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Pesticide survey in water and suspended solids from the Uruguay River Basin, Argentina

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Abstract The Uruguay River is receptor of pollutants, such as pesticides, from agriculture activities along its course. The present study reports concentration levels of organochlorinate, organophosphorus, and other pesticides in water and suspended solids in nine sampling sites of the Uruguay River. Data analyses included principal component analysis (PCA) to assess differences between sampling sites contamination. Most of the tested pesticides were ubiquitous due to the widely use in the chemical control of pests implemented in the region. Detected concentrations of aldrin, chlordane, dieldrin, endrin, heptachlor epoxide, lindane, 4,4′-DDT, endosulfan, chlorpyrifos, diazinon, methyl-parathion, and malathion were found to be over regional and international concentration level guidelines, according to the European Union, the US Environmental Protection Agency, or the Argentinean Secretariat of Environment and Sustainable Development. For this reason, future studies in Uruguay River Basin are needed.

Keywords Pesticide contamination · Water · Suspended solids · Multivariate analysis

Introduction

Several water quality problems in Argentinean lakes and rivers have been increasing in the last decades due to agricultural activities, deforestation, forestry, animal husbandry, mining, and in particular, to discharges of untreated sewage (USEPA 2001; IETC 2001; Barceló 2008; Ibarra Cecena and Corrales Vega 2011).

The Salto Grande Basin has a length of 140 km, covering an area of 78,300 ha and is located between parallels 29° 43′ and 31° 12′ south and the meridians 57° 06′ and 57° 55′ west. The Uruguay River is one of the most important rivers in South America. It represents the main tributary of the Salto Grande Basin, and it originates in Brazil, in the confluence of Pelotas and Do Peixe Rivers and discharges in the Río de la Plata River running through 2200 km, with a mean annual discharge of 4622 $m^3 s^{-1}$ (Salto Grande 2013). The basin has dendritic shape, with a central zone that covers 70% of the total area and five smaller lateral rivers that discharge on it: Itapebí, Gualeguaycito, Mandisoví, Arapey, and Mocoretá, with different characteristics. The water from the Uruguay river is used for human

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consumption and recreation, but the principal economic use of the river is energy generation through the Salto Grande Dam located between Concordia City (Argentina) and Salto City (Uruguay). The region around the Salto Grande Basin has an important agricultural development where numerous types of pesticides are used (SAGPyA 2003; MAGyP 2009; IPEC 2012; MGAP 2013). These compounds generate environmental pollution, either by drift and/or accumulation in soils, which as a result of runoff, percolation, and other transport mechanisms may enter watercourses (Konstantinou et al. 2006; Davis et al. 2007; Guo et al. 2008; Costa et al. 2010; Sasal et al. 2010; Tang et al. 2012; Hellar-Kihampa et al. 2013). The assessment of crops that grow on both sides of the river and pesticides commonly used by farmers and application times have been taken into account in the choose of monitoring sites, sampling plan, and frequency.

There are few reports on the level of contamination of the Uruguay River Basin, and considering that they are not updated after 1988 (CTM 1988) and 1994 (CARU 1994), the objective of the present study is the evaluation of organochlorinated, organophosphorus, and other pesticide concentrations in water and suspended solids, to establish the contamination in the region of Salto Grande with respect to pesticide residues and to contribute to the control and basin's diagnosis.

Materials and methods

Study area and sampling sites

Salto Grande is a large hydroelectric dam on the Uruguay River, located between the cities of Concordia, Argentina, and Salto, Uruguay, and thus is shared between the two countries. The construction of the dam began in 1974 and was completed in 1979. Power is generated by 14 Kaplan turbines, totaling the installed capacity to 1890 MW. Figure 1 shows the basin and the location of the sampling sites, which were selected according to the objectives of this monitoring investigation, considering the total extension of the Salto Grande Basin (from Monte Caseros to 1000 m after the hydroelectric dam). Samples were taken in the following sites: Monte Caseros (MC), Mocoretá (MO), Santa Ana/Federación Chanel (SA), above the mouth of the A° Itapebí (E2C), A° Center Itapebí (E9), A° Gualeguaycito Chico (E71), left margin La Toma (E95), Center Dam (E1C), and downstream Dam (E11). These nine sample sites were chosen considering that they are nearby intensive agroindustrial areas, which have direct influence into water quality of the basin. Samples were taken from all sites, once in each season, for the period 2013–2015. A total of 12 samples have been taken per sample site.

Sample collection

Samples were collected according with the general standardized guidelines of the Standard Methods for the Examination of Water and Wastewaters (APHA 1998). A total of 2 L of water was collected, at 20 cm depth, in dark glass bottles, without separating suspended solids (CTM 1988). Samples were kept in a cooler at 4 °C while transferred to the laboratory. Then, they were filtered (nylon membrane 0.45-μm pore size) immediately after arriving to the laboratory to separate suspended solids and kept at 4 °C. Analysis were carried out in the next 3 days to avoid any degradation.

Physical-chemical analysis

The following measurements were done in situ using a multi-parameter water quality monitor Hydrolab DS5 (Hach Company, USA): temperature, conductivity, turbidity, dissolved oxygen, and suspended fixed solids (SS-550 °C). These measures were performed only to have some information about each sample site.

The pesticide analysis began with the filtration of samples to separate water and suspended solids. A 0.45-μm filter was used. After that, water analysis included a liquid/liquid extraction procedure with 2 mL hexane/200 mL filtered water. Samples were agitated during 1 min, and the organic phase was separated by decantation. This layer was filtered through 0.45-μm filter.

Suspended solids were extracted with 2 mL hexane/100 mL filtered water, in an ultrasound bath ULTRAsonik 104× (Ney Dental Inc., Bloomfield, USA) during 5 min.

The extracts obtained from all samples were filtered through 0.2-μm filter, before the chromatographic determination of pesticides.

The determinations carried out in situ and in the laboratory were performed for all the samples taken from the nine sample sites.

