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Physicochemical and ecotoxicological based assessment of bottom sediments from the Luján River basin, Buenos Aires, Argentina

Leticia Peluso · Gustavo Bulus Rossini · Alfredo Salibián · Alicia Ronco

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Abstract The physicochemical analysis of bottom sediments of the Lujan River was done on samples from 14 sites situated along its course and covered grain size and organic matter, total N and P, sulfides, heavy metals, organochlorine, and pyrethroid pesticides. In addition, acute 10-day whole-sediment laboratory toxicity tests were carried with each sample, using the native amphipod *Hyalella curvispina* as test organism. In order to correlate both types of results, data were assessed by multivariate analysis, including principal component analysis (PCA). The physicochemical profile of samples resulted similar along the river course, though several anomalous data were registered in the middle course of the river, mainly in samples taken downstream a large industrial complex; with a few exceptions in upper basin sites characterized by the dominance of agricultural activities, the pesticides concentration were consistently below the analytical detection limits. Almost 50 % of the samples induced adverse effects on the amphipod when testing sublethal and lethal end points. The toxicity of the samples in terms of survival rate was extremely high in two sites, in particular in samples taken downstream the Pilar industrial complex. The integration of a selection of physicochemical and toxicological parameters of the sediments by PCA allowed discriminating areas of the river basin according the type and intensity of their particular pollution condition.

Keywords Contamination · Sediment toxicity testing · *Hyalella curvispina* · Multivariate analysis

Introduction

Sediments play a significant role in aquatic ecosystems, mediating chemical exchange among the particulate, dissolved, and biological phases. Most attention has been focused on concentrations and fates of contaminants in dissolved form (Burton 2002), with much less attention given to sediment-associated contaminants. Sediments may accumulate contaminants in concentrations higher than those observed in the water

L. Peluso · G. Bulus Rossini · A. Ronco
Centro de Investigaciones del Medio Ambiente, Facultad de Ciencias Exactas, Universidad Nacional de La Plata,
Calle 47 y 115 La Plata (1900),
Buenos Aires, Argentina

L. Peluso · A. Ronco (✉)
Consejo Nacional de Investigaciones
Científicas y Técnicas (CONICET),
Buenos Aires, Argentina
e-mail: cima@quimica.unlp.edu.ar

A. Salibián
Programa de Ecofisiología Aplicada, (PRODEA-INEDES),
Departamento de Ciencias Básicas,
Universidad Nacional de Luján,
Lujan, Buenos Aires, Argentina

G. Bulus Rossini · A. Salibián
Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC PBA),
Buenos Aires, Argentina

column (Bartlett et al. 2004), thus inducing harmful effects on the benthic biota with potential impacts via bioaccumulative or biomagnification processes. It has been demonstrated that organic or inorganic pollutants do not remain immobilized in the sediments, being remobilized by bioturbation and/or resuspension (Sprovieri et al. 2007). Sediments are contaminant sinks and could act as secondary sources of pollution (Burton and Landrum 2003; Lee et al. 2000), altering the quality of aquatic environments and aquatic life.

Many different approaches may be used in sediment quality assessment. Among them, chemical analyses and toxicity testing are the most commonly used around the world (Ingersoll et al. 2002; Kwok et al. 2010; Losso et al. 2004). Chemical analyses consist in listing de contaminants and quantifying the contaminants and their respective concentrations. Toxicity tests are considered effective tools for providing direct, quantifiable evidence of the biological consequences of contamination. These tests allow the evaluation of the interactive effect of the complex mixtures present in the sediment and can be carried out with the aqueous phase (elutriate or porewater) or in the solid phase (whole sediment) (Blaise and Férard 2005). The whole sediment tests provide a methodology to evaluate the bioavailability of contaminants to benthic organisms (Landrum and Robbins 1990; Riba et al. 2004). Amphipods are suitable and are strongly recommended as test organisms in sediment toxicity tests (ASTM 1999; USEPA 2000). In recent years, the amphipod *Hyalella curvispina*, widely distributed in South America, 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 (Anguiano et al. 2008; Giusto and Ferrari 2008; Jergentz et al. 2004; Mugni et al. 2011; Venturino et al. 2007).

The Lujan River basin is situated in the northeast of Buenos Aires Province. Approximately one million people live in the influence area of the basin. It is one of the most disturbed aquatic environments of the region. Agriculture in the upper sector (Andrade 1986; Guichón et al. 1999) and industrial activities (untreated effluents from the Luján and Pilar industrial complexes) mainly in the middle and low basin sectors are important nonpoint and point sources of pollution, with additional raw sewage discharges. Industries accounting a major recent growth are those related to petrochemical and chemical production, added of food industry and textiles (Briano et al. 2003). Water surveys evidence low-quality standards, with low dissolved oxygen, high COD values, and also high levels of nutrients, with evidence of eutrophication (Giorgi et al. 2000; Pizarro and Alemanni 2005). Also, presence of different inorganic and persistent organic pollutants had been detected (O'Farrell et al. 2002; Lobos et al. 2006; Lombardo et al. 2009), though there is scarce information on sediment quality surveys of the basin (Di Marzio et al. 2005; Ronco et al. 2008).

Taking into account the reports on the contamination of the Luján River basin and the lack of studies on sediment related biological effect assessments, the objective of the present study is the evaluation of sediment quality, integrating experimental data from: (1) sediment physical–chemical analyses, (2) toxicity data using sediment toxicity tests with *H. curvispina* as test organism, and (3) analyzing results by multivariate statistical analysis.

