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Integrated ecotoxicological assessment of bottom sediments from the Paraná basin, Argentina

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ABSTRACT

Paraná River, the six largest in the world, is receptor of pollution loads from tributaries traversing urban and industrialized areas, and extensive agriculture, particularly in its middle and low stretch along the Argentinean sector, where most of the productive activities of the country develop. Within the frame of monitoring surveys, the quality of bottom sediments from distal positions of twenty tributaries and three of the main course was evaluated. The assessment covered testing lethal and sublethal effects with the *Hyalella curvispina* based toxicity test, a benthic macrofauna survey and physicochemical variables of sediment matrix composition. A multivariate statistical analysis approach permitted integrating the obtained data from the different survey lines of evidence, explaining potential causes of the measured biological effects. The main perturbations detected were associated to tributaries in the middle sector of the basin, where anoxic conditions with high sulfide contents prevail mostly related to organic matter inputs of diverse combined activities, where sediments induce high lethality, and a consequent strong reduction of the benthic community population and diversity. The integrated survey approach proved being a robust tool in the assessment of causative—adverse effects relationships.

1. Introduction

The del Plata Basin is the second largest in South America and comprises Argentina, Uruguay, Brazil, Bolivia and Paraguay, with three large sub-basins, corresponding to the Paraná (2600,000 km^2), Paraguay (1000,000 km^2) and Uruguay Rivers (365,000 km^2). The annual discharge reaching the Atlantic Ocean is 23,000 m^3/s (Berbery and Barros, 2002). The Paraná River is the sixth largest river of the world, a mean annual discharge of 17,000 m^3/s and suspended load of 118.7 million tons/yr (Orfeo and Stevaux, 2002). The basin traverses a variety of geological units, like the Andes Mountains, the Chaco-Pampean Plains, the Eastern Plains, the Jurassic–Cretaceous Area and the Brazilian Shield (Iriondo, 1988). These well differentiated geologic and climatic environments are controlling factors in the sedimentology, clay mineralogy and matrix composition of the basin (Bertolino and Depetris, 1992). The grain size of sediments is dominated by silt and clay sizes (Iriondo, 2004; Manassero et al., 2008; Orfeo, 1999), with vast amounts of colloids and clay aggregates circulating in the basin (Konta, 1985). Most of the Argentinean productive activities and population settlements are associated to this basin. Previous monitoring campaigns have shown multiple sources of pollution along the basin. The middle and low Paraná receive heavily polluted inputs from tributaries traversing across urban and industrialized areas, added of extensive agriculture (Marino and Ronco, 2005; Peluso et al., 2013; Ronco et al., 2008, 2011; SAyDS- PNA- UNLP, 2007). Although transport of polluted mud favor mixing and recycling of particles it was possible to identify anoxic water and sediments with high sulfide and organic matter contents, changes in the composition of major matrix components and heavy metals (Ronco et al., 2011).

The dynamics of fine bottom sediments play an important role in environmental studies as they act as transporting agents and sinks of pollutants (Burton and Landrum, 2003; Camilión et al., 2003; Horowitz, 1985; Lee et al., 2000; Ronco et al., 2001). The capacity of adaptation of benthic organisms in relation to changes of environmental parameters and available food determines their distribution, growth and reproduction. Distribution and abundance are related to factors such as organic matter presence and content, substrate type and occurrence of contaminants (Wetzel and Likens, 1991). Since the bottom sediment provides nutrients and habitat to a large variety of benthic organisms, the assessment of sediment quality becomes relevant for the protection of aquatic life (Paixão et al., 2011).

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Within the frame of monitoring surveys of the Argentinean Paraguay–Paraná basin sector (between 25°21′and 34°18′ latitude), the objective of the present study is to analyze and discuss results of quality assessment of bottom sediments from distal positions of the major tributaries and the main river course, testing lethal and sublethal effects with an amphipod based toxicity test, correlating with measured physicochemical variables by means of multivariate analysis, and finally integrating the information with the screening of benthic community.

2. Materials and methods

2.1. Study area and sample collection

The sampling campaign was done in the scientific vessel SPA-1 "Dr. Leloir" of the Prefectura Naval Argentina (PNA) between June and July of 2011. Grab sediment samples were taken from a total 23 sampling points of the Paraguay and Paraná rivers (see Fig. 1) using an Eckman dredge (to an approximate depth of 10 cm). Each composite sample was obtained from at least 15 discrete grab samples per site. Twenty of the samples were taken in the confluence of the principal tributaries with the Paraná River and the rest within the main Paraná water course. Table 1 shows the sampling sites identification, corresponding abbreviations and a brief description. Also, in situ measured parameters in the water column are given.

Sediment samples were kept in a cooler at 4 °C while transferred to the laboratory. Upon arrival they were manually homogenized and sub-samples were obtained for chemical analysis and for toxicity testing. For this last case were held at 4 °C in the dark for no more than 2 weeks before the start of the toxicity tests (ASTM, 2002). A separate composite sample prepared from two sub-samples was used for the analysis of the community structure, which was previously sieved through a certified 400 mesh, and the material was fixed in 10 percent formaldehyde in the field.

