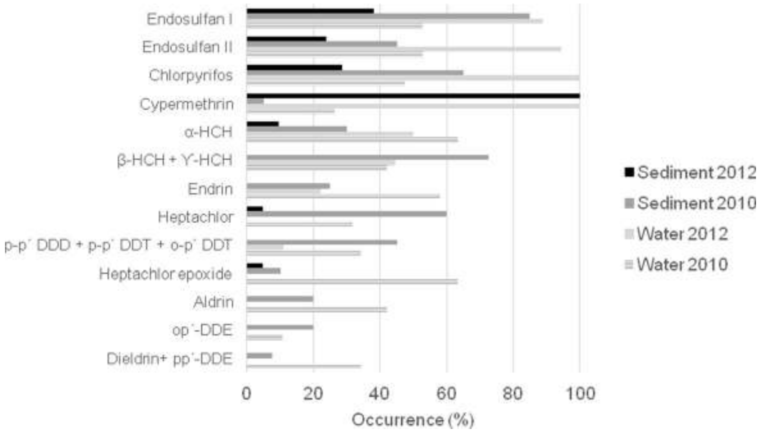

Fig. 2 Frequency of detection of compounds as a percent of the total pesticide tested in the water and sediments during both sampling campaigns. In the figure, the percent frequency is plotted on the *abscissa* for each of the pesticide-related compounds indicated on the *ordinate*. Key to the bar textures: *solid black*, sediment 2012 campaign; *solid dark gray*, sediment 2010 campaign; *solid light gray*, water 2012 campaign; *gray-and-white striped*, 2010 campaign

compounds obtained from the water and the sediment were 69.4% ± 33.5 (n = 3) and 52.0% ± 27.4 (n = 10), respectively. The respective recoveries calculated for chlorpyrifos and cypermethrin were 76.3% ± 27.6 (n = 5) and 82.2% ± 31.4 (n = 4) for the water and 82.0% ± 40.1 (n = 6) and 49.4% ± 23.1 (n = 9) for the sediments. In addition, the overall recovery for the entire procedure, without the influence of the sediment matrix and for the rotoevaporation-dryness steps were carried out. The respective recoveries of the OCl mixture, of chlorpyrifos, and of cypermethrin were 102.0% ± 22.0 (n = 4), 135.3% ± 51.0 (n = 4), and 109.3% ± 61.9 (n = 4) for the overall procedure and 95.6% ± 5.7 (n = 2), 116.9% ± 0.2 (n = 2), and 88.2% ± 10.5 (n = 4) for the concentration steps. The results indicated that the extraction of analytes from the sediment and from the chromatographic materials as well as the handling steps was satisfactory, with no substantial losses.

Occurrence of pesticides in surface water and sediments

Table 1 lists the number of pesticides and sampling sites tested with each environmental matrix for the two campaigns. The number of compounds tested varied in each sampling campaign for operational reasons. For the samples of the 2010 campaign, 95.2% and 100% of the analytes tested were detected for water and for sediments, respectively, and for the 2012 campaign 68.4% and 42.1%.

Figure 2 indicates that the endosulfans, chlorpyrifos, and cypermethrin were the compounds most frequently detected, with those being ubiquitous throughout the compartments tested in the two campaigns (analytes specifically studied in both campaigns, n, 17; Table 1). The endosulfans and chlorpyrifos exhibited higher detection frequencies (average, 60%) in both the water and the sediments, while cypermethrin was detected in all samples (i.e., 100% frequency) in the 2012 campaign. The results are in agreement with the current use of insecticides in the most widely cultivated crops of Argentina, such as the Roundup®-resistant soybean (Pengue 2001; Ablin and Paz 2004; Bejarano González and Red de Acción en Plaguicidas y sus Alternativas en México A.C., RAPAM 2008; SIIA 2015), as judged by the volumes of commercial formulations of pesticides employed. Those three compounds are the pesticides most extensively exploited in the country (Marino and Ronco 2005; Kleffmann and Partner SRL 2010; Mugni et al. 2011; Demetrio 2012; Villaamil Lepori et al. 2013), thus explaining the presence of these contami-

Table 1 Number of pesticides and sampling sites tested per sampling campaign and environmental matrix

Campaign	Sample type	Number of pesticides tested	Number of sites
2010	Water	21	19
	Sediment	20	20
2012	Water	19	18
	Sediment	19	21
Common to the two campaigns	Water	17	15
	Sediment	17	15

nants in the environments in the present study. In addition, the OCl compounds (HCH, aldrin, dieldrin, endrin, the DDT residues, heptachlor, and heptachlor epoxide) were more often detected in the 2010 campaign, with the isomers of the HCH being the most frequent. These OCl pesticides were seldom detected in water and sediment in 2012, and in particular, the two DDE isomers, aldrin, and dieldrin were not detected at all.