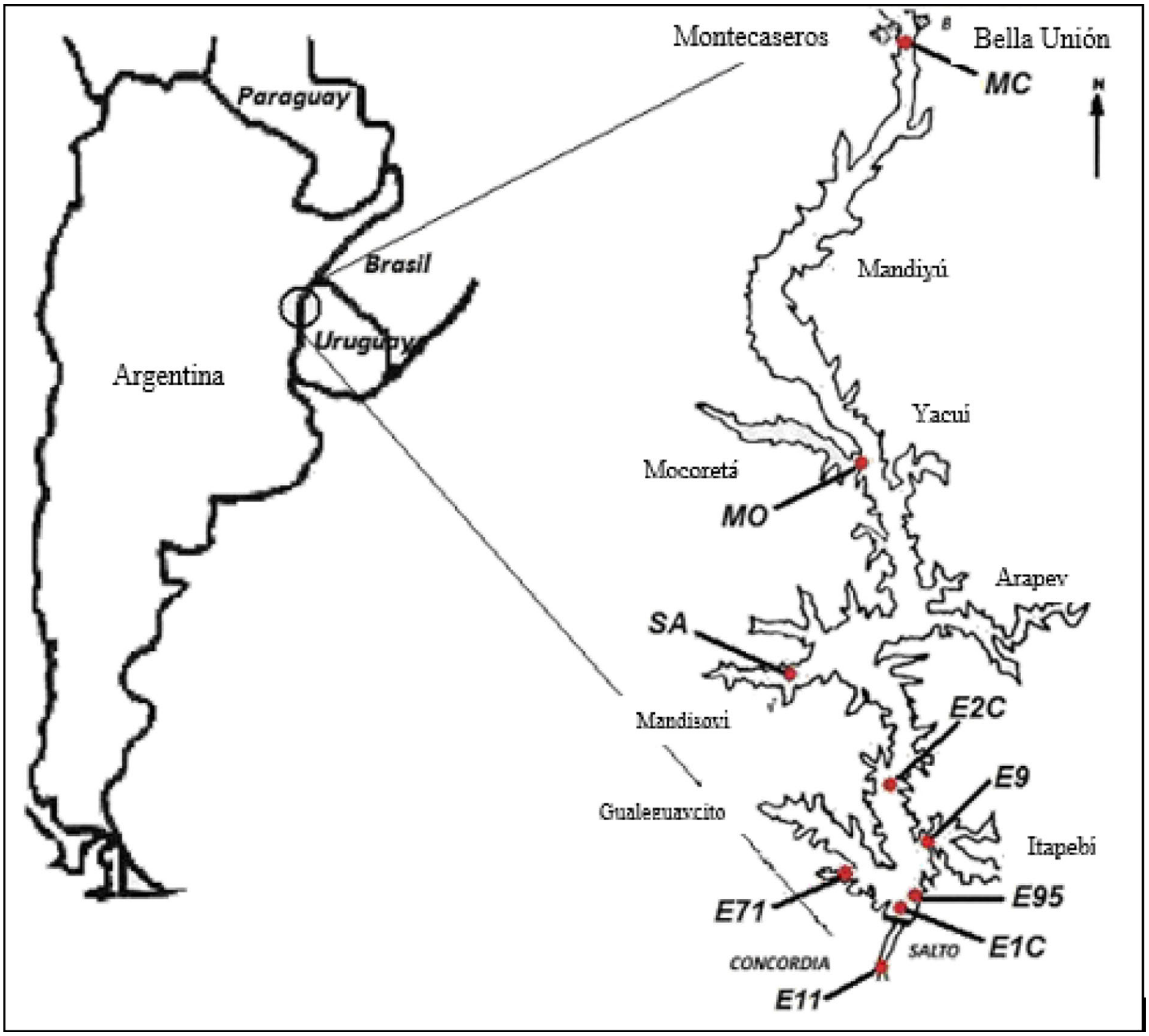

Fig. 1 Area of the study with the location of the sample stations

Reagents

Diazinon, methyl-parathion, fenitrotion, malathion, chlorpyrifos, triadimephon, penconazole, imazalil, myclobutanil, ethion, trifloxystrobin, propiconazole, bromopropylate, lindane, endosulfan, aldrin, heptachlor epoxide A, trans-chlordane, dieldrin, endrin, *p*,*p*′-DDT, and *p*,*p*′-DDD standards of high purity (>98%) were supplied by Sigma-Aldrich (Seelze, Germany). The stock solutions (1 g l^{-1}) were prepared by dissolving the standards in methanol HPLC grade (99.9%) from Sintorgan (Buenos Aires, Argentina) and stored under freezing condition (−18 °C) in dark bottles sealed with PTFE/silicone caps. The working standard solutions (50 mg l^{-1}) were prepared in hexane HPLC grade (99.9%) purchased by Sintorgan (Buenos Aires, Argentina). Deionized water obtained from an E-pure water purification system (Barnstead/Thermolyne, Bedford, MA, USA) was used for physical-chemical analysis.

Chromatographic conditions

Gas chromatographic (GC) analyses were carried out on an Agilent 6890N gas chromatograph (Agilent Technologies, Delaware, USA), equipped with a micro-electron capture detector (μECD) for lindane, endosulfan, aldrin, heptachlor epoxide A, trans-chlordane, dieldrin, endrin, *p*,*p*′-DDT, and *p*,*p*′-DDD determination; a nitrogen-phosphorous detector (NPD) for diazinon, methyl-parathion, fenitrotion, malathion, chlorpyrifos, triadimephon, penconazole, imazalil, myclobutanil, ethion, trifloxystrobin, propiconazole, and bromopropylate determination; and two split-splitless injection ports, 0.75-mm ID liners and two fused silica capillary columns HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm film thickness) from J&W Scientific (Folsom, CA, USA). Helium and nitrogen were used as carrier gas for μECD and NPD determination, respectively. They were maintained at a constant flow of 1 ml min^{-1}. Injection was done in the splitless mode at 250 °C. The detector temperature was 330 and 290 °C for μECD and NPD, respectively. The oven temperature for μECD determination was programmed as follows: initial temperature of 80 °C (0.2 min), increased at a rate of 10 °C min^{-1} up to 280 °C (3 min), and then increased at 15 °C min^{-1} up to 290 °C (1 min). The oven temperature for NPD determination was programmed as follows: initial temperature of 80 °C (0.2 min), increased at a rate of 42 °C min^{-1} up to 200 °C, and then increased at 10 °C min^{-1} up to 280 °C (9 min). For confirmation analyses, an Agilent 6890N GC coupled with an Agilent 5973 mass spectrometer (MS) supported by reference libraries and equipped with the same column was used. Electron impact (EI) mass spectra were obtained at 70 eV, and the system was programmed in selected ion monitoring (SIM) mode. Temperature of ion source was 230 °C, and MS quad temperature was 150 °C.