2.2. Physical–chemical analysis

Physical and chemical variables of the water column from each sampling site (conductivity, transparency, pH, temperature and dissolved oxygen), were measured in situ in each sampling station (multi-parameter water quality monitor HORIBA U-52). Biological Oxygen Demand (BOD5) was also determined in the laboratory according Method 5210 D (APHA (American Public Health Association), 1998). Physical characteristics of sediments samples included grain size and organic matter. Sieving and settling velocity technique, with previous cement removal (Day, 1965) was performed for grain size analysis; sediments were sieved trough a set of Standard Sieves larger than 63 μm to separate the sands. Grain size of the fraction smaller than the 63 μm was determined by the standard pipette technique (Folk, 1954). Organic matter content in the sediment was obtained by calcination (loss on ignition) in a muffle furnace at 550 °C. Sulfides were analyzed according to Method 9030 (USEPA (United States Environmental Protection Agency), 1996); nitrogen (Bremner, 1965) and phosphorus (Andersen, 1979) contents were done by colorimetric methods. Analysis of metal content (Cd, Cu, Cr, Ni, Pb and Zn) was done by atomic absorption spectrophotometry (direct flame) following acid digestion of samples according to Method 3050 (USEPA (United States Environmental Protection Agency), 1996). Mercury was extracted according Method 7471B (USEPA (United States Environmental Protection Agency), 1996) and concentration was determined by cold vapor spectrophotometry (CV-AAS). Detection limits (mg/kg) varied depending on the metal: 0.03 Hg; 0.3 Cd; 1.0 Cu; 2.0 Ni; 3.0 Pb and Zn; 10.0 Fe and Mn). Quality controls included reagent blanks, duplicate samples and certified reference material analysis (Pond Sediment 2, National Institute for Environmental Studies, Yatabe, Tsukuba Ibaraki, Japan). Reference materials analysis provided results with accuracy ranging between 80 and 95 percent. Chemicals for sample treatments or analysis of major matrix components were analytical grade. Certified standards of metals were from AccuStandard, Inc. (1000 mg/l standard stock solutions, traceable to the National Institute of Standards and Technology, USA).

2.3. Toxicity testing

Toxicity of each of the sediment samples were assessed using the amphipod *Hyalella curvispina*. In recent years, this amphipod species has been used as test organism in ecotoxicological assessments. Its easiness in breeding under laboratory conditions, sensitivity to toxicants (García et al., 2010; Peluso et al., 2011), and being part of the native fauna lead to using it in field and laboratory testing of aquatic environments of Argentina (Giusto and Ferrari, 2008; Jergentz et al., 2004). Test organisms were obtained by sieving from laboratory cultures maintained in dechlorinated tap water (hardness 220 mg/l $CaCO_3$, pH 8.2, conductivity1.10 mS/cm) (Peluso et al., 2011). Ten-day whole-sediment tests were conducted following USEPA (United States Environmental Protection Agency) (2000) standardized protocol with modifications. Toxicity test procedure was previously described by Peluso et al. (2013). Reference sediment used in testing was obtained in S2 since according to information from previous monitoring campaigns did not exhibit detectable levels of pollution (Ronco et al., 2011). Measured endpoints were survival and growth (length). Performance criteria for the control sediment required 80 percent survival. Amphipods survival higher than 50 percent in each of replicate was set for carrying out the analysis with the variable length.

2.4. Benthic community analysis

The separation and taxonomic identification of sample material was done in the laboratory under stereoscopic microscope. All taxa were categorized into functional feeding groups based on available information (Merrit and Cummins, 1996: Cummins et al., 2005). The calculated benthic index (Cornet, 1986)

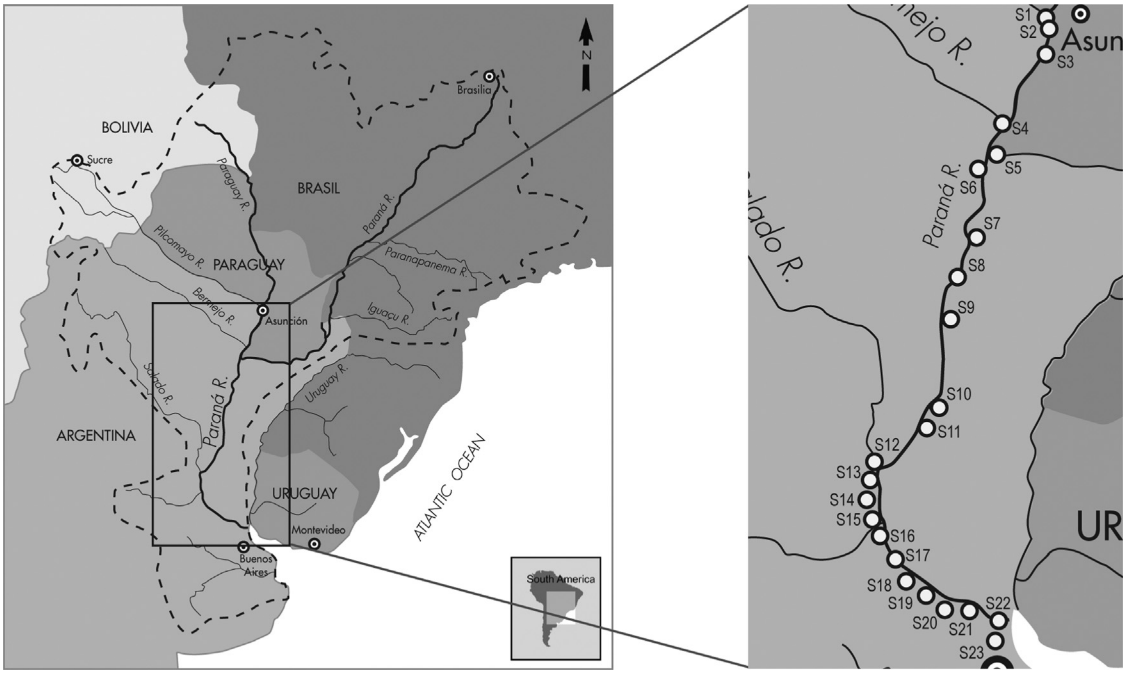

Fig. 1. Area of the study with the location of the 23 sampling sites.