Materials and methods

Study area and sampling sites

The Río Luján is situated in the northeast of the Buenos Aires Province flowing into the Río de la Plata estuary. The basin area covers 2,600 km^2, running across several local districts with a total length of 128 km (Andrade 1986). According to Sala (1972), it can be divided in three sectors. The 40 and 30 km upper and middle sectors, respectively, have a slightly higher regional slope and the last 60 km with lower slope, traverse on Quaternary deposits known as the Pampas plains. The present study was carried along the upper and middle course of the Lujan River. Figure 1 shows the location of the sampling sites. Samples were taken in the following sites: Aº Durazno (SU-1) and Aº Leones (SU-2) both from the locality of Suipacha; García bridge (SU-3); 3 de Marzo bridge, Mercedes (SU-4); Jáuregui (SM-1); A. Brown bridge, Luján (SM-2); Highway 8 intersection, Pilar (SM-3); Highway 6 intersection (SM-4); Aº Larena upstream (SM-5) and (SM-6) downstream Pilar industrial complex; Acceso Oeste intersection (SL-1); Pilar nature reserve (SL-2); and Highway 9 intersection, Escobar (SL-3) and Carmel, Pilar (SL-4).

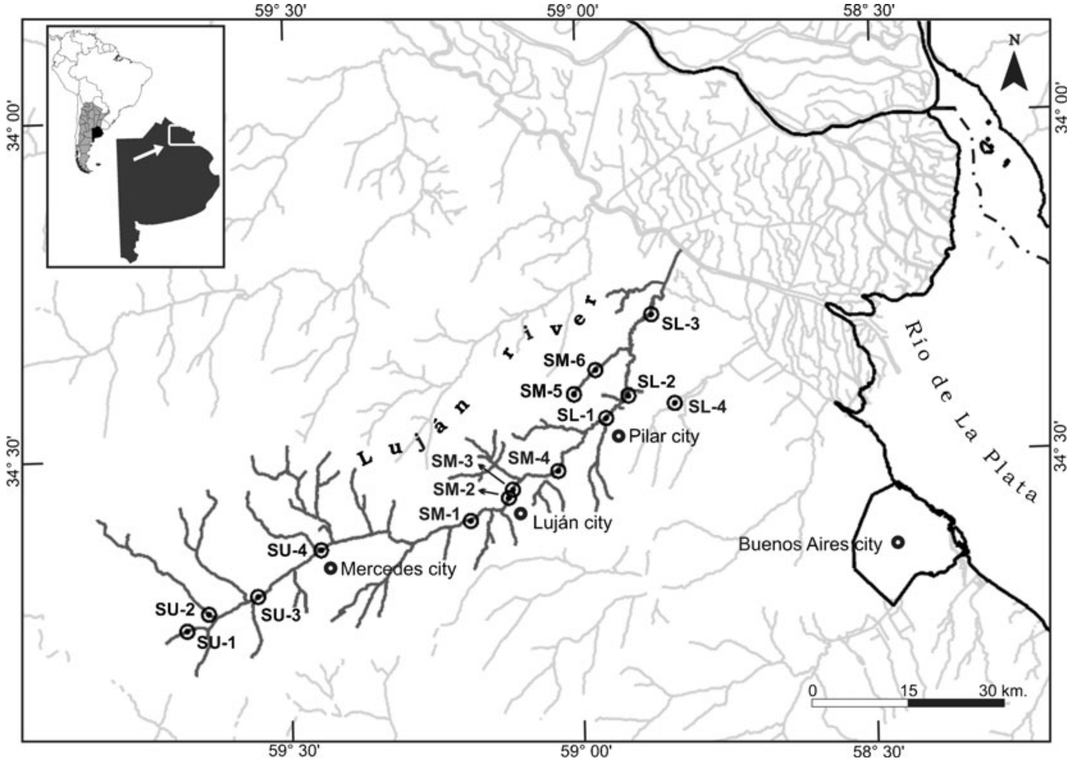


Fig. 1 Area of the study with the location of the 14 sampling stations

Sediment collection

Samples of superficial sediments were collected in 14 sampling sites and a control for toxicity tests, between July and August 2006 using an Eckman grab (to a depth of about 10 cm). Each composite sample was done from at least 15 discrete grab samples per site. Samples were kept in a cooler (4 °C) and then transferred to the laboratory. Sediments were homogenized, and sub-samples were obtained for chemical analysis and for toxicity testing. Sediments were held at 4 °C in the dark for no more than 2 weeks before the start of the toxicity tests (ASTM 2002).

