Bull Environ Contam Toxicol (2009) 83:913–919
DOI 10.1007/s00128-009-9878-2

Vertical Fluxes and Accumulation of Trace Metals in Superficial Sediments of the Río de la Plata Estuary, Argentina

L. M. Tatone · C. Bilos · C. N. Skorupka · J. C. Colombo

Received: 30 April 2009 / Accepted: 9 September 2009 / Published online: 19 September 2009

Abstract Superficial sediments and settling material collected in Buenos Aires coastal area were analyzed to evaluate the accumulation and sources of trace metals. Residual elements showed homogeneous sedimentary concentrations (Fe: 23,846 ± 4,367; Ni: 10 ± 2.7; Mn: 706 ± 314 μg g^{-1}) whereas anthropogenic metals presented exponentially decreasing offshore gradients (Zn: 98 ± 69; Cr: 28 ± 21; Cu: 19 ± 15; Pb: 18 ± 13 μg g^{-1}). Anthropogenic impact was evaluated through metal-Fe relationships, Fe-normalized enrichment factors and sediment quality guidelines. The slopes of metal-Fe regressions from background sites were comparable to upper crust metal ratios, excepted Cr which is impoverished, and Mn which is diagenetically enriched. Metal-Fe relationships also hold for most 2.5 km offshore sites but with higher slopes denoting human influence, and are completely lost in 1–2.5 km sediments and trap material which plot over the regressions and exceed sediment quality guidelines.

Keywords Heavy metals · Coastal sediments · Settling particles · Río de la Plata

L. M. Tatone · C. Bilos · C. N. Skorupka · J. C. Colombo (✉)
Laboratorio de Química Ambiental y Biogeoquímica, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Av. Calchaqui km 23500, Florencio Varela, Buenos Aires 1888, Argentina
e-mail: laqab@intervar.com.ar

L. M. Tatone
Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Av. Rivadavia 1917, City of Buenos Aires CP C1033AA, Argentina

J. C. Colombo
Comisión de Investigaciones Científicas (CIC), Calle 10 y 526, La Plata, Province of Buenos Aires 1900, Argentina

Urbanized rivers, estuaries and coastal areas are impacted by the discharge of effluents containing organic pollutants and trace metals which are of particular concern due to their specific toxicity and biogeochemical recycling from the sediment reservoir (Salomons and Förstner 1984). To distinguish between natural versus anthropogenic metal sources, enrichment factors relative to the composition of the earth crust or background sites have been used. However, the principal disadvantage of this approach are the uncertainties related to the variable composition of local sources rocks, soils, sediments and air-borne material, and cut off values to discriminate human influence (Reimann and de Caritat 2005).

The Río de la Plata (RLP) located on the eastern coast of South America (Fig. 1) drains the second largest basin in the continent (Framiñan et al. 1998). The first 80 km of the Argentinean coast is heavily populated and industrialized producing a severe environmental impact. Numerous rivers, creeks and polluted channels discharge untreated effluents directly into the coastal area. In addition, the major sewer of Buenos Aires city discharges about 2 million m^3 day^{-1} of untreated effluents 2.5 km offshore Berazategui resulting in large vertical fluxes of organic pollutants (Colombo et al. 2005, 2007). In spite of this difficult environmental situation, the fluxes and distribution of trace metals in this coastal area have not been evaluated. The sole antecedent is a study of suspended particulate matter and coastal sands (Bilos et al. 1998) which indicated a moderate pollution with urban gradients overlapping with the influence of the turbidity maximum zone, ~130 km south from Buenos Aires. In this paper we evaluate the vertical fluxes, spatial distribution and anthropogenic influence of sediment-bound metals in the coastal area from Metropolitan Buenos Aires applying a complementary approach of metal-Fe relationships, crustal and background derived enrichment factors and sediment quality guidelines.