Table 1
Sampling sites description and corresponding in situ measured water quality parameters.

Characteristics	T°	pH	Conductivity (mS/cm)	DO (mg/l)	BOD (mg/l)
S1- Río Pilcomayo mouth. Profuse aquatic vegetation in river bed and along banks. Direct influence from the City of Asunción (Paraguay) in the right margin of the Paraguay River. No evident influence of human activity in the Río Pilcomayo basin	22.0	6.5	16.4	5.4	3
S2- Río Paraguay. Downstream the City of Asunción. Boat traffic. Clear urban and industrial influence	22.6	6.6	9.1	6.5	3
S3- A° Montelindo. Profuse aquatic vegetation in river bed and along banks. Very low anthropic activity	18.4	6.3	53.8	8.4	Nd
S4- Río Bermejo. Very high water flow with high load of suspended particulate matter. Scarce vegetation in river banks, with very low anthropic activity	21.9	6.5	54.8	9.0	6
S5- Río Paraguay confluence with the Río Paraná. Profuse vegetation along banks, low anthropic activity in nearby areas. Populated areas upstream waters	21.6	6.8	13.3	7.8	Nd
S6- Río Negro. Black dark waters. Direct influence of the City of Resistencia. Fishing activity	20.9	7.0	44.0	4.8	4
S7- Río Santa Lucía. Agriculture in influence area. It drains waters from the Iberá watershed	17.3	6.8	28.4	7.8	Nd
S8- Río Paraná main water course. Downstream the Cities of Resistencia and Corrientes. Commercial and sport boat traffic. Fishing and touristic areas	20.1	6.6	9.0	8.2	3
S9- Río Corrientes. Sandy banks, with weeds and palm trees (Yatay). Traverses citric fruit cultivated areas	14.9	6.8	11.2	9.1	3
S10- Rio Guayquiraró. Sandy banks. It runs along gallery forests. Bathing touristic sectors. Sportive fishing	15.8	6.7	54.7	7.0	5
S11- Río Feliciano. Receptor of smaller water streams along the course. Vegetated and rice cultivation in margins	15.6	6.9	34.8	7.7	7.5
S12- Río Salado. Typical weed vegetation along margins. Receptor of large urbanized areas (Santa Fé- Santo Tomé, etc.) and local industries	13.5	7.5	668,0	7.5	6
S13- Río Coronda. Clay bottom sediments. It runs along typical rolling Pampas with extensive agriculture	11.7	7.4	684,0	8.6	8
S14- Río Carcarañá. Clay bottom sediments. High bank coastline. It runs along typical rolling Pampas with extensive agriculture	13.2	7.5	41.4	9.2	4
S15- Río San Lorenzo. Scarcely vegetated banks with constructed structures and roads along cost. High urbanized and industrial influence	16.1	7.3	23.3	8.6	5
S16- Río Saladillo. Important 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	15.6	7.2	30.4	7.7	12
S17- Río Paraná main water course. Circulation of transatlantic ships and smaller scale boats traffic	16.6	7.4	11.0	8.6	10
S18- A° Pavón. It runs across typical vegetation of the rolling Pampas. Extensive agriculture in influence area, also some industries nearby sampling site	13.8	7.4	298.0	11.1	8
S19- A° Ramallo. It runs across typical vegetation of the rolling Pampas with extensive agriculture. Small touristic beach area. Nearby the City of San Nicolás, holding an important industrial complex	16.4	7.0	61.7	10.2	11
S20- Río Arrecifes. Typical vegetation of the rolling Pampas with extensive cultivation along the water course	13.0	7.4	318.0	10.6	4
S21- Río Areco. Typical vegetation of the rolling Pampas with extensive cultivation along the water course	9.3	6.6	167.0	3.7	6
S22- Río Paraná de las Palmas main water course. Downstream Campana Harbor. Piers, chemicals and oil shipping	12.1	6.6	17.1	7.1	4
S23- Río Luján. Typical vegetation of the rolling Pampas with cultivation and highly urbanized and industrialized upstream	11.7	6.5	145.0	6.5	15

were: Mean Density $(D)=[\Sigma(ni/a)]/M$, with M: total number samples, ni: number of individual per sample, a: area sampled. The Shannon index (Shannon and Weaver, 1963) was used to calculate the specific diversity (H). The evenness (J') was calculated with the Pielou (1975) and Species richness (S) counting the number of species. Dominance $(Dm)=(n/N)\times 100$, with n: total number of individuals of the considered species, N: total number of individuals from all the species. Frequency $(F)=(m/M)\times 100$, with m: number of samples with the considered species, M: total number of samples. Considering the dominance and frequency (Rodriguez et al., 1980), species were classified as: (a) Dominant: $Dm\geq 1$ percent; (b) Constant: $F\geq 50$ percent; (c) Accessory: 25 percent $<F<$ 50 percent; (d) Accidental: $F<25$ percent; (e) Expansive: $F>15$ percent and $Dm>25$ percent; (f) Diffuse: $F>15$ percent and $Dm<25$ percent.