Concentration levels of pesticides in surface waters and sediments

The results of these two campaigns indicated a generalized presence of pesticides in the study region along with a wide variability in the concentrations of the OCls, OPs, and PYRs in the sites surveyed within the Paraguay-Paraná basin. We performed the following calculations taking into account only the analytes detected in both campaigns (*n* = 17; Table 1) and expressed the results in terms of the three chemical groups (cf. Section 2.2): the OCls including those originally banned (OCls old use) and the more recently banned endosulfans (sum of isomers I and II), the OP chlorpyrifos, and the PYR cypermethrin. The last three compounds were analyzed in detail since those analytes were frequently detected and were present at higher concentrations. Moreover, the number of sites used in the calculations corresponded to those surveyed in both campaigns (*n* = 15; Table 1).

The concentrations quantified expressed as the median values plus the range (minimum and maximum) for the compounds detected (i.e., the old OCls and endosulfans, the OP chlorpyrifos, and the PYR cypermethrin) are summarized in Table 2 and the box plots of Fig. 3 also showing the median values, percentiles, outliers, and extreme values.

The concentrations of the endosulfans, chlorpyrifos, and cypermethrin detected per sampling site in the two monitoring campaigns were characterized by both homogeneity and ubiquity, with the three being more prevalent in the middle and lower sector, where higher concentrations were observed (Fig. 4). On the basis of the guidelines recommended with water for the protection of the aquatic biota of the region (SRHN 2003, 2004, 2005), all of the concentrations of endosulfans, chlorpyrifos, and cypermethrin quantified in both campaigns were found to be above each corresponding reference level.

Comparisons with data from previous studies

The pesticide concentrations detected in the water were several orders of magnitude lower than in the sediments from the same sites. These results are in agreement with reports from local studies within the core productive area for extensive (Jergentz et al. 2005; Ronco et al. 2008; Di Marzio et al. 2010) and intensive crops (Demetrio 2012) those areas having water bodies under the direct influence of agriculture (the south Santa Fé, northwest Buenos Aires, and east Córdoba provinces). In particular, the range of concentration levels of endosulfans, chlorpyrifos, and cypermethrin detected in the basin is in agreement with the measured concentrations reported for the Pampean region (Jergentz et al. 2005; Ronco et al. 2008; Demetrio 2012). In contrast, Ballesteros et al. (2014) documented a concentration range of endosulfans in Mar Chiquita Lake (Córdoba) within the order of nanograms per liter in water and between one and two orders of magnitude lower in sediments and in water samples from the Suquía River basin; Bonansea et al. (2013) detected maximum concentrations of endosulfans, chlorpyrifos, and

Table 2 Quantitation of pesticides measured in the water and sediment of the Paraguay-Paraná basin sites sampled in the campaigns of 2010 and 2012

Campaign	Old OCls	Endosulfanes	Chlorpyrifos	Cypermethrin
Water (µg/l)				
2010	0.02 (0.01–0.19)	0.20 (0.10–0.31)	0.02 (0.01–0.03)	0.24 (0.23–0.25)
2012	0.01 (0.004–0.06)	0.12 (0.01–4.26)	0.11 (0.04–0.47)	0.74 (0.01–6.62)
Sediment (µg/kg dry weight)				
2010	0.61 (0.16–9.07)	3.83 (1.56–7.78)	0.80 (0.18–4.41)	8.00 (1 sample)
2012	0.64 (0.26–1.94)	1.42 (0.77–37.6)	5.18 (3.32–13.5)	9.70 (0.57–221)

The data are expressed as the median values plus the range (minimum and maximum)

