

Water quality of the main tributaries of the Paraná Basin: glyphosate and AMPA in surface water and bottom sediments

A. E. Ronco · D. J. G. Marino · M. Abelando ·
P. Almada · C. D. Apartin

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Abstract The Paraná River, the sixth largest in the world, is the receptor of pollution loads from tributaries traversing urban and industrialized areas plus agricultural expanses, particularly so in the river's middle and lower reaches along the Argentine sector. In the present study, we analyzed and discussed the main water quality parameters, sediment compositions, and content of the herbicide glyphosate plus its metabolite aminomethylphosphonic acid (AMPA) in water and sediments. Samples were obtained from distal positions in the principal tributaries of the Paraná and the main watercourse during surveys conducted in 2011 and 2012 to monitor the basin. Only 15 % of the water samples contained detectable concentrations of glyphosate at an average concentration of 0.60 µg/L, while no detectable levels of AMPA were observed.

The herbicide and metabolite were primarily present in sediments of the middle and lower stretch's tributaries, there occurring at a respective average of 37 and 17 % in samples. The mean detectable concentrations measured were 742 and 521 µg/kg at mean, maximum, and minimum glyphosate/AMPA ratios of 2.76, 7.80, and 0.06, respectively. The detection of both compounds was correlated with the presence of sulfides and copper in the sediment matrix.

Keywords Paraná Basin · Water quality parameters · Bottom sediments · Glyphosate · AMPA / Aminomethylphosphonic acid

Introduction

The del Plata Basin—the second largest in South America and comprising Argentina, Uruguay, Brazil, Bolivia, and Paraguay—contains as its principal rivers the Paraguay (2459 km long), the Paraná (4352 km long), and the Uruguay (1600 km long), with the last two flowing into the widest estuary of the world, the Río de la Plata (256 km in width). The Paraná is the sixth largest river in the world, with a basin of 1,500,000 km², a mean annual discharge of 17,000 m³/s, and a suspended load of 118.7 million tons per year (Orfeo and Stevaux 2002). The basin traverses a variety of geological features, including the Andes Mountains, the Chaco-Pampean Plains, the Eastern Plains, the Jurassic-Cretaceous Area, and the Brazilian Shield (Iriondo 1988). The bottom

A. E. Ronco, D. J. G. Marino and C. D. Apartin contributed equally to this work.

A. E. Ronco (✉) · D. J. G. Marino · C. D. Apartin (✉)
Centro de Investigaciones del Medio Ambiente, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Buenos Aires, Argentina
e-mail: cima@quimica.unlp.edu.ar
e-mail: apartin@quimica.unlp.edu.ar

A. E. Ronco · D. J. G. Marino
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Buenos Aires, Argentina

M. Abelando · P. Almada
Prefectura Naval Argentina, Dirección de Protección Ambiental, Av. E. Madero, 235 Buenos Aires, Argentina

sediments of the rivers are dominated by silt and clay particle sizes (Manassero et al. 2008), with vast amounts of colloids and clay aggregates circulating in the basin (Konta 1985). Most of the Argentine industrial and agricultural activities and population settlements are associated with this basin. Four previous monitoring campaigns (2004, 2005, 2006, and 2009) of the Argentine sector of the Basin have revealed multiple sources of pollution along the Basin (Peluso et al. 2013a; Ronco et al. 2011; SAyDS-OPS- PNA- UNLP 2007). The middle and lower Paraná tributaries traverse areas subjected to extensive agriculture (Marino and Ronco 2005; Ronco et al. 2008, 2011). That Argentina is the tenth largest agricultural nation in the world, with 31 million ha devoted to agriculture that account for 2.2 % of the world's total area under cultivation is indeed notable (Leguizamón 2014). Pesticide use increased in the last several decades as agriculture became gradually transformed into a system of high technology in order to satisfy growing demands (Heinemann et al. 2013). The adoption of transgenic crops engineered to tolerate the broad-spectrum herbicide glyphosate [*N*-(phosphonomethyl)glycine] gradually increased over the last two decades, with over 22 million ha of the cultivated land being occupied by glyphosate-tolerant corn and soybeans in the 2012–2013 growing season (CONABIO 2013). Accordingly, the two most common crop rotations of the Argentine pampas (i.e., corn vs. full-season soybeans and corn vs. wheat vs. short-season soybeans) usually require two or three applications of glyphosate (Bindraban et al. 2009). The presence of the herbicide in surface waters near agricultural fields has been documented (Aparicio et al. 2013; Lupi et al. 2015; Peruzzo et al. 2008; Primost 2013; Ronco et al. 2008), but no information on the impact of this compound at the level of the large basins of the region is currently available. Consequently, the present study was conducted first in order to analyze the main water quality parameters and sediment composition of specific sampling locations—with an emphasis on the contents of the herbicide glyphosate and the metabolite aminomethylphosphonic acid (AMPA)—and then to discuss the results obtained. Finally, we analyzed the occurrence of these contaminants in environmental compartments by means of the composition of the sediment-matrix components and regional agricultural activities.