2.5. Statistical analysis

Toxicity data were checked for normality and homoscedasticity assumptions with Shapiro–Wilk's and Bartlett's tests, respectively. The amphipod survival and growth (length) were compared by the one-way analysis of variance (ANOVA), followed by Tukey test. Percent survival data were arcsine-transformed, and length data were log-transformed before analysis (Zar, 2010). Potential relationships between measures of exposure (chemistry data) and effects (toxicity and benthic community data) were explored using bivariate and multivariate statistical analyses. PCA was performed on chemical contents of Fe, Mn, Pb, Cr, Cu, Zn, As, Hg and sulfides; fines and organic matter in the sediments, benthic index (specific diversity H, evenness J' and species richness S) and the toxicity tests data (amphipods mortality and inhibition of growth for organisms exposed to whole sediment), followed by Varimax rotation in order to make the components more interpretable. 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 considered to be significant for values >0.4. Analytes not detected in at least 50 percent of the stations were not included in the PCA. Concentrations below the detection limit were replaced with a value of one-half the corresponding limit (Delistraty and Yokel, 2007). PCA was performed using tools of the software XL-STAT (Addinsoft 2005, version 7.5.3).

3. Results and discussion

3.1. Physical–chemical analysis

Data of sediment characterization is given in Table 2. Most samples are composed by fines (over 50 percent content) with

Table 2
Physical–chemical measurements of grain size (percent), organic matter (OM percent); sulfides, Nitrates, P and metals (mg/kg dry weight) in bottom sediments.

Site	Fines	OM	Sulfides	Total P	Nitrate	Fe	Mn	Cd	Cu	Cr	Hg	Ni	Pb	Zn
S1	63.6	4.6	313	200	2.7	7,350	45	< 0.3	9.2	8.3	< 0.03	10.2	28.6	27.7
S2	14.2	8.6	10	14	2.4	840	< 10	< 0.3	< 1.0	< 3.0	0.06	< 2.0	< 3.0	1.3
S3	76.9	3.2	33	19	< 1.0	8,920	154	< 0.3	6.7	8.8	0.20	11.4	19.0	32.4
S4	92.9	3.7	18	86	3.8	14,060	270	< 0.3	13.3	14.1	0.16	19.6	34.8	46.8
S5	92.3	2.2	20	468	3.8	15,830	239	0.5	12.5	17.3	0.14	20.5	29.6	51.1
S6	99.2	2.5	46	532	3.4	11,890	210	0.3	9.9	12.9	0.05	16.5	23.4	41.6
S7	57.4	3.4	24	47	2.7	7,580	193	< 0.3	7.3	8.1	0.10	9.9	15.9	19.4
S8	74.4	17.2	19	302	5.4	7,740	101	< 0.3	4.7	8.4	0.07	10.6	13.3	18.4
S9	68.4	0.2	< 10	14	3.3	400	29	< 0.3	< 1.0	< 3.0	< 0.03	< 2.0	< 3.0	1.1
S10	19.9	2.9	32	42	4.8	2,110	161	< 0.3	2.4	< 3.0	0.18	< 2.0	6.5	10.9
S11	78.5	4.1	75	29	2.5	12,300	587	< 0.3	9.5	14.3	0.22	11.3	22.7	23.6
S12	42.4	0.7	170	319	< 1.0	4,800	128	< 0.3	4.2	6.7	0.05	6.5	13.9	13.1
S13	48.5	3.5	32	680	4.0	11,550	210	< 0.3	9.5	14.4	0.21	12.0	20.7	25.8
S14	98.9	19.5	437	287	< 1.0	7,850	149	< 0.3	8.8	11.9	0.15	8.5	15.8	30.2
S15	62.3	35.8	91	195	7.2	7,520	162	< 0.3	5.9	8.6	0.41	9.2	13.2	17.9
S16	50.0	17.2	1907	11	2.8	11,900	387	< 0.3	26.7	21.6	0.08	15.9	36.3	97.9
S17	38.1	1.2	< 10	243	2.9	4,410	47	< 0.3	2.4	< 3.0	0.15	6.1	6.4	12.3
S18	85.0	11.1	426	70	1.0	4,850	153	< 0.3	5.8	7.1	1.63	5.7	13.8	16.3
S19	96.2	15.5	490	131	9.9	13,060	218	< 0.3	13.2	20.6	0.26	12.5	29.1	49.4
S20	90.4	40.6	103	276	8.6	12,430	303	< 0.3	11.6	17.2	0.21	10.8	23.3	40.7
S21	89.6	17.1	114	62	1.6	5,660	179	< 0.3	8.9	9.3	0.25	6.5	16.3	28.5
S22	59.4	21.9	17	278	11.3	16,790	363	< 0.3	13.0	19.7	0.26	17.8	23.7	35.5
S23	71.2	4.4	762	71	1.7	12,550	152	< 0.3	19.3	30.7	0.25	10.9	27.2	61.7

dominance of silts and can be classified as silty loam. The samples from S2 and S10 exhibit a high content of sand while those from S12, S13 and S17 show a variable texture. The organic matter content of the studied sediments is variable, ranging 0.2 and 40.6 percent according OM values. Though there is a tendency indicating that the first 13 sampling sites corresponding to the upper sector tributaries exhibiting OM values below 10 percent, with the exception of S8. Paraná lower course tributaries exhibit higher levels of OM ranging 11.1 and 35.8 percent. The samples from the main course of the Río Paraná are the exception, characterized by low levels of organic matter. A similar behavior could be observed in relation to sulfide contents in sediments, with lower levels in tributaries of the upper course (almost all of them below 50 mg/kg) and higher in those of the lower course of the Paraná. A very high content of sulfides was detected in the Río Saladillo mouth reaching values of 1907 mg/kg.