Method validation

The analytical methods were validated by evaluating quality parameters such as linearity, precision (repeatability), selectivity, limits of detection, and quantification and recovery values. The extraction and chromatographic conditions were optimized using firstly standard solutions and secondly fortified water and suspended solids samples. The calibration curves were constructed with five concentration levels of spiked samples ranging from 0.05 to 1 mg L^{-1} ($n = 5$). Repeatability (expressed as relative standard deviation, RSD%) was determined by analyzing samples spiked with the different pesticides at all the concentrations used to determine the linear range ($n = 5$) on the same day. The selectivity of the proposed methodologies was evaluated by observing that there were no interfering peaks at the retention time of each pesticide for blank chromatograms of water and suspended solid samples without spiking. Limits of detection (LOD) and quantification (LOQ) were calculated as three and ten times the signal-to-noise ratio, respectively ($n = 5$). For accuracy determination, a recovery evaluation was made. Quintuplicate water and suspended solid samples were spiked with the concentration of pesticide standards used in the calibration.

Data analysis

The relationships between variables were assessed through multivariate analysis by principal component analysis (PCA) based on contents of organochlorinated and organophosphorus pesticides in water and suspended solids samples. This technique allowed finding groups of variables and reducing the dimensionality of them. This was done by means of the principal variable loading and the bi-plot of factor scores for the sampling sites to correlate both types of information. Significant factors were selected based on the Kaiser principle of accepting factors with eigenvalues >1 (Quinn and Keough 2002). Factor loadings were significant for values >0.4 (Delistraty and Yokel 2007; Peluso et al. 2013). STATGRAPHICS Centurion version XV and Origin version 8.6 were the softwares used to perform the statistical analysis.

Results and discussion

Method performance

The presence of matrix effect was observed because of the difference between the standard and spiked samples curves slopes. The ANOVA test showed that there were statistically significant differences ($p < 0.01$) for both cases. For that reason, the standard addition method was recommended for quantification studies. The performance characteristics of the analytical method are presented in Table 1. The results showed a good linearity with regression coefficient greater than 0.999 for all pesticides in both matrixes. The relative standard deviations (RSDs) of five replicates of different concentrations were lower than 10% in all cases. These values indicate that the precision of the method was satisfactory for control residue analysis (Table 1). The LOD and LOQ satisfy the MRL established by the European Union (EC 1975), the US Environmental Protection Agency (USEPA 2013), and the Argentinean Secretariat of Environment and Sustainable Development (SAyDS

Table 1 Performance characteristics of the analytical methods for water and suspended solids

	Water			Suspended solids			MS confirmation parameters	
Analyte	LOD (ng L^{-1})	LOQ (ng L^{-1})	Recovery (%) ± RSD%	LOD (ng mg^{-1})	LOQ (ng mg^{-1})	Recovery (%) ± RSD%	Quantification Ion	Qualifier ions
Lindane	2.71	8.80	96.0 ± 2.5	0.12	3.55	98.2 ± 2.1	181	183, 219
Endosulfan	4.75	15.60	95.2 ± 1.7	1.87	6.25	96.0 ± 1.2	195	197, 241
Aldrin	3.22	9.90	87.0 ± 2.6	1.28	4.00	88.2 ± 2.3	101	293, 291
Heptachlor epoxide A	2.42	8.50	90.4 ± 1.9	0.96	3.51	97.5 ± 1.5	353	355, 237
Trans-chlordane	2.90	9.30	87.3 ± 2.6	1.19	3.80	88.9 ± 3.6	373	375, 377
Dieldrin	3.02	9.12	87.3 ± 2.4	1.24	3.71	85.5 ± 2.9	108	277, 279
Endrin	3.10	9.81	94.2 ± 1.2	1.31	3.98	94.6 ± 1.8	261	281, 279
p,p′-DDD	2.90	9.63	87.0 ± 2.7	1.20	3.86	89.4 ± 2.9	235	237, 165
p,p′-DDT	2.72	9.45	86.0 ± 2.6	1.07	3.77	88.5 ± 2.1	235	237, 165
Diazinon	2.93	9.30	88.0 ± 1.9	1.22	3.83	92.0 ± 2.9	179	152, 304
Methyl-parathion	3.49	10.10	83.2 ± 2.2	1.40	4.10	93.0 ± 2.5	291	139, 123
Fenitrotion	2.98	9.44	84.3 ± 2.6	1.29	3.79	91.3 ± 2.7	277	260, 278
Malathion	3.75	12.05	81.0 ± 2.8	1.47	4.82	90.6 ± 1.3	127	158, 99
Chlorpyrifos	2.62	8.70	90.2 ± 1.8	1.10	3.50	92.5 ± 2.3	197	270, 242
Triadimephon	2.50	8.15	87.0 ± 2.1	1.05	3.25	91.2 ± 1.8	208	181, 128
Penconazole	3.11	10.20	82.6 ± 2.8	1.31	4.20	88.0 ± 1.7	159	161, 248
Imazalil	6.22	20.54	84.5 ± 3.5	2.50	8.25	89.6 ± 2.3	215	217, 54
Myclobutanil	3.42	11.27	89.0 ± 2.7	1.41	4.52	89.0 ± 2.5	288	150, 181
Ethion	2.60	8.55	91.6 ± 1.6	1.06	3.45	93.5 ± 1.9	231	384, 153
Trifloxistrobin	3.33	10.82	87.3 ± 1.8	1.35	4.35	92.3 ± 1.6	116	130, 222
Propiconazole	3.66	11.52	82.5 ± 2.4	1.50	4.65	89.0 ± 2.8	259	261, 191
Bromopropylate	6.90	22.82	80.5 ± 1.7	2.80	9.15	89.4 ± 1.5	341	185, 157

1993), and mean that the method is sufficiently sensitive. Pesticides were confirmed according to quantification ion (target ion) and two qualifier ions in SIM mode (Table 1).

Physical-chemical analysis

In situ measured parameters in the water were taken during 2013–2015 period, and the maximum, minimum, and average values are given in Table 2. Major water components characterization of each sample site allowed studying variability in time as seen in Table 2. Table 3 shows the maximum, minimum, and average values of pesticide concentrations in water and suspended solids during 2013–2015 periods.

Contamination is probably related to different and complex factors, but considering that the agricultural practices used in most parts of the studied region are the traditional ones, pesticides can arrive to watercourses through different transport mechanisms, principally rain-runoff processes and are directly related with the surrounding crops. It was observed that the greatest pesticide occurrence and maximum concentration in each sample site coincided with precipitations higher than 70 mm in the 30-day period before sampling.