Materials and methods

Study area and sample collection

The sampling campaigns were conducted in the scientific vessel SPA-1 “Dr. Leloir” of the Prefectura Naval Argentina during the months of June through July of 2011 and 2012. Separate water and sediment samples were collected from 23 specific sites in the Paraguay and Paraná rivers and their tributaries (Fig. 1 and Table 1). An Eckman dredge was used to take the sediments—down to an approximate depth of 10 cm, with each composite sample being obtained from at least five different grab samples per site. Twenty of the samples were taken in the confluence of the principal tributaries with the Paraguay or Paraná Rivers, while the rest were from the main Paraná watercourse. Table 1 provides the identification of the sampling sites, the corresponding abbreviations, and a brief description.

Whole water and sediment samples to be used for the main matrix composition parameters were kept in a cooler at 4 °C during transfer to the laboratory. The analysis of glyphosate and AMPA was performed on that water and also on a suspended fraction (in the sampling campaign of 2012). The whole water was placed into 100-mL polypropylene bottles and spiked with 500 ng of ¹³C,¹⁵N-glyphosate (¹³C, ¹⁵N-GLY). Filters containing the suspended fraction (obtained from the filtration of 100 mL whole water through 45-mm, 0.45-μm nitrocellulose filters in situ during the sampling) along with 10 g of sediment samples were also spiked with 30 or 250 ng of the ¹³C,¹⁵N-GLY, respectively. Upon arrival, all samples for chemical analysis of the herbicide were stored at -20 °C until the time of processing.

Physical-chemical analysis

The physical and chemical variables of the water column from each sampling site (i.e., conductivity, transparency, pH, temperature, and dissolved oxygen) were measured in situ at each sampling station (multiparameter water quality monitor HORIBA U-52™). Water analyses were conducted in the laboratory according to the following methodology (APHA 1998): Alkalinity was determined by titration (method 2320); chlorides by potentiometry (method 4500-Cl-D); sulfates by turbidimetric analysis (method 4500-SO42-E); nitrate by cadmium reduction (method 4500-NO3-E); total suspended

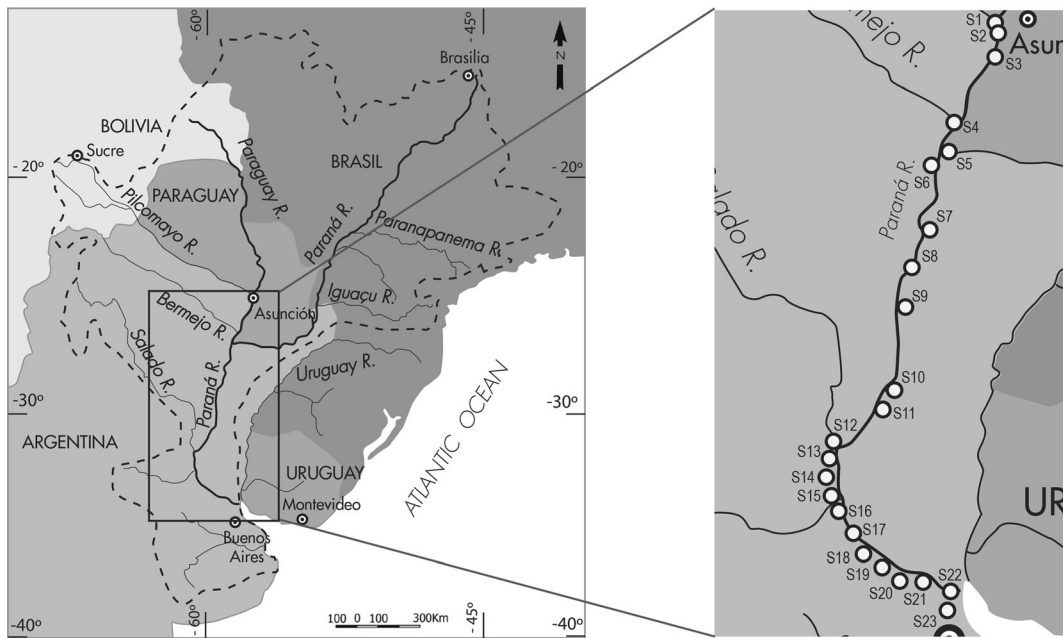


Fig. 1 Study area and sampling site locations. Table 1 lists the names of the sites and their principal geographic and ecologic features

solids and dissolved solids by methods 2540-D and C, respectively; calcium by EDTA titration (method 3500-Ca-B); and magnesium by calculation (method 3500-Mg-B). In nitric acid-digested samples (method 3030-E) sodium plus potassium along with iron, manganese, and zinc were determined by atomic absorption spectrometry (direct air-acetylene flame; methods 3111 and 3500, respectively).

The physical characteristics of the sediment samples recorded consisted in grain size and organic matter. Sieving and settling velocity with previous cement removal (Day 1965) was employed for grain size analysis after sediments were passed through a set of standard sieves larger than 63 μm to separate the sands. The organic matter content in the sediment was determined by calcination (loss on ignition, LOI) in a muffle furnace at 550 °C (APHA 1998; Heiri et al. 2001). Sulfides were analyzed according to method 9030 (USEPA 1996), while the total phosphorus content was measured by a colorimetric method following ignition of the sample (Andersen 1976). Finally, an analysis of the metal composition was conducted by atomic absorption spectrophotometry (as in the water analyses) following acid digestion of the samples (method 3050, USEPA 1996).