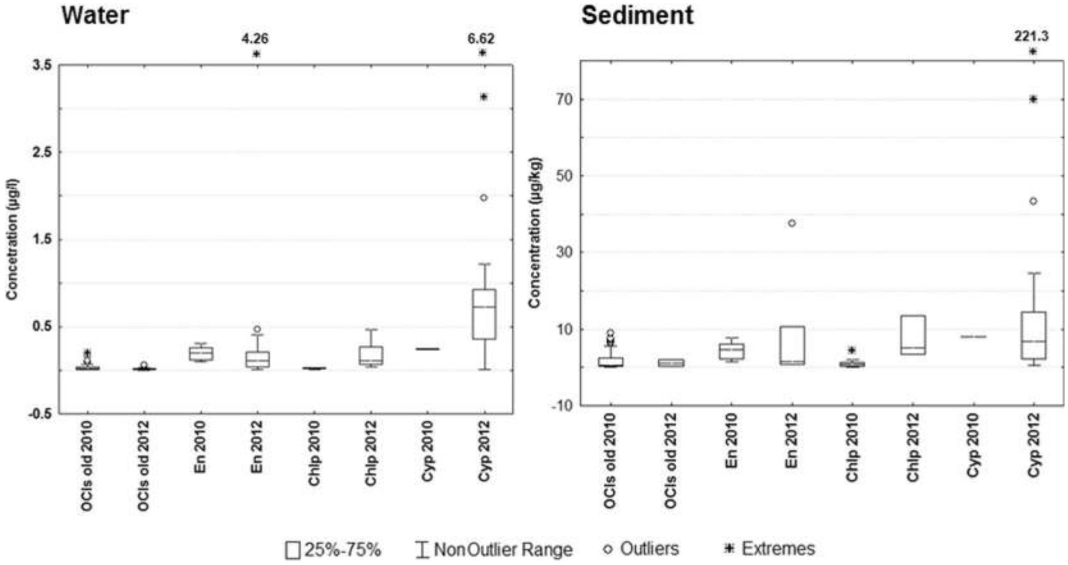

Fig. 3 Values of median concentration, percentile (25% and 75%), range, and outliers for the detection of organochlorine (old), endosulfans, chlorpyrifos, and cypermethrin. The *box plots* represent three quartiles of the data for each condition, with the range being indicated by the *brackets above and below the boxes*, the extreme values by the *asterisks*, and the median values by the *horizontal black lines within*. In the figures, the concentration of the compound indicated on the *abscissa* in micrograms per liter (for water, **a**) or micrograms per kilogram dry weight (for sediment, **b**) is plotted on the *ordinate*

cypermethrin of three, two, and one order of magnitude lower, respectively, than those observed in the present study. Marino and Ronco (2005), however, had reported concentrations of cypermethrin and chlorpyrifos in both the water and the sediments of streams adjacent to cultivated areas in the rolling Pampas of up to one or two orders of magnitude higher than those observed in the present study in the lower stretches of those same streams. In addition, in streams of the same region, Di Marzio et al. (2010) had detected concentrations of endosulfans at up to 20 µg/l in water and 553 µg/kg in sediments, with those values being one order of magnitude higher than the data from the Río Saladillo River (the highest detected in the present study). Furthermore,