Considering the concentration of residues, the presence of pesticides in different sampling sites and sampling dates, we can conclude that in the different samples of surface water and suspended solids, bromopropylate was the pesticide that was found in the maximum concentration, corresponding to the E1C and E9 sample sites, in the months of April 2014 and September 2013. Bromopropylate is used principally in citrus and vineyards, and more recently in apiculture, as an acaricide. The high concentrations of this pesticide in E1C and E9 are directly related to these agriculture

Table 2 Minimum, average, and maximum of measured water quality parameters obtained in situ in each sampling site during 2013–2015 periods

		Site								
		E1C: Center Dam	E2C: above the mouth of the A° Itapebí	E11: downstream Dam	E71: A° Gualeguaycito Chico.	E9: A° Center Itapebí	E95: left margin La Toma	MC: Monte Caseros.	MO: Mocoretá	SA: Santa Ana/ Federación Chanel
Temperature (°C)	Minimum	15.4	16.3	14.8	14.9	14.5	15.3	15.7	14.8	14.6
	Average	21.4	21.0	19.8	21.1	20.6	22.2	20.8	19.9	18.5
	Maximum	30.1	25.2	23.3	29.1	28.3	29.7	26.3	28.3	27.8
Dissolved Oxygen (mg L^{-1})	Minimum	7.2	7.3	8.5	7.5	7.7	7.6	7.6	8.2	7.3
	Average	9.3	8.7	9.0	9.6	8.9	9.6	9.8	11.3	10.8
	Maximum	13.7	9.3	10.1	11.6	10.1	13.7	11.8	12.4	11.7
Conductivity (μS cm^{-1})	Minimum	48.4	47.8	48.0	48.3	51.5	50.8	48.9	79.5	49.7
	Average	56.1	55.7	52.5	54.0	59.5	57.8	55.7	109.8	57.0
	Maximum	70.1	63.5	55.7	66.0	83.0	71.3	83.2	122.4	66.6
Turbidity (NTU)	Minimum	19.9	21.1	20.0	20.8	17.9	18.6	20.4	22.2	17.5
	Average	35.1	38.9	30.3	39.6	34.6	31.2	51.6	29.0	20.5
	Maximum	77.1	73.1	38.0	134.0	92.0	68.9	77.9	89.8	71.5
SS-550 °C (mg L^{-1})	Minimum	2.4	5.6	3.8	1.6	2.0	4.4	15.8	7.1	5.8
	Average	8.0	11.8	8.1	9.2	11.0	7.2	37.6	8.8	6.8
	Maximum	15.2	31.2	11.2	47.2	32.0	12.8	54.2	36.8	36.7

activities that represent the most important ones around the sites.

On the other hand, endosulfan was the pesticide most commonly found in the different sampling for surface water and suspended solids, respectively, because it is a wide spectrum insecticide commonly used to control worms, caterpillars, and other insects in soil and some crops from these regions such as cotton and cereals. Its maximum concentration corresponded to the sites E9 and E1C for both samples, in September 2013.

Regarding the distribution of pesticide residues in water and suspended solids, they are related to the values of the partition coefficients octanol/water (K_{OW}), because they indicate the partition in those matrices (Yu et al. 2006; Zhou et al. 2006; Vryzas et al. 2009).

The highest number of pesticides that have been detected simultaneously in both samples was 10 and correspond to the E1C sampling site during March and July 2014. These two dates were rainier than the rest of the sampling dates, allowing increment in the transportation of pesticides from the fields to surface water. Likewise, the runoff process affects the increase of turbidity and solid content in the water channel, allowing us to conclude that rains and runoff process are two factors that probably explain the greater presence of pesticides during March and July 2014.

Multivariate approach

The concentration of pesticides in water and suspended solids, in the different sample sites, was associated by PCA followed by Varimax rotation (Table 4). For the application of this method, the number of analyzed variables must be less than the number of sample sites. For this reason, pesticides with the greatest residue levels and occurrence were selected for the study (González Martín et al. 1994). They are also shown in Table 4.

The PCA method grouped the variables in four and two principal components for organophosphorous and other pesticides in water and suspended solids, respectively, and in three principal components for chlorinated pesticides in both matrixes. Components explain 81.60 and 87.03% of the total initial variance for chlorinated and phosphorous and other pesticides in water,

Table 3 Minimum average and maximum of pesticides in water and suspended solids in each sampling site during 2013–2015 periods

		Site								
		E1C: Center Dam		E2C: above the mouth of the A° Itapebí		E11: downstream Dam		E71: A° Gualeguaycito Chico.		E9: A° Center Itapebí
		Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water
Diazinon	Minimum	<LOD	<LOD	<LOD	<LOD	90	5	<LOD	<LOD	<LOD
	Average	31	9	<LOD	<LOD	138	12	48	22	3
	Maximum	140	41	<LOD	<LOD	**186**	20	97	70	12
Methyl-paration	Minimum	<LOD	<LOD	<LOD	<LOD	18	<LOD	<LOD	<LOD	<LOD
	Average	<LOD	<LOD	<LOD	<LOD	96	<LOD	<LOD	<LOD	<LOD
	Maximum	<LOD	<LOD	<LOD	<LOD	100	<LOD	<LOD	<LOD	<LOD
Fenitrotion	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	32	<LOD	<LOD	<LOD	36	<LOD	22	23	64
	Maximum	147	<LOD	<LOD	<LOD	72	<LOD	112	112	157
Malathion	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	34	15	<LOD	<LOD	36	3	205	4	<LOD
	Maximum	86	75	<LOD	<LOD	73	5	**953**	14	<LOD
Chlorpyrifos	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	5	1	133
	Maximum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	27	4	27
Triadimephon	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	10	25	<LOD	<LOD	4	2	24	10	32
	Maximum	36	126	<LOD	<LOD	8	4	47	47	128
Penconazole	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	11	7	<LOD	<LOD	8	<LOD	17	2	<LOD
	Maximum	53	36	<LOD	<LOD	15	<LOD	44	1	<LOD
Imazalil	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	426	24	<LOD	<LOD	<LOD	<LOD	857	607	557
	Maximum	1358	98	<LOD	<LOD	<LOD	<LOD	2065	2065	1929
Myclobutanil	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	62	38	<LOD	<LOD	274	3	85	61	84
	Maximum	135	125	<LOD	<LOD	547	7	217	207	228
Ethion	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	<LOD	<LOD	49	65	<LOD	12	<LOD	5	<LOD
	Maximum	<LOD	<LOD	70	85	<LOD	24	<LOD	14	<LOD
Trifloxystrobin	Minimum	<LOD	<LOD	<LOD	<LOD	121	25	<LOD	<LOD	<LOD
	Average	338	14	<LOD	<LOD	1329	226	292	27	727
	Maximum	1133	57	<LOD	<LOD	1410	280	999	66	1734
Propiconazole I	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	16	<LOD	<LOD	<LOD	2	4	15	4	<LOD
	Maximum	80	<LOD	<LOD	<LOD	50	8	75	18	<LOD