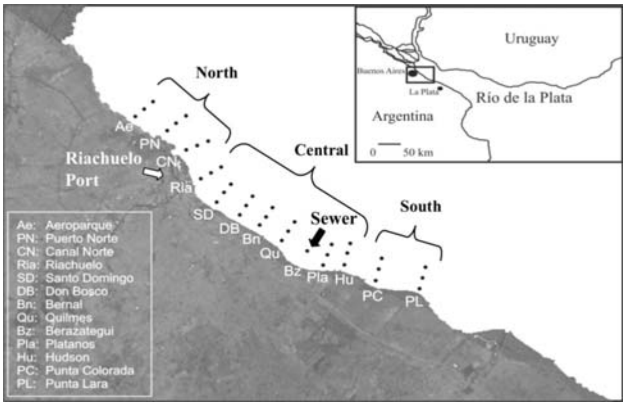

Fig. 1 Study area in the Río de la Plata estuary showing the sampling sites (based on a Landsat satellite image)

Materials and Methods

Sediment sampling was performed along 50 km in the shallow (3–5 m depth) upper Río de la Plata Estuary (Fig. 1). Superficial sediments were collected with a stainless steel grab sampler along 13 transects perpendicular to the coast at 1, 2.5 and 4 km (Colombo et al. 2005). Settling particles were collected 1.5 m below the surface during 9 trap deployments upstream and downstream the sewer (Colombo et al. 2007). Sediment samples were homogenized and splitted for the determination of the grain size composition (sieve and pipet method), total organic carbon (TOC; catalytic combustion; Thermo Finnnigan, CE FlashEA 1112) and trace metals. Sediment samples were digested with aqua regia, centrifuged and diluted to 25 mL with deionized water. Metal concentrations were determined using a Thermo Elemental Solaar M5 atomic absorption spectrophotometer with air-acetylene flame. The quantification limits ranged from 0.38 for Zn to 2.00 μg g^{-1} for Pb. Trace metals were below detection limits in blank samples. The precision of trace metal determinations as the relative standard deviation (RSD) tested through the analysis of eight duplicate samples was below 10% and the accuracy evaluated with certified soil (CRM020-050 RTC) and sewage sludge (CRM005-050 RTC) ranged from 68% to 135%. Pearson correlation analyses were performed on the entire data set to evaluate relationships between the various trace metals, fines (clay plus silt) and organic carbon contents. ANOVA analysis and the Tukey‘s multiple comparison test were used to tests significant differences ($p < 0.05$) in heavy metal concentrations.

Results and Discussion

Table 1 presents RLP trace metal concentrations in surface sediments collected at 1, 2.5 and 4 km offshore grouped in the North, Central and South areas. Río de la Plata coastal sediments consist basically of sandy silts (57 ± 22% silt, 35 ± 25% sand) with low clay (7.5 ± 4.2%) and organic carbon contents (0.6 ± 0.5%) which showed higher values in the Central Area (1.1 ± 0.5%, 0.6 ± 0.3%, 0.4 ± 0.1% at 1, 2.5 and 4 km, respectively), specially at Berazategui (1.9%) due to the sewer discharge, compared to southern (0.8 ± 0.02%, 0.3 ± 0.1%, 0.4 ± 0.2%) and north sites (0.3 ± 0.02%, 0.3 ± 0.3%, 0.5 ± 0.2%).