Physical–chemical analysis

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 through a set of Standard Sieves larger than 63 μm to separate the sand size grain. Grain size of the fraction smaller than the 63 μm was determined by the standard pipette technique (Folk 1954). Dry weight was determined after drying the material at 105 °C until a constant weight was reached. Organic matter content in the sediment was obtained through calcination (loss on ignition) in a muffle furnace at 550 °C. Sulfides were analyzed according to Method 9030 (USEPA 1996), leachable nitrate and phosphor contents according to Black (1965). Analysis of metal content was done by atomic absorption spectrophotometry (direct flame, atomic vapor, or hydride generation) following acid digestion of samples according to Method 3050 (USEPA 1996). 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 an accuracy ranging between 80 and 95 %. Analysis of organochlorinated (Alfa HCH, HCB, aldrin, lindane, dieldrin, DDTs, heptachlor, heptachlor epoxide, diazinon, chlorpyrifos, methyl parathion, malathion) and pyrethroids (cypermethrin and D-allethrin) pesticides included a solid/liquid extraction procedure by sonication with methylene chloride, filtered, rotoevaporated, taken to dryness with N_2 flow, and finally resuspended in *n*-hexane (Method 3550, USEPA 1996), and then a cleanup procedure with Florisil was done according to Method 3620 (USEPA 1996). Pesticide identification and concentrations were measured by GC-ECD with an HP5, 15 m and 0.53 mm inner diameter column, N_2 carrier, with a temperature ramp between 180 and 220 °C, and a limit of detection of 0.02 mg/l (injected sample extract) (Marino and Ronco 2005). The recovery factor was tested using pure standards on similar matrices.

Reagents Chemicals for sample treatments or analysis of major matrix components were analytical grade. Qualities of solvents used for the analysis of pesticides were HPLC grade. Certified standards of metals were from AccuStandard, Inc. (1,000 mg/L standard stock solutions, traceable to the National Institute of Standards and Technology, USA). Pesticide standards were from SENASA (Argentinean National Service of Agricultural Food Health and Quality).

Toxicity tests

H. curvispina test organisms were obtained by sieving from laboratory cultures maintained in dechlorinated tap water (hardness 220 mg/l $CaCO_3$, pH 8.2, conductivity 1.10 mS/cm) (Peluso et al. 2011). Ten-day whole-sediment tests were conducted following USEPA (2000) standardized protocol with modifications. Five replicates were used for each sediment sample; 100 ml of sediment and 175 ml of overlying water were placed in each replicate, with ten individuals each. Test amphipods (7–14 days old) were previously separated and fed with fish food (McShullet®) and boiled lettuce ad libitum. Exposure was conducted for 10 days at 21 °C on a 16:8 light/dark photoperiod. At the start of the exposure, about 20 amphipods were kept in a solution of 4 % formaldehyde for measurement of length. At the beginning and ending of testing, the following parameters were measured in the overlying water: dissolved oxygen, pH, and conductivity with sensors (Lutron® YK-200PDO, YK-2001PH, and YK-200PCT, respectively), ammonia (commercial kit Aquamerck®), hardness, and alkalinity by titration methods (Methods 2340C and 2320, APHA, AWWA, WEF 1998). Measured endpoints were survival and growth (length). On day 10 of the exposure, sediments in each beaker were sieved through a #50 sieve (300-μm opening). Surviving amphipods were counted and preserved for later length measurements. Sediment of an unpolluted stream (Aº Juan Blanco) was used as the control in the experiments. Performance criteria for the control sediment required 80 % survival. Survival higher than 50 % was set for carrying out the analysis with the variable length.

Data 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 Dunnet's test. Percent survival data were arcsine-transformed, and length data were log-transformed before analysis (Zar 2010). The relationships between variables were assessed through multivariate analysis by principal component analysis (PCA). PCA was based on chemical contents of Fe, Mn, Pb, Cr, Cd, Cu, Zn, As, Hg, organochlorinated and pyrethroids pesticides, sulfides and organic matter in the sediments, and the toxicity tests data (amphipods mortality exposed to whole sediment). 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 in an attempt 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. Statistical analysis was performed using tools of the software XL-STAT (Addinsoft 2005, version 7.5.3).

Results and discussion

The different approaches to assess the extent of pollution in bottom sediments include data from physicochemical analyses, biological effects with toxicity tests, biomarkers of exposure or effects, concentration of residues in organism tissues, and also biological indexes of benthic communities. The present study considered a physicochemical and ecotoxicological approach, taking into account data from toxicity test with *H. curvispina* on whole sediment.

Physical–chemical and toxicity data

Physicochemical and sedimentological parameters of tested samples of the Río Luján basin are shown in Table 1. Texture of sediments indicates a very similar composition along the river course, with a high predominance of silts, and can be accordingly classified as silty loam. The organic matter content in tested samples ranged between 2.6 and 12.1 %. An exception was the sample corresponding to Reserva Pilar (sample SL-2), with an organic matter content of 23.2 %. The sulfide concentration levels were within the range of 20 and 310 mg/kg, with the exception of the sample from Aº Larena (sample SM-6) exhibiting a concentration of 1,409 mg/kg, in accordance with the black aspect of the sample. Concentrations of Fe were between 14.4 and 32.8 g/kg, except for the sample of Aº Larena, duplicating the value and reaching a concentration of 68.3 g/kg. The tested sediments showed different concentrations of pesticides and metals (Table 2), being Cr, Cu, Pb, and Zn higher than background levels in samples SU-4, SM-1, SM-2, and SM-6. Most of the tested pesticides in the sediment samples of the studied basin were below the detection limits, with the exception of cypermethrin, detectable in some of the sites where the predominance of agriculture was associated. Additionally, detectable levels of heptachlor-epoxide were observed in the middle sector of the basin (SL-1 to SL-4).