Table 3 (continued)

		Site								
		E1C: Center Dam		E2C: above the mouth of the A° Itapebí		E11: downstream Dam		E71: A° Gualeguaycito Chico.		E9: A° Center Itapebí
		Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water
Bromopropylate	Minimum	<LOD	<LOD	<LOD	<LOD	130	70	<LOD	<LOD	<LOD
	Average	8426	580	<LOD	<LOD	5472	3134	1957	2140	1454
	Maximum	17,993	1063	<LOD	<LOD	5840	3400	4533	4533	5013
Lindane	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	17	18	9	206	<LOD	3	<LOD	19	18
	Maximum	**65**	120	**28**	606	<LOD	10	<LOD	80	**18**
Aldrin	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	11	9	16	2	70	<LOD	10	4	63
	Maximum	**50**	65	**29**	9	**138**	<LOD	**33**	24	**19**
Heptachlor epóxide A	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	30	10	9	4	111	1	50	22	21
	Maximum	**93**	69	**28**	13	**315**	5	**229**	92	**92**
Trans-chlordane	Minimum	<LOD	<LOD	22	<LOD	<LOD	<LOD	<LOD	<LOD	26
	Average	99	27	854	1	290	1	133	7	133
	Maximum	**258**	109	**2474**	4	**595**	6	**718**	46	**273**
Dieldrin	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	63	8	149	12	35	1	40	6	753
	Maximum	**158**	52	**382**	36	**89**	7	**153**	23	**5049**
Endrin	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	14	9	74	24	33	1	21	208	23
	Maximum	**76**	44	**158**	72	**51**	6	**107**	164	**96**
Endosulfan	Minimum	<LOD	<LOD	57	<LOD	<LOD	<LOD	<LOD	<LOD	83
	Average	110	22	120	37	67	17	97	37	154
	Maximum	**344**	81	**239**	90	**106**	27	**316**	109	**239**
p,p′-DDD	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	<LOD	50	<LOD	1	4	<LOD	<LOD	13	3
	Maximum	<LOD	350	<LOD	7	12	<LOD	<LOD	77	23
p,p′-DDT	Minimum	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Average	8	1	133	49	227	1	6	<LOD	7
	Maximum	**54**	10	**399**	143	**670**	10	**42**	<LOD	**50**

	Site								
	E9: A° Center Itapebí	E95: left margin La Toma		MC: Monte Caseros		MO: Mocoretá		SA: Santa Ana/Federación Chanel	
	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids
Diazinon	<LOD	<LOD	<LOD	10	<LOD	29	<LOD	20	<LOD
	3	25	22	43	6	65	2	28	11
	10	71	91	106	39	97	35	52	37
Methyl-paration	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Fenitrotion	<LOD	<LOD	<LOD	<LOD	<LOD	12	<LOD	<LOD	<LOD
	34	36	7	<LOD	1	18	2	<LOD	<LOD
	123	178	26	<LOD	21	32	27	<LOD	<LOD
Malathion	<LOD	<LOD	<LOD	17	<LOD	30	<LOD	16	<LOD
	<LOD	<LOD	16	26	4	25	1	31	3
	<LOD	<LOD	78	44	32	57	22	46	28
Chlorpyrifos	<LOD	<LOD	<LOD	<LOD	<LOD	10	<LOD	9.	<LOD
	15	20	2	<LOD	4	17	<LOD	14	1
	33	**98**	7	<LOD	8	32	<LOD	30	15
Triadimephon	<LOD	<LOD	<LOD	<LOD	4	<LOD	<LOD	<LOD	<LOD
	<LOD	<LOD	1	<LOD	4	<LOD	1	<LOD	<LOD
	<LOD	<LOD	7	<LOD	18	<LOD	10	<LOD	<LOD
Penconazole	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	14	<LOD
	94	210	8	<LOD	<LOD	<LOD	<LOD	17	<LOD
	374	1036	30	<LOD	<LOD	<LOD	<LOD	37	<LOD
Imazalil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	29	65	156	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	116	261	625	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Myclobutanil	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	8	781	30	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	30	2987	68	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Ethion	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	10	<LOD
	36	4	7	<LOD	1	<LOD	1	17	1
	86	18	23	<LOD	9	<LOD	7	38	7

Table 3 (continued)

	Site								
	E9: A° Center Itapebí	E95: left margin La Toma		MC: Monte Caseros		MO: Mocoretá		SA: Santa Ana/Federación Chanel	
	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids
Trifloxystrobin	4	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	213	243	29	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	576	972	97	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Propiconazole I	<LOD	<LOD	<LOD	28	6	16	<LOD	39	10
	238	19	12	112	8	59	8	142	13
	954	93	62	199	38	100	29	177	36
Bromopropylate	<LOD	1044	86	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	19,007	6228	1115	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	74,585	15,023	2362	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Lindane	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	34	<LOD	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	187	<LOD	5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Aldrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	7	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	9	**27**	5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Heptachlor epóxide A	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	1	20	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	8	**80**	8	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Trans-chlordane	<LOD	12	<LOD	17	<LOD	27	<LOD	18	<LOD
	5	127	5	45	<LOD	76	1	37	<LOD
	18	**476**	21	**68**	<LOD	**90**	10	**71**	<LOD
Dieldrin	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	4	35	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	10	**82**	9	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
Endrin	<LOD	<LOD	<LOD	40	8	<LOD	<LOD	14	5
	1	19	<LOD	208	10	<LOD	2	29	9
	7	**96**	<LOD	**290**	35	<LOD	17	**41**	15
Endosulfan	<LOD	<LOD	<LOD	<LOD	<LOD	18.95	<LOD	<LOD	<LOD
	101	111	64	<LOD	<LOD	25	2	<LOD	<LOD

Table 3 (continued)

	Site								
	E9: A° Center Itapebí	E95: left margin La Toma		MC: Monte Caseros		MO: Mocoretá		SA: Santa Ana/Federación Chanel	
	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids	Water	Suspended Solids
	428	**222**	18	<LOD	<LOD	**48**	9	<LOD	<LOD
p,p′-DDD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<LOD	<LOD	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	<LOD	<LOD	5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
p,p′-DDT	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	10	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Pesticide concentration that exceeds legislation is shown in bold format. The concentration is expressed in ng L^{-1} and ng mg^{-1} for water and suspended solids, respectively

LOD limit of detection

respectively, and 88.06 and 75.13% of the total initial variance for chlorinated and phosphorated and other pesticides in suspended solids, respectively. The loadings of the variables and percentage of the total variance for these factors are represented in Table 4.