The grand mean trace metal concentrations follow their natural abundance decreasing from Fe (23,846 ± 4,367 μg g^{-1}) > Mn (706 ± 314 μg g^{-1}) > Zn (98 ± 69 μg g^{-1}) > Cr (28 ± 21 μg g^{-1}) > Cu (19 ± 15 μg g^{-1}) ~Pb (18 ± 13 μg g^{-1}) > Ni (10 ± 2.7 μg g^{-1}). Trace metal variability differs markedly between major components such as Fe with a very low dispersion (RSD = 18%), Ni (26%) and Mn (45%), and trace metals with anthropogenic sources like Cu, Cr, Pb and Zn which display spatial gradients and larger variability (RSD = 71–77%). The correlation analysis of trace metals, TOC and grain size (fines: silt + clay) show that anthropogenic metals display a significant positive correlation among them (i.e. Zn, Cr, Cu and Pb; r: 0.82–0.93, $p < 0.05$), but not with Fe and Mn, denoting different sources. Both metals series show also a contrasting behavior against organic carbon, with no association for Fe and Mn and a significant positive correlation (r: 0.74–0.92, $p < 0.05$) for anthropogenic metals supporting common sources, i.e. effluent discharges. The impact of coastal pollution sources from Metropolitan Buenos Aires area is indicated by offshore-decreasing gradients of anthropogenic metals, and lower concentrations in the North area upstream major sources (Fig. 2). Zn, Cr, Cu and Pb show significant exponential trends with distance offshore (metal = a. e^{k*km}; k = −0.40 ± 0.13; R^2 = 0.81–0.99), indicating a rapid attenuation of coastal inputs by differential settling of particulated matter close to major outputs.

Most anthropogenic metals peak at 1 km from the coast at the most polluted Central Riachuelo-Sewer area (Ria-Bz), with some indication of southward transport for Zn whose maximum value is registered in the South area (PC-PL). The highest average concentrations registered at 1 km are roughly equivalent in the Central and South areas with Cr displaying the most clear single peak (84 μg g^{-1}) close to the polluted Riachuelo port. In addition to these coastal sources, the sewer area 2.5 km offshore Berazategui constitutes a distinct hotspot with the highest concentrations of anthropogenic metals (Table 1). These concentrations exceed most values reported for other sewage polluted sediments, i.e. Victoria, Canada; Sydney, Australia; Gulf of Mexico; Massachusetts, USA; Sao Paulo, Brazil (Chapman et al. 1996; Matthai and Birch 2000; Soto-Jiménez et al. 2001; Bothner et al. 2002; Abessa et al. 2005).

Table 1 Concentration of trace metals in Río de la Plata sediments collected a 1, 2.5 and 4 km offshore

	1 km							2.5 km						
	Fe (μg g^{-1} dry weight)	Mn	Zn	Cr	Cu	Pb	Ni	Fe	Mn	Zn	Cr	Cu	Pb	Ni
North area														
Aeroparque	22,943	1,759	59.5	13.1	9.6	10.7	8.9	28,257	1,577	56.7	14.5	7.6	8.5	9.6
Puerto Norte	16,791	653	40.1	11.7	9.0	7.8	6.8	21,689	682	43.4	10.9	5.8	5.6	6.5
Canal Norte	21,021	1,314	56.8	13.6	10.0	11.8	8.5	27,237	842	61.8	16.5	15.2	9.0	12.9
Mean	20,252	1,242	52.1	12.8	9.5	10.1	8.1	25,728	1,033	53.9	14.0	9.5	7.7	9.7
SD	3,148	556	10.5	1.0	0.5	2.0	1.1	3,534	477	9.5	2.9	5.0	1.8	3.2
Central area														
Riachuelo	24,625	441	156.7	84.3	37.0	30.3	11.7	27,582	788	80.9	21.9	19.1	14.1	13.9
Sto. Domingo	23,759	343	120.8	35.7	18.8	21.7	7.9	19,709	800	58.7	13.2	9.7	16.8	8.0
Don Bosco	29,343	369	121.8	32.6	14.5	16.9	7.1	23,390	743	63.8	15.8	11.8	11.6	10.4
Bernal								24,643	498	100.1	41.7	20.7	20.6	11.2
Quilmes	40,103	777	241.2	72.8	41.7	37.6	12.7	25,045	554	164.2	42.4	34.3	27.3	11.6
Berazategui								19,425	252	205.1	54.6	70.1	60.9	16.0
Platanos	23,609	612	247.0	70.2	49.8	40.9	15.4	30,837	611	97.2	27.2	24.6	20.3	11.0
Hudson	25,521	551	209.6	70.3	46.7	33.8	15.7	27,014	1,016	70.1	16.1	11.2	11.6	10.0
Mean	27,827	515	182.8	61.0	34.7	30.2	11.7	24,706	658	105.0	29.1	25.2	22.9	11.5
SD	6,370	165	57.4	21.4	14.7	9.3	3.6	3,890	232	52.4	15.3	19.9	16.2	2.5
South area														
Pta. Colorada	27,702	956	298.3	53.1	36.7	35.9	15.8	26,629	473	83.1	20.0	13.5	15.6	8.1
Punta Lara	23,073	505	186.5	48.0	33.4	30.0	11.3	26,099	609	66.1	15.4	9.1	12.0	7.7
Mean	25,387	730	242.4	50.6	35.1	32.9	13.5	26,364	541	74.6	17.7	11.3	13.8	7.9
SD	3,274	319	79.0	3.6	2.3	4.2	3.2	375	96	12.1	3.2	3.1	2.5	0.3
Mean (km)	25,317	753	158.0	45.9	27.9	25.2	11.1	25,197	726	88.6	23.9	19.4	18.0	10.5
SD	5,901	438	86.3	26.5	15.8	11.9	3.5	3,373	320	46.3	13.7	17.1	14.1	2.7
Avg traps	22,821	337	303.9	105.7	119.1	93.9	26.9							
SD	4,132	97	129.0	44.6	89.2	93.9	9.8							
Fluxes (mg m^{-2} day^{-1})	9,034	134	133	45	55	44	9.3							
SD	2,762	52	94	28	61	64	8.8							