To assess the contamination level with heavy metals and the potential impacts of anthropic activities in different areas of the basin, it was calculated an enrichment factor (EF) of the tested sediments. Data on metal levels was normalized against iron concentration in each sample to differentiate pollution loads from background levels (Mucha et al., 2003). According to Sinex and Helz (1981) and Rubio et al. (2000) the metal enrichment factor (EF) is defined as follows:

$$\mathrm{EF} = (\mathrm{M}/\mathrm{Fe})_{\mathrm{sample}}/(\mathrm{M}/\mathrm{Fe})_{\mathrm{background}}$$

where EF is the enrichment factor, $(\mathrm{M}/\mathrm{Fe})_{\mathrm{sample}}$ is the ratio of metal and Fe concentration of the sample, $(\mathrm{M}/\mathrm{Fe})_{\mathrm{background}}$ is the ratio of metal and Fe concentration of a background. Existent data on concentrations of metals in bottom sediments from rivers and streams of South America with low anthropic impacts (Merlo et al., 2011; Peluso et al., 2013; Ronco et al., 2007, 2008; Weber et al., 2013) and pristine sediments (Solomons and Förstner, 1984) indicates that values are within the range of average earth crust (Martins and Meybeck, 1979; Viers et al., 2009). Additionally, due to a lack of sediment guideline values in Argentina, a comparison with existent Canadian Sediment Quality Guidelines (CCEM, 2002) was done taking into account both the interim sediment quality guideline (ISQG) and the probable effect level (PEL). In the present study we employed the metal average earth crust levels to calculate EF of the study metals except for Cd and Hg. Cadmium was below the detection limit in almost all samples with the methodology of analysis employed, and Hg did not correlate with Fe concentrations. Mercury exhibited very variable concentrations below or near 0.25 mg/kg (Table 2) in most sampling places, being over the ISQG for this metal, except for S15 with 0.41 mg/kg and S18 reaching a concentration of 1.63 mg/kg; in this last case being over the PEL value. Measured concentrations of Cu, Cr, Ni, Pb and Zn were all below the ISQG (CCEM, 2002), with the exception of Pb that was over the level in sample S16. Table 3 shows metal EFs for the 23 sampling sites of the studied tributaries and Paraná main course. According Zhang and Liu (2002), EF values between 0.5 to 1.5 indicate that the metal concentration is associated to earth crust provenance while values over 1.5 suggest anthropic sources disturbance. In our study, Pb exhibits EF values over 5, suggesting significant enrichment in most tributaries near the confluence

Table 3
Enrichment factor (EF) values of heavy metals from sediments samples.

Site	Cu	Cr	Ni	Pb	Zn
S1	1.40	0.57	1.02	8.73	1.07
S2	NC	NC	NC	NC	0.44
S3	0.84	0.50	0.94	4.78	1.03
S4	1.06	0.51	1.02	5.56	0.94
S5	0.89	0.55	0.95	4.20	0.91
S6	0.93	0.55	1.02	4.42	0.99
S7	1.08	0.54	0.96	4.71	0.72
S8	0.68	0.55	1.00	3.86	0.67
S9	NC	NC	NC	NC	0.78
S10	1.28	NC	NC	6.91	1.46
S11	0.87	0.59	0.67	4.14	0.54
S12	0.98	0.71	0.99	6.50	0.77
S13	0.92	0.63	0.76	4.02	0.63
S14	1.26	0.77	0.79	4.52	1.09
S15	0.88	0.58	0.90	3.94	0.67
S16	2.52	0.92	0.98	6.84	2.33
S17	0.61	NC	1.01	3.26	0.79
S18	1.34	0.74	0.86	6.40	0.95
S19	1.13	0.80	0.70	5.00	1.07
S20	1.05	0.70	0.64	4.21	0.93
S21	1.76	0.83	0.84	6.46	1.42
S22	0.87	0.59	0.78	3.17	0.60
S23	1.73	1.24	0.64	4.86	1.39

NC: not calculated.

with the Paraná main course. Copper is also enriched in samples from S16, 21 and 23, with a maximum EF of 2.5. These sediments correspond to sampling sites under industrial influence (see Table 1).

3.2. *Toxicity testing*

Survival results obtained after the acute 10-day toxicity test with *H. curvispina* are shown in Fig. 2. The highest average percentage of survival of 94 percent corresponds to the control sediment, meeting the acceptance criteria recommended by USEPA (United States Environmental Protection Agency) (2000) for whole sediment toxicity testing. Overlying water quality characteristics were similar among treatments. Dissolved oxygen in the overlying water was at or above acceptable levels of 2.5 mg/l in all treatments throughout the study (USEPA (United States Environmental Protection Agency), 2000). ANOVA test showed significant differences ($p < 0.05$) between S15, S16 and S18 samples with the control, with survival of test organisms below 35 percent, being 0 percent in the sample S16.

Growth of amphipods as body length was assessed in samples showing survival over 50 percent. The percentage of growth of amphipods after 10 days of the control group was 24 percent respect to initial time. Exposed organisms to studied samples exhibited a variable growth. Fig. 3 shows the percentage of growth of sediment exposed *H. curvispina* respect to the initial group. Results indicate significant differences for samples S3, S7, S8, S22 and S23 exhibiting a reduction of growth while sediments from S11 and 17 induced an increment of growth. Previous studies using *H. curvispina* as test organisms in moderately or not contaminated sediments from rivers and streams of the Pampean region it was possible to detect 20 and 35 percent of growth respect to the initial group (Peluso et al., 2011, 2013; Giusto et al., 2012). From 20 of the studied samples of the Paraná tributaries in which was possible to assess growth, eight of them exhibited inhibition (respect to the initial group) (Fig. 3).