Analysis of glyphosate and AMPA

Glyphosate and AMPA were analyzed by high-performance liquid chromatography and mass spectrometry (HPLC-MS) following derivatization with 9-fluorenylmethoxycarbonyl chloride (FMOC-CL; Sancho et al. 1996). Water samples were pretreated by adjusting 2-mL aliquots to pH 9 with sodium tetraborate (40 mM), followed by the immediate addition of 2 mL of FMOC-Cl solution in acetonitrile (1 mg/mL). The solution was then kept overnight in the dark at room temperature (Ibáñez et al. 2005). The extraction of the nitrocellulose filters containing the suspended fraction was effected by sonication in 3 mL of 100 mM K₂HPO₄ (Miles and Moye 1988), followed by centrifugation. Next, 2 mL of the extract were used for derivatization with FMOC-Cl as in the water samples. Of the wet sediment, 10 g was extracted with 25 mL of 100 mM K₂HPO₄ by sonication for 15 min. The derivatization with FMOC-Cl was performed on a 2-mL centrifuged sample adjusted to pH 9. The extractions and derivatizations of the different types of samples were carried out in polypropylene tubes (Miles and Moye 1988). The preparation of standard solutions for constructing calibration curves was done under operational conditions equivalent to those used for the testing

Table 1 Description of the sampling sites, in situ measured water quality parameters and solids (average data of the campaigns 2011–2012). Tributaries of Paraguay and Paraná rivers were sampled nearby each respective confluence

Site characteristics	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	TSS (mg/L)
<i>S1-Pilcomayo River</i> (tributary of Paraguay River). Profuse aquatic vegetation in river bed and along banks. Direct influence from the City of Asunción (Paraguay) on the right margin of the Paraguay River. No evident influence of human activity in the river's basin	6.5	222	96	285
<i>S2-Paraguay River</i> (main watercourse). Downstream from the City of Asunción. Boat traffic. Clear urban and industrial influence	6.9	125	62	132
<i>S3-Montelindo Stream</i> (tributary of Paraguay River). Profuse aquatic vegetation in river bed and along banks. Very low anthropic activity	6.9	500	411	136
<i>S4-Bermejo River</i> (tributary of Paraguay River). Very high water flow with high load of suspended particulate matter. Scarce vegetation in river banks, with very low anthropic activity	7.4	507	372	539
<i>S5-Paraguay River</i> confluence with the Río Paraná. Profuse vegetation along banks, low anthropic activity in nearby areas. Populated areas upstream waters	6.9	154	80	104
<i>S6-Negro River</i> (tributary of Paraná River). Dark black water. Direct influence from the City of Resistencia. Fishing activity	7.1	291	242	302
<i>S7-Santa Lucía River</i> (tributary of Paraná River). Agriculture at influence. River drains waters from the Iberá watershed	7.3	173	176	91
	7.2	90	188	300

Table 1 (continued)

Site characteristics	pH	Conductivity ($\mu\text{S}/\text{cm}$)	TDS (mg/L)	TSS (mg/L)
<i>S8-Paraná River</i> (main watercourse). Downstream the Cities of Resistencia and Corrientes. Commercial and sport boat traffic. Fishing and touristic areas				
<i>S9-Corrientes River</i> (tributary of Paraná River). Sandy banks, with weeds and palm trees (Yatay). Traverses citric fruit cultivated areas	6.8	92	154	94
<i>S10-Guayquiraró River</i> (tributary of Paraná River). Sandy banks. It runs along gallery forests. Bathing touristic sectors. Sportive fishing	6.7	547	473	43
<i>S11-Feliciano River</i> (tributary of Paraná River). Recipient of smaller streams along the course. Vegetated with rice cultivation on margins	7.2	295	297	163
<i>S12-Salado River</i> (tributary of Paraná River). Typical weed vegetation along banks. Recipient from large urbanized areas (e. g., Santa Fé, Santo Tomé) and local industries	8.0	3900	2276	128
<i>S13-Coronda River</i> (tributary of Paraná River). Clay bottom sediments. River runs along typical rolling pampas with extensive agriculture	7.4	336	248	65
<i>S14-Carcaraña River</i> (tributary of Paraná River). Clay bottom sediments. High banked coastline. River runs along typical rolling pampas with extensive agriculture	7.8	3960	1606	25
<i>S15-San Lorenzo River</i> (tributary of Paraná River). Scarce vegetated banks with constructed structures and roads	7.6	334	334	294

Table 1 (continued)