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 93.5 % corresponds to the control sediment (Aº Juan Blanco), meeting the acceptance criteria recommended by USEPA (2000) and OECD (2004) for whole sediment toxicity testing. Overlying water quality characteristics were generally 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 2000). ANOVA test showed significant differences ($p<0.05$) between SU-1, SU-4, SM-1, SM-6, and SL-2 samples. Additionally sites SU-4 and SM-6, the differences with the control site were highly significant ($p<0.01$), with survival of test organisms below 10 %. Growth of amphipods as body length was assessed in samples showing survival over 50 %. The amphipods of the control site sediment evidenced an average growth increment of 38 % after 10 days respect to the initial stage. The only samples inducing a significant effect on growth ($p<0.05$) were those exposed to sediments from Jauregui (SM-1) and Pilar (SM-3), with an average growth of 14 and 7 %, respectively, with respect to the initial group.

Due to a lack of sediment guideline values in Argentina, a comparison with existent Canadian Sediment Quality Guidelines (CEQG 2002) was done taking into account both the threshold effect level (TEL) and the probably effect level (PEL). Samples from sites SU-1, SU-2, and SU-3 did not exhibit concentrations over the TELs. The three first stations correspond to upper basin sites, with a prevalence of agricultural activities in neighboring areas, though sample SU-4, located by the city of Mercedes, showed

Table 1 Physical–chemical measurements of grain size, organic matter, and water (% dry weight); sulfides, N, and P (in milligrams per kilogram dry weight) in sediments samples

	Site														
	Ref S	SU-1	SU-2	SU-3	SU-4	SM-1	SM-2	SM-3	SM-4	SM-5	SM-6	SL-1	SL-2	SL-3	SL-4
Grain size															
Sand	14.8	30.2	16.5	25.2	29.0	24.8	31.7	30.6	21.7	20.4	19.7	21.5	17.4	27.6	20.8
Silt	48.7	61.3	80.3	66.2	61.8	64.9	55.4	62.1	65.0	55.8	52.0	73.9	69.0	56.1	73.9
Clay	36.4	8.6	3.4	6.0	8.5	9.8	8.6	7.3	13.9	23.8	27.8	4.8	12.2	15.4	23.6
OM	12.0	2.7	2.9	2.6	10.2	6.6	7.7	3.5	3.6	3.8	12.1	3.6	23.2	3.4	4.3
Water	67	36	35	28	52	49	58	36	35	56	64	42	70	43	45
Sulfides	<20	176	220	130	215	20	<20	34	27	20	1,409	310	98	23	<20
Nitrate	<1.0	<1.0	<1.0	<1.0	3.0	3.6	1.4	<1.0	1.5	<1.0	<1.0	5.0	4.6	<1.0	<1.0
Total P	469	2,420	5,911	2,212	4,809	2,111	2,235	3,038	3,388	3,150	4,789	982	4,964	2,031	2,379

Table 2 Measured contaminant concentrations of investigated sediments and classification according to sediment quality guidelines (according to CEQG 2002)

	Site															SQG	
	Ref S	SU-1	SU-2	SU-3	SU-4	SM-1	SM-2	SM-3	SM-4	SM-5	SM-6	SL-1	SL-2	SL-3	SL-4	TEL	PEL
Metals																	
As	9.0	11.2	8.6	7.2	14.6	9.8	14.3	8.1	18.5	3.9	3.9	6.6	17.3	17.0	6.5	5.9	17.0
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	23.4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	3.5
Cr	<2.5	9.4	13.3	17.0	807.3	149.5	219.7	19.5	5.8	35.7	51.4	40.9	60.0	28.1	40.0	37.3	90.0
Cu	15.8	23.3	18.8	20.3	126.6	31.4	98.8	23.1	37.2	25.1	466.0	24.3	142.1	25.8	27.3	35.7	197
Hg	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	11.0	<0.05	<0.05	<0.05	<0.05	0.17	0.48
Pb	37.3	23.6	24.3	26.2	64.1	73.3	57.1	33.0	34.9	24.6	104.9	172.4	63.8	29.1	31.1	35.0	91.3
Zn	69.9	39.0	32.0	22.0	190.0	170.0	196.0	75.0	145.0	68.0	751.0	38.0	265.0	79.0	98.0	123	315
Fe	24,301	20,945	26,692	26,701	28,750	24,804	20,714	16,094	25,308	n.d	68,125	28,017	20,750	25,219	32,818		
Mn	n.d	206	535	476	542	351	316	343	198	n.d	281	1214	387	446	759		
Pesticides																	
Lindane	<0.8	0.88	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	0.94	1.38
Dieldrin	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	2.85	6.67
Total DDTs	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	6.1	20.3
Heptachlor epoxide	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	6.2	<0.8	21.4	5.3	18.5	6.3	7.3	0.6	2.7
Diazinon	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	4	<4.0	<4.0	4.6	<4.0	<4.0	<4.0	n.d	n.d
Cypermethrin	<2.0	30.1	5.5	9.6	<2.0	3.5	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	25.4	53.9	n.d	n.d
D-Allethrin	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	n.d	n.d

Metals concentrations in milligrams per kilogram dry weight and pesticides in micrograms per kilogram dry weight

SQG sediment quality guidelines, *TEL* threshold effect level, *PEL* probably effect level