For water samples, the first factor, F1, accounted for 26.89% of the variance for organophosphorous and other pesticides and combines the concentration of propiconazole with a negative value, and chlorpyrifos and triadimephon with positive values, and accounted for 40.56% of the variance of chlorinated pesticides, combining the concentration of aldrin and endosulfan with positive values. The second factor accounted for 25.35% of the total variance of phosphorous and other compounds and is positively correlated with diazinon, myclobutanil, and bromopropylate. The F2 accounted for 25.88% of the variance of chlorinated pesticides, positively correlated with heptachlor epoxide A and *p,p′*-DDT, and negatively correlated with lindane and dieldrin. The third factor accounted for 19.99% of the total variance of phosphorous and other compounds, and is positively correlated with malathion and negatively with ethion. This factor accounted for 15.15% of the variance for chlorinated pesticides and is positively correlated with trans-chlordane and endrin. The F4 accounted for 14.78% of the total variance of phosphorous and other compounds, and is positively correlated with chlorpyrifos and propiconazole, and negatively with malathion and ethion.

For the case of suspended solids, F1 accounted for 48.01% of the variance for phosphorous and other pesticides and combines the concentration of chlorpyrifos, bromopropylate, and propiconazole with positive values. Also, it accounted for 41.69% of the variance of chlorinated pesticides, combining the concentration of aldrin, heptachlor epoxide A, and dieldrin, with positive values. The F2 accounted for 27.12% of the total variance of phosphorous and other pesticides and is positively correlated with bromopropylate and myclobutanil. The F2 accounted for 29.88% of the variance of chlorinated pesticides and is positively correlated with lindane and *p,p′*-DDT. The F3 accounted for 16.48% of the total variance for chlorinated pesticides and is positively correlated with endrin and negatively correlated with trans-chlordane.

Figure 2 presents the biplot obtained by the PCA (with Varimax rotation) showing the distribution of pesticides and sample sites defined by the first two factors for water and suspended solids. It is seen in

Table 4 Factor loading and percentage of the total variance explained for 2, 3, and 4 components

	Water				Suspended Solids		
	F1	F2	F3	F4	F1	F2	F3
Eigenvalue	2.15	2.03	1.56	1.18	3.84	2.17	
Variance%	26.89	25.35	19.99	14.78	48.01	27.12	
Diazinon	−0.21	**0.45**	0.30	−0.05	−0.31	0.33	
Malathion	0.11	0.10	**0.58**	**−0.51**	−0.35	0.32	
Chlorpyrifos	**0.52**	−0.25	−0.02	**0.45**	**0.41**	0.39	
Triadimephon	**0.61**	−0.11	0.30	−0.07	−0.29	0.33	
Myclobutanil	0.13	**0.49**	−0.35	0.18	−0.29	**0.47**	
Ethion	−0.11	−0.35	**−0.47**	**−0.54**	0.32	−0.11	
Propiconazole	**−0.48**	−0.15	0.30	**0.46**	**0.43**	0.36	
Bromopropylate	0.19	**0.58**	−0.19	−0.05	**0.40**	**0.40**	
Eigenvalue	3.25	2.07	1.21		3.34	2.39	1.32
Variance%	40.56	25.88	15.15		41.69	29.88	16.48
Lindane	0.35	**−0.43**	0.16		0.34	**0.50**	0.03
Aldrin	**0.48**	0.15	−0.17		**0.42**	−0.31	−0.34
Heptachlor epoxide A	0.31	**0.47**	−0.36		**0.41**	−0.32	0.39
Trans-chlordane	0.26	0.19	**0.66**		0.30	−0.39	**−0.49**
Dieldrin	0.38	**−0.40**	0.02		**0.52**	0.21	−0.07
Endrin	−0.21	0.09	**0.58**		0.28	−0.25	**0.67**
Endosulfan	**0.45**	−0.25	0.05		0.14	0.07	−0.20
p,*p*′-DDT	0.31	**0.55**	0.18		0.29	**0.54**	0.03

Only loadings equal to or greater than 0.40 are shown in bold format

Fig. 2a that E2C is represented by aldrin and trans-chlordane, E11 by *p*,*p*′-DDT and heptachlor epoxide A, E9 by endosulfan, dieldrin, and lindane, and MC, SA, MO, E95, and E71 by endrin, for organochlorinated pesticides in water. In Fig. 2b, E11 is represented by diazinon, E95 by myclobutanil and bromopropylate, E71 and E1C by malathion, E9 by chlorpyrifos and triadimephon, SA, MC, and MO by propiconazole, and E2C by ethion, for orgnophosphorous pesticides in water. Figure 2c, d shows the biplot for organochlorinated and organophosphorous pesticides in suspended solids, respectively. In the first one, E2C is represented by lindane, dieldrin, and *p*,*p*′-DDT, E9 by endosulfan, and E1C and E71 by trans-chlordane, aldrin, heptachlor epoxide A, and endrin. In the second one, E9 is represented by ethion, chlorpyrifos, bromopropylate, and propiconazole, E2C by ethion, and E1C, E71, and E95 by myclobutanil, diazinon, triadimephon, and malathion.

In general, the use of different pesticides from the same kind is a common practice in the field. For instance, two sample sites with the same kind of crops in each region could be characterized by a different insecticide or fungicide. It is directly related with the agronomic practices chosen for pest control.

The three pesticides that characterized E2C were probably transported by a runoff process related with the rains around this region, from nearness rivers such as Mandisoví. Aldrin and trans-chlordane are almost prohibited and could be used only to termite control. However, they have been used as insecticide in the past and their degradation is very slow and it could remain in the soil for more than 20 years. Probably, they were transported from soil to water courses through this process and can be found in fish, birds, and mammals. Ethion is used to control mites, cochineals, spiders, and other insects in vineyards, citrus, sorghum, and during seeds storage but, in this region, is principally used to control the fruit fly *Ceratitis capitata* in citrus.