Site characteristics	pH	Conductivity (μS/cm)	TDS (mg/L)	TSS (mg/L)
along cost. High urban and industrial influence				
<i>S16-Saladillo River</i> (tributary of Paraná River). Major industrial influence from the southern sector of the City of Rosario densely populated area. Sampling site is located next to a packing house and other industries	7.4	262	194	53
<i>S17-Paraná River</i> (main water course). Circulation of transatlantic ships and smaller scale boat traffic.	7.4	110	100	12
<i>S18-Pavón Stream</i> (tributary of Paraná River). It runs across typical vegetation of the rolling pampas. Extensive agriculture at influence, also some industries near sampling site	7.8	3580	2132	110
<i>S19-Ramallo Stream</i> (tributary of Paraná River). It runs across typical vegetation of the rolling pampas with extensive agriculture. Small touristic beach area. Near the City of San Nicolás, holding a major industrial complex	7.8	914	566	140
<i>S20-Arrecifes River</i> (tributary of Paraná River). Typical vegetation of the Rolling Pampas with extensive cultivation along the watercourse	8.2	3180	1932	942
<i>S21-Río Areco</i> (tributary of Paraná River). Typical vegetation of the rolling pampas with extensive cultivation along the water course.	7.8	1580	968	94
<i>S22-Paraná de las Palmas River</i> (main watercourse). Downstream Campana Harbor. Piers, chemicals and oil shipping	7.2	168	154	88

Table 1 (continued)

Site characteristics	pH	Conductivity (μS/cm)	TDS (mg/L)	TSS (mg/L)
<i>S23-Luján River</i> (tributary of the Paraná Delta-Río de la Plata system). Typical vegetation of the rolling pampas with cultivation, but highly urbanized and industrialized upstream	7.1	1445	840	125

of the samples. All derivatized samples were finally extracted with 5 mL dichloromethane and centrifuged and the aqueous phase passed through 0.45-μm filters for HPLC-MS determination. The runs were carried out with pressure generated from a binary Agilent 1100™ pump (Agilent Technologies Inc., Miami, FL, USA) coupled to a mass-quadrupole VL mass spectrometer with an electrospray ionization source (ESI Agilent Technologies Inc., Miami, FL, USA). Chromatographic separation was performed in a C18 X-SELECT™ column (75 mm × 4.6 mm and 3 mm pore size, from Waters Corp., Milford, MA, USA) kept at 25 ± 1 °C. A methanol-water gradient was used (with mobile phases previously conditioned with 5 mM ammonium acetate) at a flow rate of 0.5 mL/min. Nitrogen was applied as an auxiliary gas at 8 L/min and 330 °C. According Meyer et al. (2009), selected ion monitoring in the negative ionization mode was applied for the detection of GLY-FMOC, ¹³C,¹⁵N-GLY-FMOC, and AMPA-FMOC. The ion settings corresponded to the deprotonated compounds and two daughter ions for quantification and identification, respectively. Data acquisition and analysis were conducted by means of Agilent Chemstation LC-MSD Rev 10A.02.

The solvents used in the chromatography were of HPLC grade, while the salts were analytical grade (JT Baker-Mallinckrodt Baker Inc., USA). Nanopure water was obtained in the laboratory by means of a Sartorius Arium water purification system (Sartorius AG, Göttingen, the Netherlands). Standards of glyphosate (99 %) and AMPA (98.5 %) were acquired from Sigma Aldrich (St. Louis, MO, USA).

Quality controls and quality assurance

Quality controls during the analysis of the major components involved the use of reagent blanks, duplicate

samples, and certified reference material (Pond Sediment 2, National Institute for Environmental Studies, Yatabe, Tsukuba, Ibaraki, Japan). The analysis of reference materials provided results at an accuracy between 80 and 95 %. The chemicals for sample treatments or the analysis of major matrix components were of analytical grade. The certified standards of metals (1.00 g/L standard stock solutions) were obtained from Accu Standard, Inc. (New Haven, CT, USA).

The quality control and assurance in the analysis of glyphosate and AMPA was done according to the International Conference on Harmonisation of Technical Requirements for Registration of Pharmaceuticals for Human Use guidelines (ICH 2005). The linearity, reproducibility, detection and quantification limits, matrix effect, and recovery were accordingly tested. Isotopically labeled glyphosate (^{13}C , ^{15}N -GLY) was used to evaluate the holding time and recovery for the complete procedure.

Analysis of data

The principal water components were plotted in a Piper diagram by means of the program *Diagrammes*: Logiciel d'hydrochimie (<http://www.lha.univ-avignon.fr>). The type of distribution of sediment data was verified using a normality test followed by principal components analysis (PCA) of the chemical contents of the matrix components Fe, Mn, Cu, total phosphorous, sulfides, fines, LOI, and the concentrations of glyphosate and AMPA. Additionally, Varimax rotation to increase the participation of the variables with higher contribution and by simultaneously reducing that of the variables with lesser contribution was applied (Helena et al. 2000). 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 based on the Kaiser principle of accepting Eigen values >1 (Quinn and Keough 2002), and the component loading of the matrix correlation was considered to be significant for values that exceeded a critical level for $n = 23$. Concentrations below the detection limit were replaced with a value of one-half of the corresponding limit. Statistical analysis was performed by means of the XL-STAT software (Addinsoft 2005, version 7.5.3).