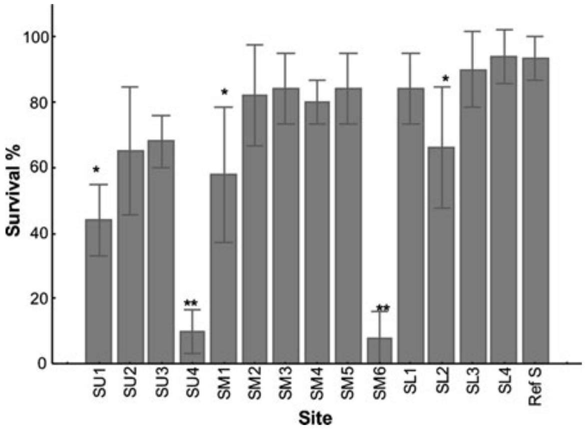


Fig. 2 Average values of the five replicates and standard deviation of amphipods survival percentage after 10 days of exposure to sediments from the study areas. *Asterisks* indicate significant difference regarding the control site Ref S (**p*<0.05, ***p*<0.01)

high contents of As, Cr, Cu, Pb, and Zn, over the TELs for those metals. Particularly, Cr concentrations in the site are almost 10-fold over the PEL for this metal. Sample from this site induced high toxicity on *H. curvispina* (10 % survival), being this level of effect in agreement with previous reports for the same area of the basin (Di Marzio et al. 2005). This basin sector is receptor of urban and industrial discharges with scarce or no treatment. The site SM-1 from Jauregui exhibited concentrations of Zn and Pb over the TELs and Cr over the PEL possibly associated with a tanning factory located in the influence area. Even though metal and pesticide concentrations were under the PELs, the sample exhibited moderate toxicity. The Larena stream was studied up (site SM-5) and downstream (SM-6) of the Pilar Industrial Complex, with industries located along its banks (Rodríguez et al. 2008). The downstream sampling sites showed concentrations of Cu, Zn, Pb, and Hg over the PELs. The sediment sample for the site SM-6 showed the highest toxicity, being the survival <10 %. The rest of the studied sites exhibited high concentrations of different metals depending on the place (see Table 2), in correspondence with the type of activity developed in the influence area for each site. For example, the sediment sample for the site SM-3 showed a concentration of Cd six times over the PEL for that metal, although this sediment sample did not induce effects on survival but determined significant effects on growth inhibition on exposed organisms. Sediment from Pilar Reserve (SL-2) induced toxic effect on the test species; however, concentrations of Cr, Cu, Pb, and Zn exceed TELs for these metals but not PELs.

Physical–chemical and biological responses integration

Concentrations of metals, pesticides, and organic matter in sediments together with the biological effects measurements were associated by PCA (Table 3). The PCA grouped the 14 variables in four principal components which explain to 77.5 % of the total initial variance. The loadings of the variables and percentage of the total variance for these factors are represented in Table 3. The first factor, F1, accounted for 40.8 % of the variance and is positively correlated with the concentrations of metals (except As, Cr, and Mn which were explained in other factors), organochlorinated pesticides, sulfides, organic matter, and amphipods mortality. The F1 suggested that the biological effect could be related to the metals (Cu, Zn, and Hg) and organochlorinated pesticides contents. The second factor, F2, accounted for 17.8 % of the variances including As and organic matter contents, though does not

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

	F1	F2	F3	F4
Eigenvalue	5.72	2.49	1.46	1.20
Variance %	40.8	17.8	10.4	8.51
Fe	**0.49**	**0.62**	−0.28	0.35
Mn	0.24	−0.52	0.26	**0.59**
As	−0.03	**0.87**	0.17	−0.13
Cd	−0.15	0.05	**−0.58**	−0.27
Cr	0.20	0.35	**0.75**	−0.17
Cu	**0.97**	−0.13	−0.02	−0.10
Hg	**0.87**	**−0.43**	−0.12	−0.13
Pb	**0.47**	−0.06	0.10	0.34
Zn	**0.95**	−0.09	−0.07	−0.11
OC pesticides	**0.83**	0.30	−0.32	−0.13
Pyrethroids	−0.34	−0.22	−0.03	**−0.51**
OM	**0.67**	**0.64**	−0.10	0.17
Sulfides	**0.88**	**−0.41**	−0.02	−0.09
Mortality	**0.70**	0.02	**0.47**	−0.36