The pesticides that characterized E11 were probably transported to that point through the dam. But also, they

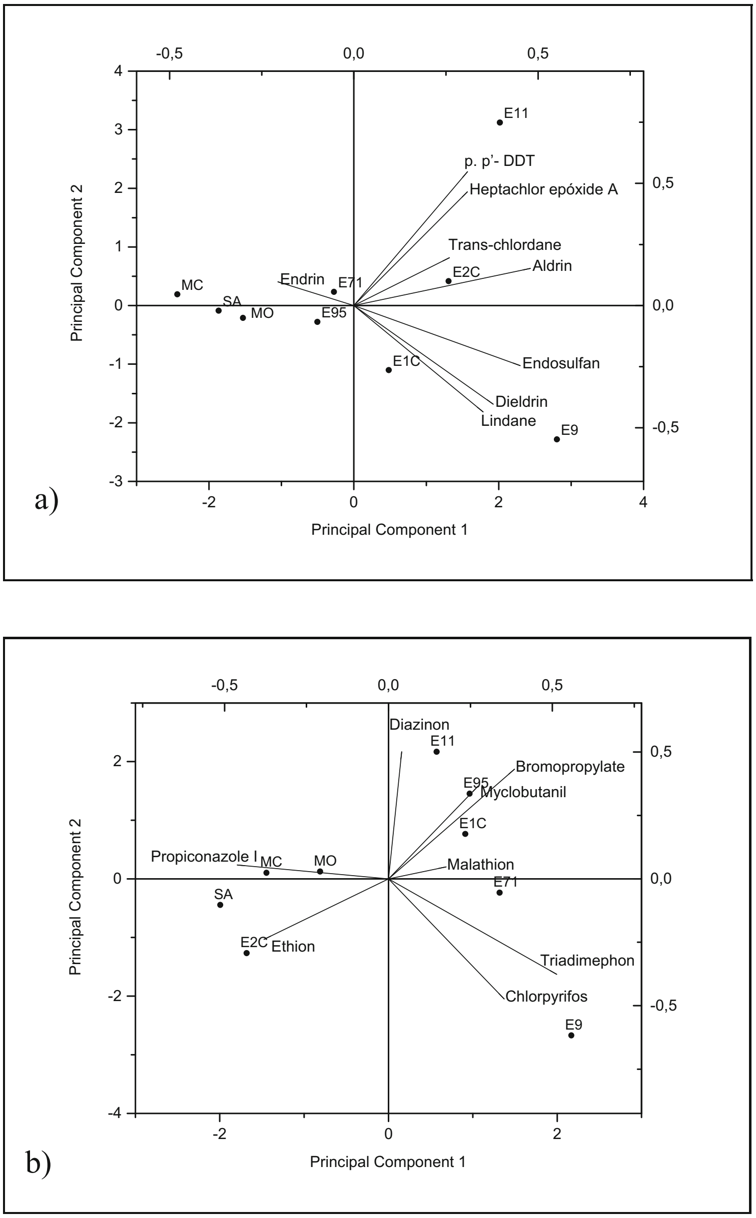

Fig. 2 Principal components analysis biplot of variables and the studied sites for the first two meaningful principal components. **a** Chlorinated pesticides in water. **b** Organophosphorous pesticides in water. **c** Chlorinated pesticides in suspended solids. **d** Organophosphorous pesticides in suspended solids

can appear in this region because of their use around E11. Diazinon is widely used against ants in different crops, and particularly in citrus against mites and black citrus aphid (*Toxoptera aurantii*). On the other hand, although the utilization of both chlorinated compounds has been restricted, they are used against ants and mosquitos in several crops (eucalyptus, pines, citrus, blueberries, cereals, etc.) that exist in both margins of the river. Their degradation is slow in soil and water and that is probably the reason of its importance in this sample point.

As what happened with aldrin in E2C, dieldrin that is one of the pesticide that characterized E9 is only permitted to termite control and its presence is probably related with this application or its slow degradation. Lindane is used in the pre-harvest season to avoid soil

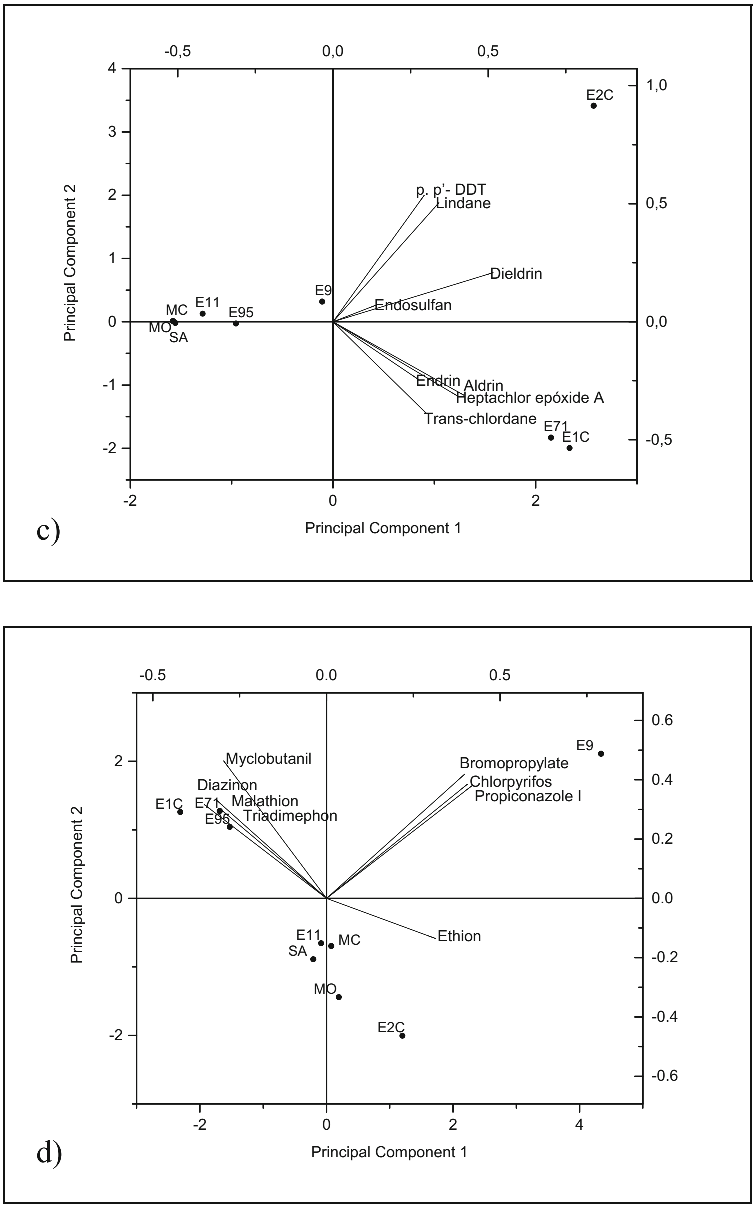

Fig. 2 (continued)