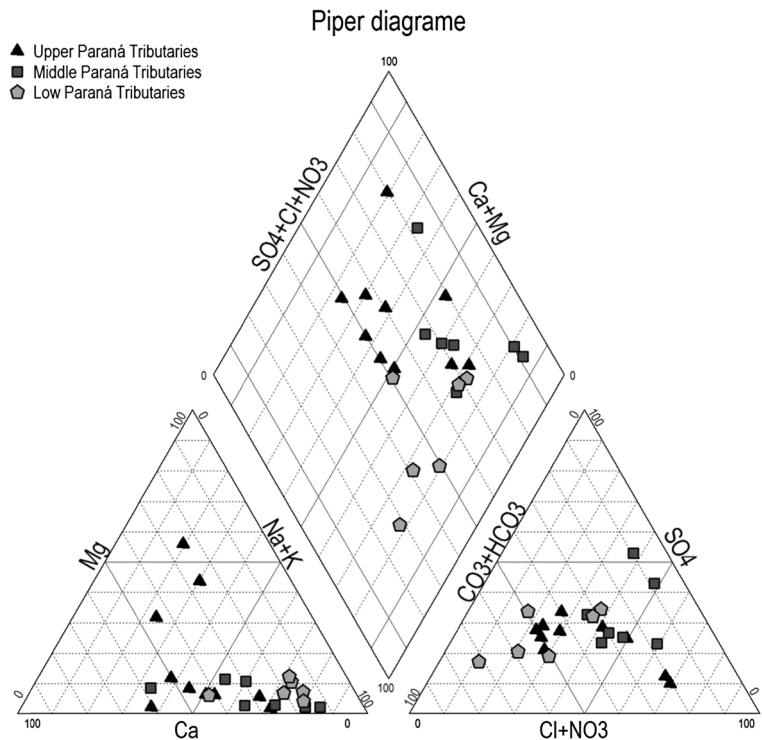
Results

Physicochemical parameters

The water composition of the tributaries (Table 1 and Fig. 2) exhibited a wide variability in the total dissolved solids at from <100 mg/L (the Paraguay and Pilcomayo rivers) up to 2000 mg/L (the Salado and Carcarañá rivers). The piper diagram in Fig. 2 shows the percentages of the main ions and their classification according to distribution, with those plots mostly indicating a central tendency for bicarbonated, sulfated, and chlorinated water and for calcium- and sodium-rich water. The concentration ranges in milligram per liter were as follows: bicarbonate, 24–326; sulfates, 11–1800; chlorides, 2–1250; nitrates, 0.05–2.8; calcium, 7.7–170; magnesium, 0.9–15.4; sodium, 3.3–1100; and potassium, 2–25. The extreme low and high values correspond to the Paraguay-Paraná main course and the Salado-Carcarañá, respectively. The suspended solids were ubiquitous in the basin, with most tributaries and the main Paraná watercourse containing over 100 mg/L and with the Arrecifes or Bermejo rivers reaching almost 1000 mg/L. The Bermejo River was the tributary that contributed the most solids to the basin owing to the river's high flow rate and type of provenance materials within its upper stretch (Manassero et al. 2008). That the Carcarañá River exhibited the lowest content of total suspended solids (at 25 mg/L), with most being present in the dissolved form, is noteworthy. Bicarbonate dominated the tributaries of the lower stretch, although that anion was variable and lower in other sectors relative to the chlorides and sulfates (e.g., in the Salado and Carcarañá rivers). The content of iron and manganese (in whole water) was between 0.6 to 8.9 and 0.005 to 0.3 mg/L, respectively, with the Bermejo River having the highest contents of both metals. All values detected were within those observed in the earlier monitoring campaign that we carried out (Ronco et al. 2011) and the data reported from recent studies on the middle stretch of the Paraná (Campodonico et al. 2015).

Table 2 summarizes the data on sediment characterization. Most samples were composed of fine particles (over 50 % content and up to 99 %), with a dominance of silts that could be classified as silty loam. The exceptions were samples from the main Paraná watercourse: those exhibited lower contents of fine particles, organic matter, and sulfides. Samples from the sandy banks of the left margin tributaries also exhibited low levels of

Fig. 2 Piper diagram of major water components



those parameters. The average content of organic matter varied from 0.2 to 9 % according to the LOI values. The sampling sites corresponding to the upper stretches of the basin tributaries tended to exhibit LOI values below 3 %, with the sole exception of S8. The tributaries of the lower stretch of the Paraná contained higher levels of LOI that became as high as 9 %. A similar pattern was observed in the sulfide contents of the sediments, where lower levels were present in the tributaries of the upper stretch of the Paraná (with almost all having <50 mg/kg) and higher levels in the lower stretch. A very high content of sulfides was detected in the mouth of the Río Saladillo, where the values reached 1907 mg/kg. The total phosphorus content did not follow any clear pattern, with concentrations ranging between 10 and 1162 mg/kg. The iron composition of the samples ranged from 1 to 15 g/kg, followed by Mn and Cu, at concentrations between 24 and 480, and <1 and 22 mg/kg, respectively. Lower levels of metals were observed in sediments from the main course of the Paraná and from the sandy banks of the left-margin tributaries (i.e., the Corrientes and Guayquiraró rivers).