3.3. *Benthic community analysis*

Density of the community varied between 25 and 6,588 individuals/m^2 being maximum and minimum values for sites S8 and S15, respectively. A total of 24 taxa were registered, though the systematic study was done for the most relevant in the samples. Results are shown in Table 4. Richness varied between 1 and 11 (for sites S8 and S19, respectively), diversity with values between 0.25 and 2.35 (for sites S23 and S7) and evenness between 0.10 and 0.79 (for sites S19 and S9, respectively). According González del Tanago and García Jalón (1984) sites showing low diversity can indicate presence of communities under extreme conditions, where only few species that adapt can survive, proliferating respect to the rest of the species from the community. Rodrigues Capítulo et al. (1997) registered low diversity in sediments with higher organic matter content for the Río de la Plata, concluding that in this type of water system, the high perturbation given by its hydrodynamic determines low specific diversity, regardless of the presence of pollution sources.

Within the functional feeding groups (FFG) identified in the benthic group (Table 5) in the studied sites of the upper and middle basin tributaries, predominate the collectors-gatherers, represented by oligochaete and chironomid (dominant and constants) and collectors-filterers, represented by bivalves, particularly *Limnoperna fortunei*. Tributaries of the lower basin sector are represented by scrapers gasteropods. The ratio oligochaete and chironomid in relation to other taxa confirm their dominance over other groups in this type of environments, observations in agreement with Marchese and Ezcurra de Drago (1992, 1999) and Rodrigues Capítulo et al. (2001). According Kerans and Karr (1994) an increment of anthropic perturbation will be associated

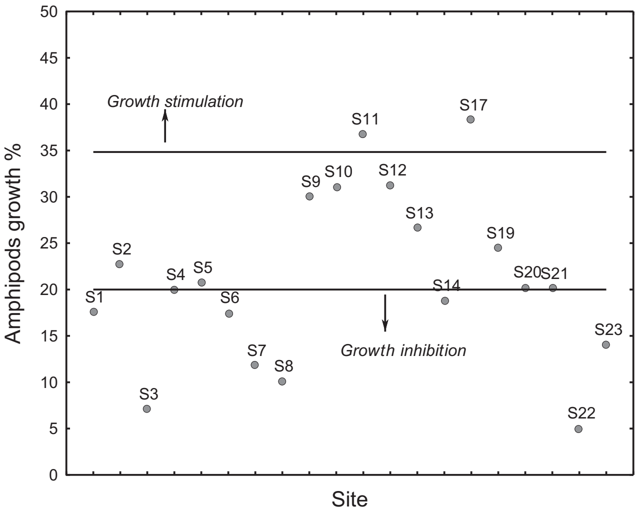

Fig. 3. *H. curvispina* percentage of growth for 10-d exposed organisms to sediments from the study sites respect to initial group. Horizontal lines mark the bounds for stimulation and inhibition of measured end point.

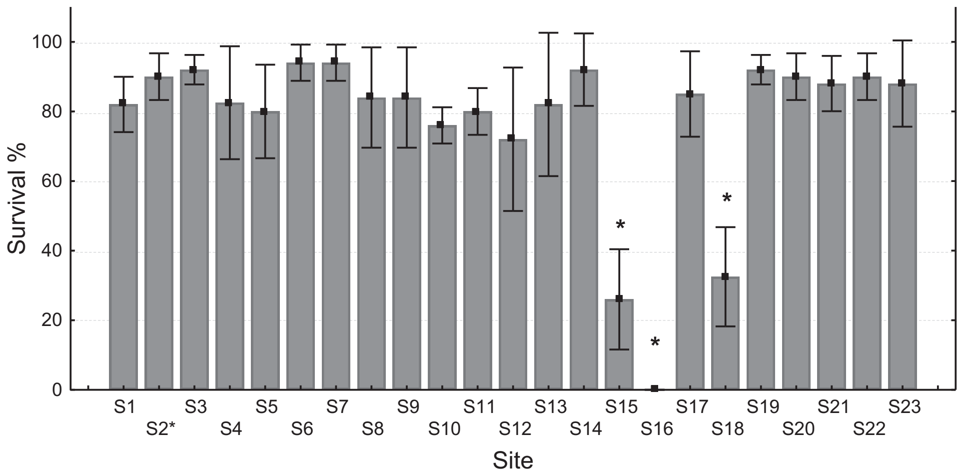

Fig. 2. Average values of the five replicates and standard deviation of amphipods survival percentage after 10 days of exposure to sediments from the study areas. Asterisks indicate significant difference regarding the control site (S2*) ($^*p < 0.05$).

Table 4
Values of the average density (ind/m^2), specific richness, species richness (S' index), diversity (H' index), evenness (J' index) and oligochaetes/chironomids/other taxa ratio (percent).