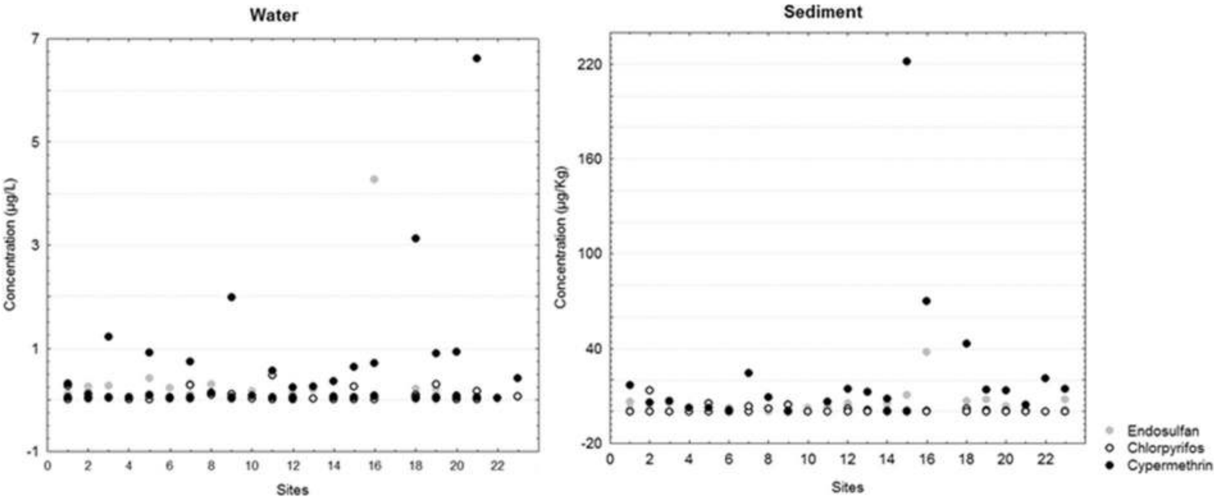

Fig. 4 Concentrations of endosulfans, chlorpyrifos, and cypermethrin detected in water (**a**) and sediments (**b**) during the sampling campaigns. In the figure, the concentration of endosulfans (*gray circles*), chlorpyrifos (*white circles*), and cypermethrin (*black circles*) in micrograms per liter (**a**) or micrograms per kilogram dry weight (**b**) is plotted in the *ordinate* for each of the sampling sites indicated on the *abscissa*

recent reports in the soybean-production regions of South America (Hunt et al. 2016) also indicated that the most commonly detected insecticides in sediments from three intensive soybean-production regions of Argentina, Paraguay, and Brazil were these most heavily used pesticides: chlorpyrifos, endosulfan (and its degradation product endosulfan sulfate), cypermethrin, and lambda cyhalothrin findings completely in agreement with the results obtained in our study.

The presence of pesticide residues such as OPs, carbamates, triazines, and PYRs among others has been reported in surface water close to areas of agricultural production in different Latin-American countries such as Venezuela, Colombia, Ecuador, and Mexico and, in most instances, the concentrations detected exceeded the standard limits established by the relevant national and international organizations (Molina Morales et al. 2012; Benítez Díaz and Miranda Contreras 2013). This precedent is in accordance with our survey in the Paraguay-Paraná basin. Chlorpyrifos has also been shown to be a common surface water contaminant in North America (Ding et al. 2010; Starner and Goh 2013). This information provides evidence of the occurrence of OCl, OP, and PYR pesticides in aquatic environments associated with agroecosystems of this basin as well as with those of other parts of the world, thus demonstrating the relevance of the problem of pollution with pesticides that affects the quality of surface water at the regional level worldwide.

Statistical analysis

Since the data set obtained for the sediment and water did not conform to a normal distribution ($\alpha = 0.05$), nonparametric statistics were used (i.e., the Mann-Whitney test). When the pesticide concentrations detected in water and sediments were analyzed to compare the data between the two campaigns, the analysis demonstrated that the endosulfans and cypermethrin did not manifest significant differences ($\alpha = 0.05$). Chlorpyrifos, however, exhibited a significant elevation in prevalence in the water (Fig. 2) and overall abundance in both environmental matrices (Table 2; Fig. 3) between the 2010 and 2012 campaigns. These results are in agreement with commercial reports of pesticide products with chlorpyrifos being the main active ingredient used (at over 11 million l/kg in 2012). In contrast, the commercial use of cypermethrin and endosulfans dropped during that period (Kleffmann and Partner SRL 2012).

Multivariate approach

Because, as mentioned above, the sediment data set obtained did not fit a normal distribution ($\alpha = 0.05$), the PCA was solved through the use of a Spearman correlation matrix in order to explore possible correlations between the pesticides (i.e., old OCls, endosulfans, chlorpyrifos, and cypermethrin) in the sediment in the sampling sites during both of the campaigns. The PCA grouped the eight variables into two principal components (65.7% of cumulative variance) with eigenvalues greater than 1.0. Table 3 lists the eigenvalues, loadings of the variables, and percentages of the total variance for these factors. The first principal component or first factor (F1) accounted for 45.4% of the total variance; this parameter combines the concentrations of old OCls, endosulfans, and chlorpyrifos of the 2010 campaign and the endosulfans and cypermethrin from the 2012 campaign with positive values. The second factor accounted for 20.3% of the total variance and was positively correlated with the total pesticides of the 2010 campaign (Table 3). Figure 5 depicts the biplot obtained by PCA showing the distribution of sediment samples and space variables defined by the first two factors. The factors explain representative features of a sample when its score is greater than 0. The figure indicates that S15 and S16 notably detach from the rest of the sampling sites, with high values for the first and second factors, indicating relevant correlations with the presence of endosulfans and cypermethrin for the 2012 samples. Previous studies (Ronco et al. 2011; Peluso et al. 2013) had demonstrated that those tributaries (the San

Table 3 The eigenvalues, factor loading, and proportion of the total variance explained for the first two principal components