	4 km						
	Fe (μg g^{-1} dry weight)	Mn	Zn	Cr	Cu	Pb	Ni
North area							
Aeroparque	20,579	703	50.37	13.2	9.9	6.2	9.8
Puerto Norte	23,021	537	50.64	15.7	13.3	5.8	11.7
Canal Norte	23,690	587	51.81	15.6	12.4	6.6	10.1
Mean	22,430	609	50.9	14.8	11.9	6.2	10.6
SD	1,637	85	0.8	1.4	1.8	0.4	1.0
Central area							
Riachuelo	17,782	395	54.97	19.5	13.3	30.5	10.2
Sto. Domingo	17,026	751	43.81	9.9	6.7	16.1	5.8
Don Bosco	21,670	862	51.35	14.2	10.9	8.4	10.2
Bernal	21,552	597	52.84	14.6	11.7	7.6	11.4
Quilmes	22,225	599	57.92	16.8	13.0	8.2	11.6
Berazategui							
Platanos	21,305	660	56.04	15.6	11.6	8.7	10.7

Table 1 continued

	4 km						
	Fe ($\mu g\ g^{-1}$ dry weight)	Mn	Zn	Cr	Cu	Pb	Ni
Hudson	21,152	721	45.18	12.3	7.6	6.2	6.8
Mean	20,387	655	51.7	14.7	10.7	12.2	9.5
SD	2,077	148	5.4	3.1	2.6	8.7	2.3
South area							
Pta. Colorada	21,481	845	53.48	13.2	9.3	10.0	8.4
Punta Lara	20,935	430	54.28	16.3	12.1	8.0	10.7
Mean	21,208	637	53.9	14.8	10.7	9.0	9.6
SD	386	293	0.6	2.3	1.9	1.4	1.6
Mean (km)	21,035	641	51.9	14.7	11.0	10.2	9.8
SD	1,913	146	4.1	2.4	2.2	7.0	1.9

In contrast to the offshore gradients observed in the Central and South areas, in the North sector anthropogenic trace metals do not show any clear spatial trend with very flat surfaces denoting background concentrations 3–5 times lower than in the Central-South area and absence of significant impact. Mn is the only element that shows a clear enrichment in Northern sediments with concentrations which duplicates those observed at the Central and South sectors at 1 km ($1{,}242 \pm 556$ vs. 515 ± 165 and $730 \pm 319\ \mu g\ g^{-1}$, respectively), possibly associated to the preservation of Mn oxides under oxic conditions (brownish sediments) compared with Mn reduction and diffusion to the water column in the reducing and polluted Central sediments. The North–South spatial patterns are attenuated at 4 km offshore where trace metals level off to more uniform concentrations.