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

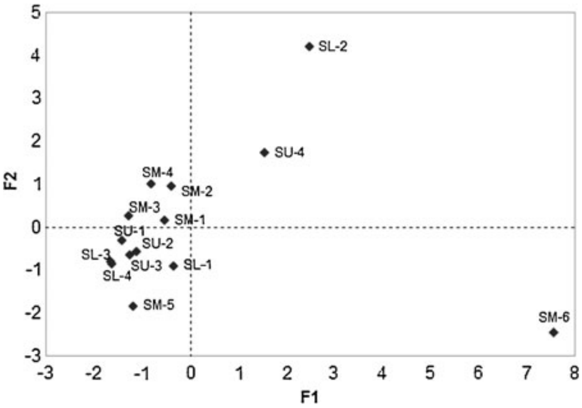


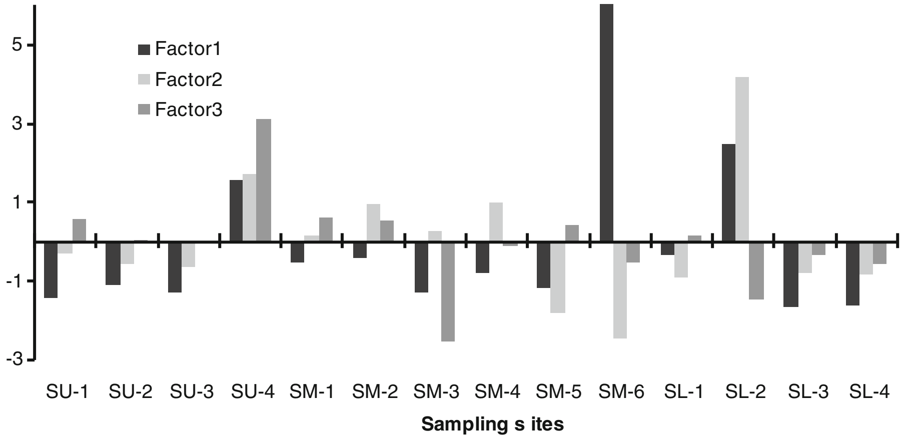
Fig. 3 Principal component score plot of sampling sites

show a good correlation with mortality. The third factor, F3, explains 10.4 % of the variance and shows significant correlation with the toxicity of sediments and total Cr concentration indicating that this metal was responsible of the tested effects. It is important to point out that concentration of pollutants exceeding the reference sediment guidelines is in accordance with the presence of effects as tested with the amphipod and the species sensitivity (Milani et al. 2003; Giusto and Ferrari 2008; Peluso et al. 2012).

Since the first two factors explain most of the variability associated to metal, organochlorinated pesticides, organic matter, and sulfides, it was evaluated the distribution of the sediments in the space defined by them (Fig. 3). It can be observed a sector plot with F1 and F2 values below zero, being represented by the less contaminated sampling sites of the basin. The first three sites (SU-1, SU-2, and SU-3) in the upper course and the ones corresponding to low sector basin (SM-5, SL-1, SL-3, and SL-5) are grouped in the plot, in accordance with the observed sediment pollution. On the other hand, most samples from the middle sector basin (SM-1, SM-2, SM-3, and SM-4) are grouped in the sector plot with F1 values below zero and positive F2, indicating no contamination by metals or organochlorinated pesticides.

Factors explain representative features of a sample when its score is greater than 0. Figure 4 shows the distribution of the factor scores for the 14 sites evaluated. Samples SM-1 and SM-2 exhibit positive F3 values that can be associated to high contents of Cr from a tanning factory in the vicinity doubling the guideline levels for aquatic life (PEL) (CEQG 2002). Although sediments from those sites did not induce high mortalities, a decreased survival and growth respect to controls were seen, suggesting that the presence of Cr could be responsible for the observed effects. Particularly the sediment from SU-4, though exhibits high positive values for F1 and F2 (Fig. 3), presents a much higher value for F3 (Fig. 4), indicating a clear Cr burden, added of high contents of Cu, Zn, and toxicity. In this sense, the concentration level of Cr is 10-fold over the PEL. Additionally, the concentrations of Cu and Zn in the sample are in the order of the LC50 values for *Hyalella azteca* (Milani et al. 2003; Galar-Martínez et al. 2008) and of effects on growth for *Hyalella pseudoazteca* (Giusto and Ferrari 2008). The SM-6 sample detaches from the rest with a very high F1 value, but near zero values in the other factors (Fig. 4). This is related with the presence of Cu, Zn, Pb, Hg, and organochlorinated pesticides, being in all cases over the levels of probable effect added of high content of sulfides, inducing high

Fig. 4 Factor score values after performing the PCA for the 14 sampling sites of Río Luján



mortality on the exposed amphipods, and showing the influence of the industrial complex nearby upstream the sampling site (Briano et al. 2003).

Conclusions

The assessment of physical–chemical and ecotoxicological parameters of sediments allowed detecting different types of pollutants in the Lujan River Basin. It was possible to detect associated biological effects testing with *H. curvispina*, observing high toxicity in sediments with high metal concentrations. The sectors most affected are the middle section of the course in which is located the most active industrial production. A decrease in pollution load in the bottom sediments at the final section was also observed. The combined analysis of physical–chemical and toxicological data by multivariate analysis allows identification of the variables that contribute most to the toxicity of the sediments. The study contributes with useful information to be used in management programs and environmental control of water courses in the region. We recommend the employment of the present assessment strategy in the implementation of sanitization programs of the water system to evaluate potential adverse impacts during the decontamination process (i.e., dredging with potential resuspension of pollutants, decision making steps, between others).

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References

Andrade, M.I. (1986). *Factores de deterioro ambiental en la cuenca del Río Luján*. Buenos Aires: Contribución del Instituto de Geografía, Facultad de Filosofía y Letras (UBA), 224 p.

Anguiano, O. L., Ferrari, A., Soleño, J., Martínez, M. C., Venturino, A., Pechen de D'Angelo, A. M., & Montagna, C. M. (2008). Enhanced esterase activity and resistance to azinphosmethyl in target and nontarget organisms. *Environmental Toxicology and Chemistry, 27*, 2117–2123.

APHA, AWWA, WEF. (1998). *Standard methods for examination of water and wastewater*. Washington, DC: American Public Health Association.

ASTM. (1999). Standard test methods for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates. E1706-95b. In *Annual book of ASTM standards*, Vol. 11.05, Philadelphia, PA.

ASTM. (2002). *Standard guide for collection*, *storage*, *characterization*, *and manipulation of sediments for toxicological testing*, E1391-02. West Conshohocken: ASTM.