	F1	F2
Eigenvalue	3.63	1.63
Variance (%)	45.4	20.3
Cumulative variance (%)	45.4	65.7
OCls old/10	0.469	0.093
En/10	0.412	0.291
Chlp/10	0.280	0.359
Cyp/10	–0.049	0.539
OCls old/12	–0.378	–0.088
En/12	0.338	–0.481
Chlp/12	–0.330	–0.219
Cyp/12	0.404	–0.448

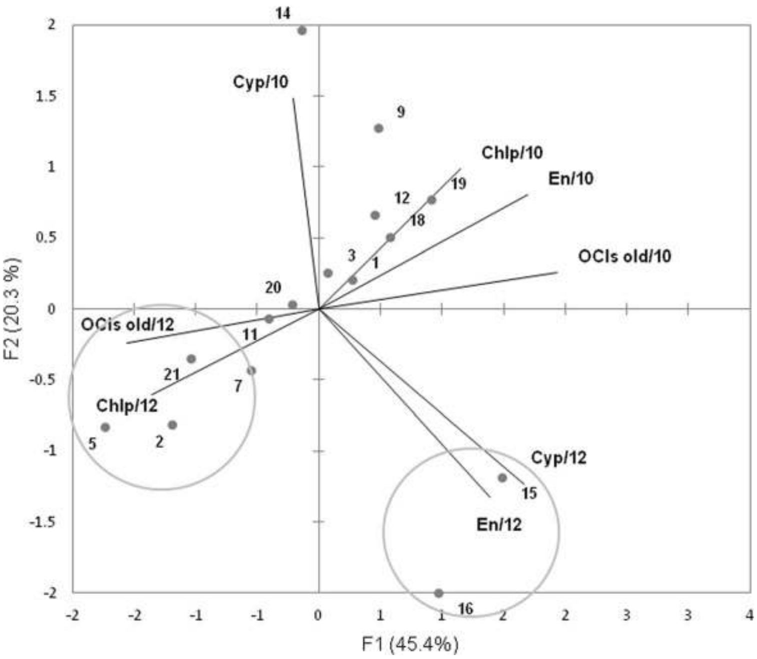

Fig. 5 Principal components analysis biplot of variables and the sites sampled for the first two meaningful principal components. Abbreviations used: *OCls* organochlorine pesticides, *En* endosulfans, *Chlp* chlorpyrifos, *Cyp* cypermethrin, *10* campaign of 2010, *12* campaign of 2012. The *Arabic numbers adjacent to the data points* denote the associated sampling sites. In the figure, the first principal component (*F1*) is plotted on the *ordinate* and the second principal component (*F2*) on the *abscissa*

Lorenzo and Saladillo streams) are characterized by multiple sources of pollution. The sediments were the most highly affected compartment characterized by high levels of toxicity and anaerobic conditions, thus leading to high sulfide contents and organic matter. In addition, the high levels of pesticides in the sediment samples from both sites also contribute to the differential behavior of the data. Furthermore, S14 in particular (the Carcarañá River) exhibited high positive values for F2 indicating a clear cypermethrin burden as revealed in the 2010 campaign. This tributary runs across agricultural areas, and samples from that site had been found to induce lethal effects in toxicity-testing surveys (González 2013). Furthermore, sites S2, S5, S7, and S21—those detaching from the rest of the sites studied—exhibited high negative values in the PCA that correlated with the presence of OCls old and chlorpyrifos at the sites in 2012. The Areco River (S21) is characterized by a typical vegetation of the rolling Pampas with extensive cultivation along the watercourse. Sites S2 (the Paraguay River) and S5 (the confluence of the Paraguay with the Paraná River) lie on productive areas of Argentina and Paraguay. Paraguay, in particular, has had a large growth in agricultural development, in recent years becoming the fourth exporting country and the sixth soybean producer worldwide (Bejarano González and Red de Acción en Plaguicidas y sus Alternativas en México A.C., RAPAM 2008; CAPECO 2015), thus explaining the high levels of pesticides detected in the influence area. A similar result was observed in sites like S21 with a history of agricultural production. The high concentration levels of pesticides detected in S7 (the Santa Lucía River) are in agreement with the activities in the area. An increase in agricultural development in the influence area of this basin has been reported, where the total area of rice production doubled between 2009 and 2011 (SIIA 2015). Moreover, tobacco plantations are common in that region, which crops together with rice requiring high loads of chemical pesticides for pest-control management (Díaz Romo and Salinas Álvarez 2002; Blanco et al. 2006; Bernardos and Zaccagnini 2008).