insects and to control some tree pests such as the wood beetle. Other common use of this pesticide is the disinfection of industries, trucks, and packing houses, alone or combined with chlorpyrifos. This last compound appears in E9 probably because it is a citrus and forest region, and it is used to control mites and *Ceratitis capitata* from October to March, and eucalyptus weevil (*Gonipterus scutellatus*), mycosphaerella leaf spots and worms (*Agriotes* spp.) in cereals, during spring and autumn. Triadimephon is a wide spectrum fungicide used against powdery mildew and leaf rust in citrus, blueberries, and vineyards during spring and summer.

The main crops found around MC and SA sample points are similar to those found in another region. However, the selection of pesticides realized by the agronomic personnel is different, being propiconazole the principal fungicide used against powdery mildew and leaf rust in citrus, blueberries, cereals, and vineyards during spring and summer. Endrin is the insecticide that characterized this site. Despite it is prohibited in several

Table 5 Concentration limits (ng L^{-1}) established in different legislations

Pesticide/legislation	EC	USEPA	SAyDS	
	Human consumption water with conventional treatment	Aquatic life protection	Human consumption water with conventional treatment	Aquatic life protection
Lindane + parathion + dieldrin	2500	ND	ND	ND
Aldrin	ND	3000	30	4
Lindane	ND	950	3000	10
Chlordane	ND	2400	300	6
Endrin	ND	86	200	2,3
Heptachlor epoxide	ND	520	100	10
α-Endosulfan	ND	220	138,000	20
Dieldrin	ND	240	30	4
4,4′-DDT	ND	1100	1000	1
Diazinon	ND	170	20,000	ND
Chlorpyrifos	ND	83	90,000	ND
Malathion	ND	ND	190,000	100

From EC (1975), USEPA (2013), and SAyDS (1993)

ND no data

countries, its half life time in soil is approximately 12 years. It is only used to control termites, like other prohibited insecticides such as aldrin and dieldrin.

Myclobutanil is a fungicide that has been used in the cultivated region around E95 to avoid powdery mildew and leaf rust in citrus, blueberries, and vineyards, during the last decade.

The region around E71 is highly cultivated, principally with citrus, blueberries, forests, and soybean. Malathion is the preference as insecticide in these areas, controlling *Ceratitis capitata* and some mealybugs and aphids in citrus, and ball bug (*Okaticus platensis*) in forests.

E1C represents the point where the water from all the Salto Grande Basin arrives, acting the dam as a contention barrier. This could explain the high pesticide concentration and occurrence in this area, related to the different agronomic activities, along all the basin region.

The pesticides that characterized the suspended solids are in general the same that appear in water samples. The reasons that justified this and the transport mechanism are probably the same too. Considering the equilibrium partitioning coefficient Kow for studied pesticides, it could be seen tan this value could justify the pesticide distribution between water and suspended solids (Yu et al. 2006; Zhou et al. 2006; Vryzas et al. 2009). For instance, the concentration of ethion, with a Log *P* value of 5.07, is bigger in suspended solids than in water, for all the samples taken. On the other hand, the concentration of malathion and imazalil, with a Log *P* value of 2.75 and 2.56, respectively, is bigger in water samples than in suspended solids.

The contamination of the different sample sites was compared with the information published by CTM (1988) and CARU (1994). Several pesticides measured in water and suspended solids were found in those studies, principally chlorinated ones. The concentration of these compounds was analogous too. Similar results were observed in other hydrological resources from the La Plata River Basin (Lenardon et al. 1984; CTM 1988; AGOSBA-OSN-SIHN 1994; CARU 1994; Rovedatti et al. 2001). Likewise, Gariboglio et al. (2014) studied water and sediment samples from the Corrientes River finding similar profiles of chlorinated pesticides. Some strobilurines and triazoles were found in this study by the first time, in the Uruguay River Basin, probably because they have been used since the last years. The presence of studied pesticides in both matrixes could be related to different factors. For instance, the presence of endosulfan could be related to its high spectrum action as insecticide, used in several crops in the basin region, as citrus, vineyards and other fruit trees, olive, corn, soybean, sugar cane, etc. (CASAFE 2007). Some crops become resistant to pesticides with time. Bromopropilate is an acaricide used commonly to replace them and is used in the same crops than endosulfan (CASAFE 2007).

Some pesticide concentrations in the different sampling sites are higher than those established by the European Union (EC 1975), the US Environmental Protection Agency (USEPA 2013), and the Argentinean Secretariat of Environment and Sustainable Development (SAyDS 1993), thus alerting on pesticide pollution and associated risks in the studied region. The concentration limits established in legislation are presented in Table 5. Aldrin, chlordane, dieldrin, endrin, and heptachlor epoxide were found in higher concentrations than those permitted for human consumption water with conventional treatment, according to SAyDS (1993). The same behavior was observed for these compounds plus lindane, 4,4′-DDT, endosulfan, and malathion, for aquatic life protection. The European Union (EC 1975) established that the concentration of lindane, dieldrin, and methyl-parathion together should not be higher than 2.5 ng l^{-1} in surface water sources for potable water production. According to USEPA (2013), the following pesticides have been found at higher concentrations than the permitted for aquatic life protection: endosulfan, chlorpyrifos, diazinon, dieldrin, endrin, and heptachlor epoxide.

Conclusion

The assessment of physicochemical parameters in samples of water and suspended solids allowed detecting different types of pollutants in the Uruguay River Basin. Based in a thorough analysis of the available literature, the present study provides updated data on pesticide contamination of this river. The presence of the different pesticides in both matrixes evaluated could be explained by different factors such as the use of these compounds in the agriculture production of the region. Most of them are widely used for pest control in citrus, olive, blueberries, corn, sorghum, soybean, wheat, etc. along the region. Water seems to be the principal vector for transport of most pesticides from agricultural fields to the receiving water body. Since some of the pesticides found reached concentrations above the limits established by the European Union, EPA, and SAyDS, we consider that future research in the Uruguay River Basin will be relevant for control and preventive taking decisions.

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