Glyphosate and AMPA

The method of HPLC-MS for the analysis of glyphosate and AMPA in the environmental matrices studied produced satisfactory results (giving linear values between 1 and 2000 µg/L, with a correlation coefficient > 0.99, a relative standard deviation between 2 and 10 % for both analytes, and levels of detection (Table 3) comparable to those reported for similar types of samples (Aparicio et al. 2013; Primost 2013). The recoveries of ¹³C, ¹⁵N-GLY were over 95 % for whole/surface water, between 90 and 95 % for water-suspended particles (over the entire procedure), and between 75 and 85 % for the sediments. The results provided in the tables were corrected by each corresponding recovery factor upon consideration of the expected and measured concentrations of ¹³C, ¹⁵N-GLY. The sediment samples containing higher levels of organic matter affected the detection of glyphosate and AMPA during the ionization step of the analytical procedure causing a suppression of the signal down to 80 % (Taylor 2005); but the addition of the ¹³C, ¹⁵N-GLY internal standard to each sample enabled an effective correction to be introduced for that damping of the detector response (Ibáñez et al. 2005).

Table 2 Physical-chemical measurements of grain size (%), organic matter (OM, %), and sulfide, total phosphorus (TP) and metals (mg/kg dw) in bottom sediments (average values from the two campaigns)

Site	Fines	OM	Sulfide	TP	Fe	Mn	Cu
S1	63.6	5.1	313	348	15,757	92	19.4
S2	14.2	6.1	10	248	6697	187	4.7
S3	76.9	2.8	33	71	7684	129	6.3
S4	92.9	2.8	18	350	12,184	245	12.1
S5	92.3	2.0	20	577	13,364	239	12.1
S6	99.2	3.0	46	750	13,226	261	12.6
S7	57.4	3.6	24	108	7074	204	7.7
S8	74.4	9.6	19	262	6844	82	4.2
S9	68.4	0.2	10	12	476	35	<1.0
S10	19.9	2.9	16	21	1055	81	2.4
S11	78.5	3.1	75	20	8026	478	7.2
S12	42.4	1.7	170	281	7400	361	8.0
S13	48.5	3.1	32	560	10,609	261	10.6
S14	98.9	13.7	437	846	11,641	367	16.8
S15	62.3	22.1	91	1162	10,409	283	19.7
S16	50.0	17.2	1907	10	5950	194	21.9
S17	38.1	1.2	<10	122	2205	24	2.4
S18	85.0	8.1	426	544	6913	299	11.4
S19	96.2	11.1	490	276	11,516	301	14.3
S20	90.4	22.5	103	612	10,692	408	13.1
S21	89.6	10.2	114	128	12,191	167	13.8
S22	59.4	12.2	17	492	14,873	316	12.8
S23	71.2	4.9	762	449	11,546	200	21.4

Only 15 % of the samples contained detectable concentrations of glyphosate in the water at an average value of 0.60 µg/L (Table 3). AMPA was not detected in these samples. The detection sensitivity in water-suspended matter, being about one order of magnitude more sensitive than for the whole water, enabled the quantification of glyphosate and AMPA in 39 % and 9 % of the samples, respectively, in the 2012 sampling campaign. In this instance, the average detectable concentrations were 0.1 and 0.04 µg/L for the two compounds, respectively.

Analysis of the sediment samples (Table 3) indicated detectable levels of both compounds mostly in the middle and lower stretch tributaries of the basin sectors under investigation, with 39 and 17 % of the samples being positive in the 2011 campaign and 35 and 17 % in the 2012 for glyphosate and AMPA, respectively. The mean concentrations detected were 742 and 521 µg/kg,

respectively; while the maximum, minimum, and mean glyphosate-to-AMPA ratios were 7.80, 0.06, and 2.76, respectively. The highest concentration was detected in the Luján River, containing over 3000 µg/kg of glyphosate and 5000 µg/kg of AMPA.

Analysis of data

Since the sediment data set obtained did not adjust to a normal distribution ($\alpha = 0.05$), nonparametric statistics were used and the PCA was solved through the use of a Spearman correlation matrix at a threshold value of 0.415. The variables contributing most to factor 1 were glyphosate, AMPA, sulfides, organic matter, Cu, and Mn (Table 4), with those parameters explaining 36.8 % of the variance. Figure 3 shows that the majority of the sediment samples grouped together and were distributed along factor 2, except for S16 and S23, which sites were sequestered along factor 1. These latter two samples exhibited the highest contents of glyphosate, AMPA, sulfide, and Cu, thus differentiating them from the other much greater group of sediment samples—which, for their part, were mostly correlated with the contents of fine particles, total phosphorus, and Fe. In addition, Table 5 indicates a satisfactory correlation between the content of glyphosate plus AMPA and the high concentrations of sulfides, Mn, and Cu in the sediments (cf. rows 1 and 2 of the table vs. columns 5, 8, and 9). The pairing of Cu and sulfide, moreover, exhibited a substantial correlation at a value of 0.815.