Fate of endosulfans, chlorpyrifos, and cypermethrin

Since endosulfans, chlorpyrifos, and cypermethrin were the three most relevant pesticides in the region, we focused on characterizing the partitioning of those compounds in order to identify the relevant sink. Figure 6 illustrates the distribution of each compound (expressed as a percent of the total) between the water and the sediments. The calculation took into consideration only the sites where we could detect the pesticides in both matrices ($n = 16$ for endosulfans, $n = 18$ for cypermethrin, and $n = 10$ for chlorpyrifos). We considered the density of water to be 1 g/cm^3 in order to

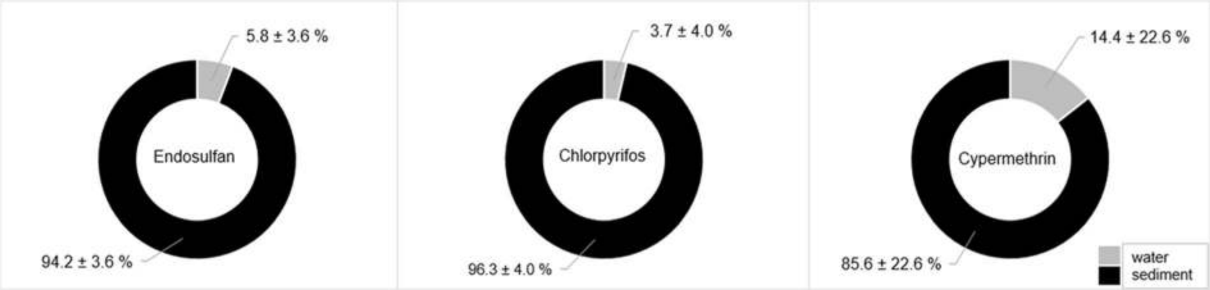

Fig. 6 Mean percent distribution ± standard deviation of endosulfans, chlorpyrifos, and cypermethrin between the water and the sediments in the Paraguay-Paraná basin sampling sites (both sampling campaigns). The *pie charts* illustrate the partitioning of endosulfans (**a**), chlorpyrifos (**b**), and cypermethrin (**c**) between the two environmental matrices with the *gray fraction* indicating the water and the *black* the sediment

estimate the mass densities and express all concentrations as micrograms per kilogram. The total data were used to calculate the partitioning of each pesticide through an estimation of the percentages in water $((C_w/(C_w + C_s))*100)$ and sediment $((C_s/(C_w + C_s))*100)$ and the corresponding average distribution in the water column.

The results indicated that the distribution of endosulfans, chlorpyrifos, and cypermethrin possessed a greater affinity for the sediments, exhibiting a partitioning of over 85% in that matrix. Since these compounds have low water solubilities and are hydrophobic, with high values of octanol-water partition and sorption coefficients (PPDB 2015); a binding of the three compounds to hydrophobic organic matter in sediments would be expected (Racke 1993; Katagi 2006; Loewy 2011; Gebremariam et al. 2012; Ondarza 2012). Previous reports from surveys in the Pampean region have reported similar trends in pesticide distribution in water and sediments to those detected here (Peruzzo et al. 2003; Jergentz et al. 2005; Marino and Ronco 2005; Ronco et al. 2008; Di Marzio et al. 2010; Demetrio 2012; Ballesteros et al. 2014). A similar calculation of the partitioning of those earlier data to that described here verified that the average distribution followed the same pattern, indicating a partitioning of 9% in water and 91% in sediments with a standard deviation of 11.3%.

Conclusions

We were able to measure the concentrations of organochlorine, organophosphorus, and pyrethroid pesticides in whole water and sediments in the Paraguay and Paraná rivers and their tributaries with endosulfans, chlorpyrifos, and cypermethrin being the most frequently detected compounds and those at the highest concentrations. The high pesticide levels in water and sediment and, in particular, those of the endosulfans are an example of how banned chemicals can still represent a hazard to aquatic organisms and subsequently to human health. The middle and lower stretches of the Paraná tributaries with intensive agriculture contribute significant loads of pesticides that reach the main watercourse and, in spite of the high dilutions associated with the discharge rates, nevertheless lead to detectable concentrations in that watercourse. These findings indicate the urgent need for management of pesticide application in the basin presently being affected by regional agricultural activity.

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