Bartlett, A. J., Borgmann, U., Dixon, D. G., Batchelor, S. P., & Maguire, R. J. (2004). Accumulation of tributyltin in *Hyalella azteca* as an indicator of chronic toxicity: survival, growth, and reproduction. *Environmental Toxicology and Chemistry, 23*, 2878–2888.

Blaise, C. & Férard, J.-F (eds.) (2005). *Small-scale freshwater toxicity investigations*, Vol. 2. Berlin: Springer.

Burton, G.A. (2002). Sediment quality criteria in use around the world. *Limnology*, *3*, 65–75.

Black, C. A. (1965). *Methods of soil analysis*. *Part 2. Chemical and microbiological properties*. Madison: American Society of Agronomy, 770 p.

Burton, P. A., & Landrum, P. F. (2003). Encyclopedia of sediments and sedimentary rocks. In G. V. Middleston, M. J. Church, M. Corigilo, L. A. Hardie, & F. J. Longstaffe (Eds.), *Toxicity of sediments* (pp. 748–751). Dordrecht: Kluwer Academic.

Briano, L., Fritzche, F., & Vio, M. (2003). El lugar de la industria. Parques industriales de la Región. Metropolitana. *Revista Eure, 29*, 109–135.

CEQG. (2002). *Summary of existing Canadian Environmental Quality Guidelines*. www.ccme.ca/assets/pdf/e1_06.pdf

Day, P. (1965). Particle fractionation and particle size analysis methods of soil analysis. In C. Black (Ed.), *Methods of soil analysis, part 1* (pp. 545–566). Wisconsin: American Society of Agronomy.

Di Marzio, W. D., Sáenz, M., Alberdi, J., Tortorelli, M., & Galassi, S. (2005). Risk assessment of domestic and industrial effluents unloaded into a fresh water environment. *Ecotoxicology and Environmental Safety, 61*, 380–391.

Folk, R. L. (1954). The distinction between grain size and mineral composition in sedimentary rock nomenclature. *Journal of Geology, 62*, 344–359.

Galar-Martínez, M., Gómez-Oliván, L. M., Amaya-Chávez, A., & Vega-López, A. (2008). Responses of three benthic organisms (*Hyallela azteca*, *Limnodrillus hoffmeisteri* and *Stagnicola attenuata*) to natural sediment spiked with zinc when exposed in single or multi-species test systems. *Aquatic Ecosystem Health and Management, 11*(4), 432–440.

García, M. E., Rodrigues-Capítulo, A., & Ferrari, L. (2010). Age-related differential sensitivity to cadmium in *Hyalella curvispina* (Amphipoda) and implications in ecotoxicity studies. *Ecotoxicology and Environmental Safety, 73*, 771–778.

Giorgi, A. D. N., García, M. E., Feijoó, C. S., Cuevas, W. O., & Gómez Vázquez, A. (2000). Estudio comparativo de los principales arroyos afluentes del río Luján (Argentina). In J. E. Péfaur (Ed.), *Ecología Latinoamericana* (pp. 99–105). Mérida: Universidad de Los Andes.

Giusto, A., & Ferrari, L. (2008). Copper toxicity on juveniles of *Hyalella pseudoazteca* Gonzalez and Watling, 2003. *Bulletin of Environmental Contamination and Toxicology, 81*, 169–173.

Guichón, M. L., Angelini, M., Benitez, A., Serafini, C., & Cassini, M. H. (1999). Caracterización ambiental de la cuenca del río Luján. *Revista de Teledetección (España), 11*, 5–12.

Ingersoll, C. G., Macdonald, D. D., Brumbaugh, W. G., Johnson, B. T., Kemble, N. E., & Kunz, J. L. (2002). Toxicity assessment of sediments from the Grand Calumet River and Indiana Harbor Canal in Northwestern Indiana, USA. *Archives of Environmental Contamination and Toxicology, 43*, 156–167.

Jergentz, S., Mugni, H., Bonetto, C., & Schulz, R. (2004). Runoff-related endosulfan contamination and aquatic macroinvertebrate response in rural basins near Buenos Aires, Argentina. *Archives of Environmental Contamination and Toxicology, 46*, 345–352.

Kwok, C. K., Yang, S. M., Mak, N. K., Wong, C. K. C., Liang, Y., Leung, S. Y., Young, L., & Wong, M. H. (2010). Ecotoxicological study on sediments of Mai Po marshes, Hong Kong using organisms and biomarkers. *Ecotoxicology and Environmental Safety, 73*, 541–549.

Landrum, P. F., & Robbins, J. A. (1990). Bioavailability of sediment-associated contaminants to benthic invertebrates. In R. Baudo, J. P. Giesy, & H. Muntau (Eds.), *Sediments: chemistry and toxicity of in-place pollutants* (pp. 237–263). Ann Arbor: Lewis.

Lee, B.-G., Lee, J.-S., Luoma, S. N., Choi, H. J., & Koh, C.-H. (2000). Influence of acid volatile sulfide and metal concentrations on metal bioavailability to marine invertebrates in contaminated sediments. *Environmental Science and Technology, 34*, 4517–4523.

Lobos J., Rodríguez, A. & Sabels, J. (2006). Evaluación de la Calidad de las Aguas de la Cuenca del Río Lujan. Convenio de Colaboración Técnica "Municipalidad de Luján, Comisión de Ecología y Medioambiente de la Cámara de Diputados de la provincia de Buenos Aires-Instituto Nacional del Agua".