Site	Mean density	Specific richness	H' index	J' index	Oligochaeta	Chironomidae	Others
S1	100	3	1.30	0.67	0.0	0.0	100.0
S2	138	5	1.67	0.49	0.0	18.2	81.8
S3	200	3	1.41	0.75	0.0	50.0	50.0
S4	800	5	1.55	0.43	2.0	0.0	98.0
S5	50	2	0.81	0.83	75.0	0.0	25.0
S6	750	3	0.49	0.30	91.7	0.0	8.3
S7	750	10	2.35	0.43	9.8	14.8	75.4
S8	25	1	0.00	NC	0.0	100.0	0.0
S9	75	3	1.46	0.79	33.3	0.0	66.7
S10	125	4	1.85	0.78	20.0	30.0	50.0
S11	1075	5	0.49	0.15	93.0	1.2	5.8
S12	225	4	1.66	0.64	12.5	12.5	75.0
S13	950	6	1.53	0.34	66.3	8.8	25.0
S14	5613	6	1.16	0.23	10.9	6.7	82.4
S15	6588	4	0.54	0.21	90.5	0.0	9.5
S16	538	5	1.35	0.36	11.6	4.7	83.7
S17	0	0	0.00	NC	0.0	0.0	0.0
S18	1467	5	1.09	0.27	0.0	4.5	95.5
S19	4525	11	0.98	0.10	7.2	0.6	92.3
S20	1111	5	1.60	0.46	30.0	6.0	64.0
S21	975	5	1.74	0.53	56.4	0.0	43.6
S22	0	0	0.00	NC	0.0	0.0	0.0
S23	1044	2	0.25	0.47	95.7	0.0	4.3

NC: not calculated.

Table 5
Functional feeding group and faunal features of Paraná and Paraguay rivers, Abbreviation: FFG, functional feeding group; P, predators; C-g, collectors-gatherers; C-f, collectors filterers; Scr, scrapers.

Taxa	FFG	Frecuency (%)	Dominancy	Fauna characteristics
Ostracoda	C-g	9.5	0.8	Accidental
Copepodos	C-f	9.5	0.1	Accidental
Cladocera	C-f	14.3	17.4	Dominant, accidental
Hyalella curvispina	Shr	4.8	0.8	Accidental
Limnoperna fortunei	C-f	42.9	1.6	Dominant, accidental, diffuse
Cyanocyclas sp	C-f	28.6	0.7	Accessory, diffuse
Pisidium sp	C-f	4.8	0.2	Accidental
Biomphalaria sp	Scr	33.3	1.1	Dominant, accessory, diffuse
Asolene sp	Scr	28.6	0.6	Accessory, diffuse
Heleobia sp	Scr	47.6	24.6	Dominant, accessory, diffuse
Uncancylus sp	Scr	4.7	0.1	Accidental
Ceratopogonidae	P	9.5	0.2	Accidental
Chironomidae	C-g	66.7	3.6	Dominant, constant, diffuse
OLIGOQUETA	C-g	76.2	42.2	Dominant, constant, expansive
Hexagenia sp	C-g	19.0	1.8	Dominant, accidental, diffuse
Caenis sp.	C-g	9.5	1.3	Dominant, accidental
NEMATODA	P	14.3	0.6	Accidental
Smicridea sp	P	4.8	1.7	Dominant, accidental
ACAROS	P	4.8	0.0	Accidental
HIRUDINEA	P	4.8	0.2	Accidental
Phyllocycla sp	P	4.8	0.2	Accidental
Perlestidae	P	4.8	0.1	Accidental
Libellulidae	P	4.8	0.1	Accidental
Elmidae	C-g	4.8	0.1	Accidental

with an increment in the proportion of collectors gatherers and filterers and a decrement in the proportion of scrapers, shredders and predators (except for Tanypodina and Hirudinea). Though Marchese (1997) considers that the large number of collectors gatherers in these environments is due not only by contamination but also to the fact that these organisms are typical from rivers and streams of plains characterized by a high proportion of fines associated to organic matter.

3.4. Multivariate approach

For a better understanding of the relationship between chemicals and toxicity, possible correlations between physicochemical concentrations measured in the sediments and the survival and growth assessed in amphipods exposed to those sediments were investigated. Concentrations of metals, sulfides, total P, fines and organic matter in sediments together with the biological effects measurements (amphipods mortality and inhibition growth) and benthic community index were associated by PCA followed by Varimax rotation. The PCA grouped the 17 variables in four principal components (75.4 percent of cumulative variance) of which eigenvalue were more than 1.0. The loadings of the variables and percentage of the total variance for these factors are represented in Table 6. The first factor accounted for 35.4 percent of the total variance; this combines the concentrations of Fe, Mn, Zn, Cu, Ni, Pb, Cr and fines with positive values. This factor could represent the sedimentary matrix and include Fe, Mn and fines. The second factor accounted for 16 percent of the total variance and is positively correlated with sulfides contents and toxicity (amphipods mortality and inhibition growth), and positively correlated but with fewer loadings with Cu and Zn concentrations (Table 6). Factor 2 suggests that lethal toxicity detected by the amphipod test may be due to high sulfide content since concentrations of Cu and Zn do not reach the ISQG level values nor the sensitivity of *Hyalella* (Milani et al., 2003; Giusto and Ferrari, 2008; Peluso et al., 2013). The third factor is highly correlated with evenness and less correlated with diversity; besides is positively correlated with mercury and negatively correlated with organic matter contents. Finally, the fourth factor (10.7 percent of total variance) is correlated with diversity and richness.

Fig. 4 correspond the biplot obtained by the PCA (with Varimax rotation) showing the distribution of sediment samples and space variables defined by the two first factors. It can be seen that S16 detaches from the rest of the sampling places, with high values for the first two factors, particularly *F*2. This factor is represented by sulfide concentration and lethality of amphipods. Additionally, higher contents of metals in S16 explain the factor loading on *F*1.

Table 6
Factor loading and percentage of the total variance explained for 4 components.