Discussion

The Paraná Basin is primarily affected by pollution in the middle and lower stretches of the Argentine portion, during which sectors the most industrial activities and urbanization predominate. Within this part of the basin tributaries run through areas of extensive agriculture with genetically modified Roundup-resistant crops—with the production in tonnage being 10,000-fold higher than those of the upper stretch. Previous studies on a local scale in surface water streams of this core soybean production area revealed glyphosate levels ranging from undetectable to up to 700 µg/L in water and from undetectable to as much as 1850 µg/kg in sediments (Peruzzo et al. 2008). Recently, Primost (2013) detected glyphosate and AMPA in a study on a local scale in small surface water streams traversing soybean-cultivated

Table 3 Glyphosate and AMPA concentrations in the sediments, whole water, and suspended matter of the sampling sites

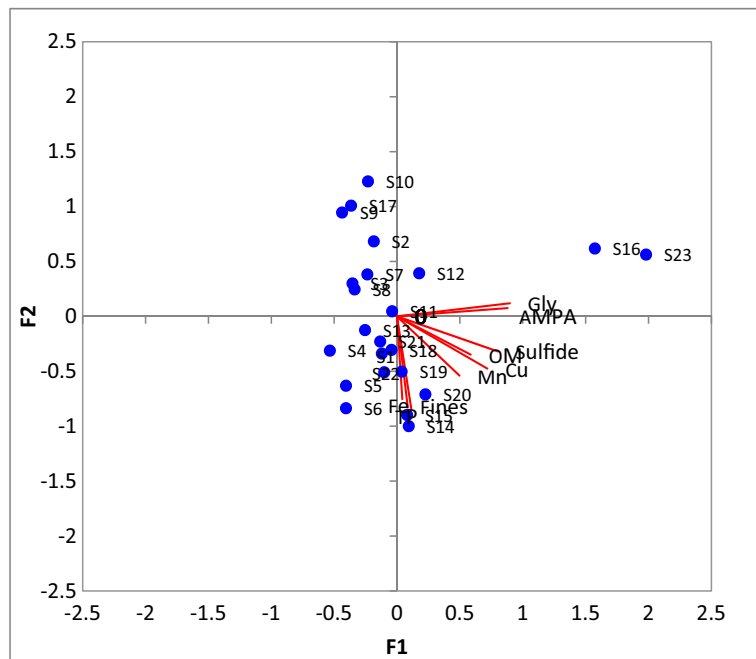
Site	Sediment (µg/kg dw)				Whole water (µg/L)				Suspended matter (µg/L)	
	Glyphosate		AMPA		Glyphosate		AMPA		Glyphosate	AMPA
	2011	2012	2011	2012	2011	2012	2011	2012	2012	
S1	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	0.10	0.04
S2	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S3	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S4	<2	<2	<2	<2	0.5	<0.3	<0.3	<0.3	0.03	<0.02
S5	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S6	<2	<2	<2	<2	0.4	<0.3	<0.3	<0.3	<0.02	<0.02
S7	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S8	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S9	<2	<2	<2	<2	0.5	<0.3	<0.3	<0.3	<0.02	<0.02
S10	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S11	359	2	88	2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S12	500	448	57	215	<0.3	0.5	<0.3	<0.3	0.10	<0.02
S13	35	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	0.21	<0.02
S14	223	<2	105	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S15	<2	<2	<2	<2	<0.3	0.6	<0.3	<0.3	0.12	<0.02
S16	1818	351	472	257	–	<0.3	<0.3	<0.3	0.04	<0.02
S17	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S18	33	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	0.08	<0.02
S19	<2	<2	<2	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S20	129	285	101	214	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S21	60	<2	44	<2	<0.3	<0.3	<0.3	<0.3	<0.02	<0.02
S22	<2	<2	154	<2	<0.3	<0.3	<0.3	<0.3	0.14	<0.02
S23	3004	719	5374	2724	1.2	0.7	<0.3	<0.3	0.06	0.04

Table 4 Coordinates of the variables analyzed for the first two factors after Varimax rotation, the Eigen values of each factor, and the percentages of the explanation and the accumulated variance

Variable	Factor 1	Factor 2
Glyphosate	0.906	0.112
AMPA	0.885	0.064
Fines	0.034	-0.748
OM	0.564	-0.442
Sulfide	0.797	-0.332
TP	0.071	-0.830
Fe	0.104	-0.841
Mn	0.490	-0.543
Cu	0.705	-0.493
Eigen value	4.23	1.90
% total variance	36.8	31.3
% accumulated variance	36.8	68.1

areas flowing into the de Galeguay River of the Entre Ríos Province within this same basin, with the research being performed during the spraying season. For the two compounds, the authors observed the following concentration ranges in water and sediments, respectively: 0.2–1.8 for glyphosate and 0.1–1.9 µg/L for AMPA and 52–3294 for glyphosate and 180–7220 µg/kg for AMPA. That these latter data from streams influenced by direct farming activities exhibited similar concentration levels of the herbicide in the sediments to those detected in the distal-tributary sediments in which our study demonstrates the impact of agriculture on the main Paraná watercourse. In addition, the monitoring of several rivers, canals, and streams from the southeastern sector of the Buenos Aires Province, an agricultural area within the region, revealed detectable levels of glyphosate and AMPA in 35 and 33 % of the water samples, respectively,