Lombardo, R., O'Farrell, I., & dos Santos Afonso, M. (2009). Spatial and temporal ion dynamics on a complex hydrological system: the Lower Luján River (Buenos Aires, Argentina). *Aquatic Geochemistry, 16*, 293–309. doi:10.1007/s10498-009-9064-5.

Losso, C., Arizzi Novelli, A., Picone, M., Marchetto, D., Pessa, G., Molinaroli, E., Ghetti, P. F., & Volpi Ghirardini, A. (2004). Evaluation of surficial sediment toxicity and sediment physicochemical characteristics of representative sites in the Lagoon of Venice (Italy). *Journal of Marine Systems, 51*, 281–292.

Marino, D., & Ronco, A. E. (2005). Cypermethrin and chlorpyrifos concentration levels in surface water bodies of the Pampa Ondulada, Argentina. *Bulletin of Environmental Contamination and Toxicology, 75*, 820–826.

Milani, D., Reynoldson, T. B., Borgmann, U., & Kolasa, J. (2003). The relative sensitivity of four benthic invertebrates to metals in spiked-sediment exposures and application to contaminated field sediment. *Environmental Toxicology and Chemistry, 22*, 845–854.

Mugni, H., Ronco, A., & Bonetto, C. (2011). Insecticide toxicity to *Hyalella curvispina* in runoff and stream water within a soybean farm (Buenos Aires, Argentina). *Ecotoxicology and Environmental Safety, 74*, 350–4.

OECD (Organization for Economic Co-operation and Development). (2004). *Sediment–water chironomid toxicity test using spiked sediment. Guideline for testing of chemicals No. 218*. Paris: Organization for Economic Co-operation and Development.

O'Farrell, I., Lombardo, L., De Tezanos Pinto, E., & Loez, C. (2002). The assessment of water quality in the Lower Lujan River (Buenos Aires, Argentina): phytoplankton and algal bioassays. *Environmental Pollution, 120*, 207–218.

Peluso, L., Giusto, A., Bulus Rossini, G. D., Ferrari, L., Salibián, A., & Ronco, A. E. (2011). *Hyalella curvispina* (Amphipoda) as a test organism in laboratory toxicity testing of environmental samples. *Fresenius Environmental Bulletin, 20*, 372–376.

Peluso, L., Salibián, A. & Ronco, A. (2012). Toxicity and bioavailability of mercury in spiked sediments on *Hyalella curvispina* Shoemaker, 1942. *International Journal of Environmental and Health*, in press.

Pizarro, H. & Alemanni, E.E. (2005). Variables físico-químicas del agua y su influencia en la biomasa del perifiton en un tramo inferior del Río Luján (Provincia de Buenos Aires). *Ecología Austral*, *15*, 73–88.

Quinn, G.P. & Keough, M.J. (2002). *Experimental design and data for biologists*. Cambridge: Cambridge University Press, 537 pp.

Riba, I., Casado-Martínez, M. C., Forja, J. M., & DelValls, T. (2004). Sediment quality in the Atlantic coast of Spain. *Environmental Toxicology and Chemistry, 23*, 271–282.

Rodríguez, A., Ruggerio, C. & Fernández, L. (2008). Actividades productivas en la cuenca del río Luján. Su impacto sobre el agua. *Revista Dlocal* Nº5, CEDet, UNSAM.

Ronco, A. E., Peluso, M. L., Jurado, M., Bulus Rossini, G., & Salibián, A. (2008). Screening of sediment pollution in tributaries from the southwestern coast of the Río de la Plata estuary. *Latin American Journal of Sediment Basin Analysis, 15*, 129–142.

Sala, J.M. (1972). *Contribución al conocimiento geohidrológico de la porción oriental de la cuenca del río Luján y las correspondientes a los arroyos Escobar*, *Garin*, *Claro y de Las Tunas*. Consejo Federal de Inversiones, 1–49, EASNE, Buenos Aires.

Sprovieri, M., Feo, M. L., Prevedello, L., Manta, D. S., Sammartino, S., Tamburrino, S., & Marsella, E. (2007). Heavy metals, polycyclic aromatic hydrocarbons and polychlorinated biphenyls in surface sediments of the Naples harbour (southern Italy). *Chemosphere, 67*, 998–1009.

USEPA (United States Environmental Protection Agency). (1996). *Method 9030 (acid-soluble and acid-insoluble sulfides: distillation), 3050 (acid digestion of sediments, sludges and soils), 3550 (ultrasonic extraction) and 3620 (clean-up procedure). Test methods for evaluating solid waste, vol. 1B: laboratory manual, physical/chemical methods (SW-846)* (3rd ed.). Washington, DC: US Government Printing Office (Update 3, Revision 0).

USEPA (Environmental Protection Agency). (2000). *Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates*, 2nd Ed. Office of Science and Technology Office of Water. Report: EPA 600/R-99/064.

Venturino, A., Montagna, C.M. & De D'Angelo, A.M.P. (2007). Risk assessment of Magnacide-« H herbicide at Río Colorado irrigation channels (Argentina). Tier 3: Studies on native species. *Environmental Toxicology and Chemistry*, *26*, 176–182.

Zar, J. H. (2010). *Biostatistical analysis*. Upper Saddle River: Prentice-Hall. 944pp.