	*F*1	*F*2	*F*3	*F*4
Eigenvalue	6.52	2.52	2.33	1.43
Variance %	35.40	15.98	13.27	10.72
OM	0.13	0.28	**−0.70**	0.14
Total P	0.26	**−0.47**	−0.17	−0.37
Sulfides	0.37	**0.82**	0.01	0.09
Fines	**0.59**	−0.27	−0.29	0.16
Zn	**0.85**	**0.44**	0.10	−0.01
Cu	**0.87**	**0.44**	0.00	0.01
Ni	**0.91**	−0.09	0.03	−0.23
Pb	**0.95**	0.14	0.08	0.03
Cr	**0.88**	0.17	−0.16	−0.05
Fe	**0.95**	−0.11	−0.13	−0.16
Mn	**0.67**	0.09	−0.16	0.09
Hg	0.09	0.01	**0.78**	0.05
H'	−0.20	0.03	**0.43**	**0.80**
Richness	0.13	−0.01	−0.12	**0.91**
J'	−0.14	−0.02	**0.78**	0.26
Growth inhib	0.17	**0.68**	−0.38	−0.05
Mortality	0.01	**0.85**	−0.10	−0.05

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

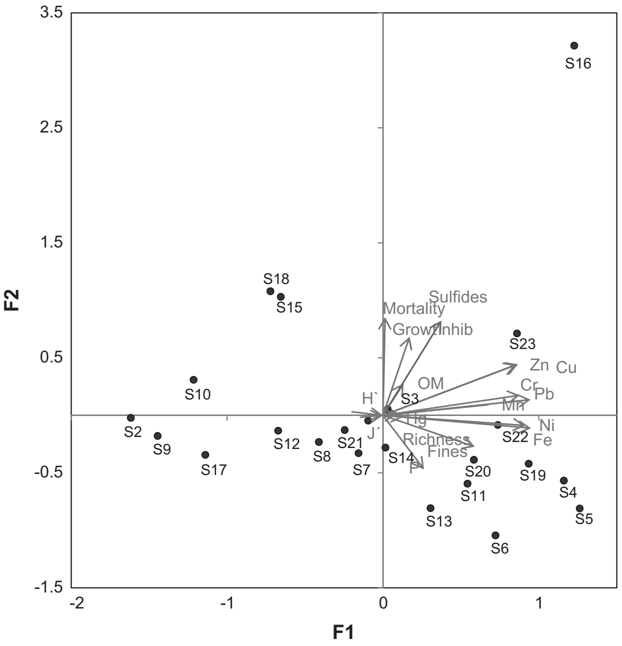

Fig. 4. Principal components analysis (with Varimax rotation) biplot of variables and the studied sites for the first two meaningful principal components.

The S16 corresponds to the tributary Río Saladillo, receptor of industrial discharges from a highly densely populated area of Rosario City (Table 1). Sulfide content from S16 is between one and two orders of magnitude over the rest of the study tributaries and the main course of Paraná River. The S15 and S18 sediments also detach from the rest, exhibiting positive values only for the *F*2. A possible association of the observed lethality in the sample from Pavón stream (S18) could be the high sulfide content. Although, sample from S15 exhibits lower sulfide levels, is one of the sediments with higher content of OM. This last site is under the influence of different industrial activities with a potential input of a wide range of chemical pollutants, some of them not being characterized (i.e., the OM characteristics) contributing to its high toxicity. Sediment from site S23, although is showing positive *F*1 and *F*2 values, also detaches from the rest of the sites. This sample induced growth inhibition on exposed amphipods. The site corresponds to the middle sector of Río Luján, with agricultural, urban and industrial activities (City of Luján and Pilar Industrial Complex) (Peluso et al., 2013). A range of values of both factors were detected for the rest of the tested sediments. Sites with fine contents below 10 percent and low metal concentrations corresponding to the main Paraná course (S2 and S9) in one extreme and sites with high fine contents from the upper and middle course of Paraná (S4, S5 and S6) (Fig. 4). The sampled tributaries have a high sediment transport capacity and high content of fines i.e., S4 correspond to sediments from Río Bermejo, a tributary that inputs between 50 and 80 percent of the total solid of the Paraná Basin (Bertolino and Depetris, 1992), reaching concentrations of 4500 mg/l (Drago and Amsler, 1988).

In relation to the other factor loadings (Table 6), *F*3 and *F*4 allowed explaining the benthic community variability. The samples from S3, S4, S5 and S10 exhibit positive *F*3 values while S1, S2, S7, S9 and S12 show low positive values, mainly characterized by the low OM content and high evenness. These sites correspond to tributaries of the upper sector of the Paraná, with low influence of urbanized or industrialized areas. The *F*4, represented by the richness and diversity of the benthic community exhibits positive values in sites S7, S19, S20 and S21, the three last corresponding to streams of the rolling pampas sector, all with similar features. Additionally, negative values of the *F*4 for samples S8, S17 and S22 (corresponding to the main course of the Paraná River), characterized by a very poor benthic community and low content of the physicochemical measured variables may be associated with its characteristic high flow rates and periodic dredging interventions to maintain navigation.

4. Conclusion

The study provides for the first time an integrated quality assessment survey of bottom sediments from tributaries of the Argentinean sector of a major surface water system like the Paraná basin. The multiple assessment approach, covering matrix characteristics and composition, associated biological effects assessed by means of a standardized toxicity test with a representative organism of the particular ecosystem, together with a survey of the benthic community allowed detecting critical sites contributing with toxicant loads into the system. A multivariate statistical approach permitted integrating data from the different survey lines of evidence, explaining potential causes of the measured biological effects. The main perturbations detected were originated from urbanized and industrialized areas associated to tributaries in the middle sector of the basin. Further steps of future research in the basin will include the influence of large areas under intensive and extensive agricultural land use, introducing other stressors such as pesticides associated to the chemical control of pests strategies used in the agriculture production of the region.

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