Fig. 3 Principal components analysis (with Varimax rotation) biplot of variables and the study sites for the first two meaningful principal components



and in 66 % of the sediments, at respective concentration ranges of 0.5–4 and 0.5–2.3 µg/L for glyphosate and 5.7–221 and 5.1–235 µg/kg for AMPA (Aparicio et al. 2013). Furthermore, Lupi et al. (2015) found similar frequencies of detection in water and sediment samples in the same region, although with concentration levels of both glyphosate and AMPA in water ranging from nondetectable up to 0.5 µg/L. Sediments from the preapplication period indicated relatively lower pesticide levels, with concentrations of glyphosate ranging from 7 to 14 µg/kg and AMPA from 2 to 13 µg/kg, consistent with the less intensive agriculture at that time.

Degenhardt et al. (2012) have observed in wetland environments that degradation and sorption were the more main pathways for the dissipation of glyphosate from the water column. Our findings also demonstrate a similar pattern in the partitioning of glyphosate and AMPA into the sediments. For example, in the present study, the Luján River, where the respective concentrations of the two compounds were determined for all compartments, the glyphosate levels were three to four orders of magnitude higher in the sediments than in the whole water. Furthermore, statistical analyses demonstrated that the concentrations of glyphosate and AMPA

Table 5 Correlation parameters of concentrations data. *Numbers in italics* indicate significant differences for an $\alpha = 0.050$ (bilateral test)

	Gly	AMPA	Fines	OM	Sulfide	TP	Fe	Mn	Cu
Gly	1.000	<i>0.833</i>	0.042	0.283	<i>0.661</i>	0.044	0.010	<i>0.439</i>	<i>0.454</i>
AMPA		1.000	0.008	0.372	<i>0.522</i>	0.021	0.163	<i>0.439</i>	<i>0.503</i>
Fines			1.000	0.178	0.369	<i>0.426</i>	<i>0.575</i>	0.401	0.246
OM				1.000	<i>0.519</i>	0.321	0.225	0.402	<i>0.695</i>
Sulfide					1.000	0.237	0.314	<i>0.445</i>	<i>0.815</i>
TP						1.000	<i>0.622</i>	<i>0.538</i>	<i>0.439</i>
Fe							1.000	0.412	<i>0.522</i>
Mn								1.000	0.383
Cu									1.000

were well correlated with the sulfide levels in the sediment samples (Table 4; Fig. 3; also cf. Table 5, rows 1 and 2 vs. column 4). The inputs of sulfur-containing additives (e.g., ammonium sulfate, gypsum) used with glyphosate during the weed control practices could explain these results (Nalewaja and Matysiak 1993; Faircloth et al. 2004). After entering the environment, sulfates are reduced to sulfides bacteriologically in the anaerobic compartments of the aquatic systems—particularly in those rivers that are recipients of high loads of organic matter such as the Río Saladillo and the Luján tributaries (Peluso et al. 2013a, b; Ronco et al. 2011), where the concentrations of sulfides, glyphosate, and AMPA are accordingly high. Moreover, according to the United States Environmental Protection Agency (USEPA 2008), the half-life of glyphosate in anaerobic sediments is two orders of magnitude longer than in the aqueous compartment, where the dissipation is extremely rapid. This differential degree of degradation is in agreement with our results. Sediments with higher loads of sulfides are necessarily located in the anaerobic compartments that as such provide conditions of oxidative stability and therefore contain higher levels of the herbicide.

An association of the herbicide and its metabolite was also observed in relation to Cu (Table 5, cf. rows 1 and 2 vs. column 9). Morillo et al. (2000) had reported that the presence of Cu enhanced herbicide adsorption to soil particles via Cu-glyphosate complexes. Sediment materials originating from soils containing such complexes could explain the association of the herbicide observed with the bottom sediments (e.g., in the Saladillo and Luján rivers). Furthermore, the organic matter, total phosphorus, Cu, and sulfides in the sediments were well correlated. Peluso et al. (2013a), upon taking into account the combined biologic effects (as assessed by toxicity tests and benthic community indices) along with the physical chemistry of the sediments from the same tributaries of the Paraná Basin, demonstrated the role of sulfides in contributing to toxicity in the samples they tested. The sediment from the Saladillo River, in particular, exhibited a high and acute lethal toxicity against the test organisms used.

Conclusions

This study provides the first survey of glyphosate and its metabolite AMPA in water and sediments from the

Paraná River on a basin-wide scale. The results revealed higher levels of these compounds in the middle- and lower-course tributaries in accordance with the intensive agriculture in those regions. Bottom sediments were found to be the main sinks of both compounds in the sampling sites investigated. The high flow rates and dilution capacity of the main watercourse of the Paraná attenuates the tributary inputs, although AMPA could be detected in sediments and suspended particulate matter throughout the river's lower stretch. These results provide information that is highly relevant to the management programs and environmental control of watercourses in the Paraná Basin, indicating the need for particular attention to agricultural practices associated with the chemical control of pests in the agronomically productive areas of the region.

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