The traps collected a substantial amount of material averaging a total flux of $411 \pm 104\ g\ m^{-2}\ day^{-1}$ and a sedimentation rate of $5.5 \pm 2.1\ cm\ year^{-1}$ (density: $2.65\ g\ cm^{-3}$). The TOC content of the settling material is relatively high averaging $8.0 \pm 5.6\%$, compared to 0.9% in bottom sediments. The concentration of metals in the settling material show a comparable abundance order than sediments decreasing from Fe ($22{,}821 \pm 4{,}132\ \mu g\ g^{-1}$); to Mn ($337 \pm 97\ \mu g\ g^{-1}$); Zn ($304 \pm 129\ \mu g\ g^{-1}$); Cu ($119 \pm 89\ \mu g\ g^{-1}$); Cr ($106 \pm 45\ \mu g\ g^{-1}$); Pb ($94 \pm 94\ \mu g\ g^{-1}$) and Ni ($27 \pm 10\ \mu g\ g^{-1}$). Similarly, the variability was lower for major components such as Fe and Mn (RSD: 18–29%), and increased for Ni, Cr and Zn (RSD: 37–42%) and especially for Cu and Pb (RSD: 75–100%). Compared to bottom sediments, the settling material appears enriched in most metals, especially in those from anthropogenic sources (Table 1). The combination of high total mass fluxes and relatively high trace metal concentrations results in very large metal fluxes which range from 5 to 393 $mg\ m^{-2}\ day^{-1}$ for minor elements and from 3.9–15 $g\ m^{-2}\ day^{-1}$ for Fe.

In order to critically evaluate trace metal sources and anthropogenic impact we implemented a complementary strategy based on the comparison of metal-Fe relationships and Fe-normalized enrichment factors relative to the upper crust (Wedepohl 1995; EF_{crust}) and background sites (EF_{bkd}) in the Río de la Plata ($EF = (Me/Fe)_{sample}/(Me/Fe)_{crust\ or\ background}$), and on possible toxicological concerns according to Canadian Interim Sediment Quality Guidelines (ISQG) for Protection of Aquatic Life (CCME 2001). The rationale of EFs is that low values (~ 1.0) characteristic of lithogenic material increase due to anthropogenic sources. To overcome the uncertainties related to the variability of local rock composition and the EF cutoff values for anthropogenic influence (i.e. $EF > 1$ to 20 have been reported; Reimann and de Caritat 2005), the calculation of EFs relative to local background sites has been also proposed (Blaser et al. 2000). Both strategies could be combined in the regressions of metals against a major lithogenic component such as Fe which show slopes differing according to the magnitude of anthropogenic sources.

Fig. 3 presents Río de la Plata sediment trace metal-Fe relationships discriminating sampling sites located 1, 2.5 and 4 km offshore. Crust derived enrichment factors are indicated above 1 km and some 2.5 km data points. The regressions showed in the figure were calculated for background North sites and for 2.5 km stations not affected by the sewer. In the case of Zn, Cu, Pb and Ni the metal-Fe regressions for background North sites present slopes which are essentially the metal/Fe ratio of the crust (Zn: 0.0015 vs. 0.0017; Cu: 0.0006 vs. 0.0005, Pb: 0.0007 vs. 0.0006; Ni: 0.004 vs. 0.0006; slope vs. crust ratio). The

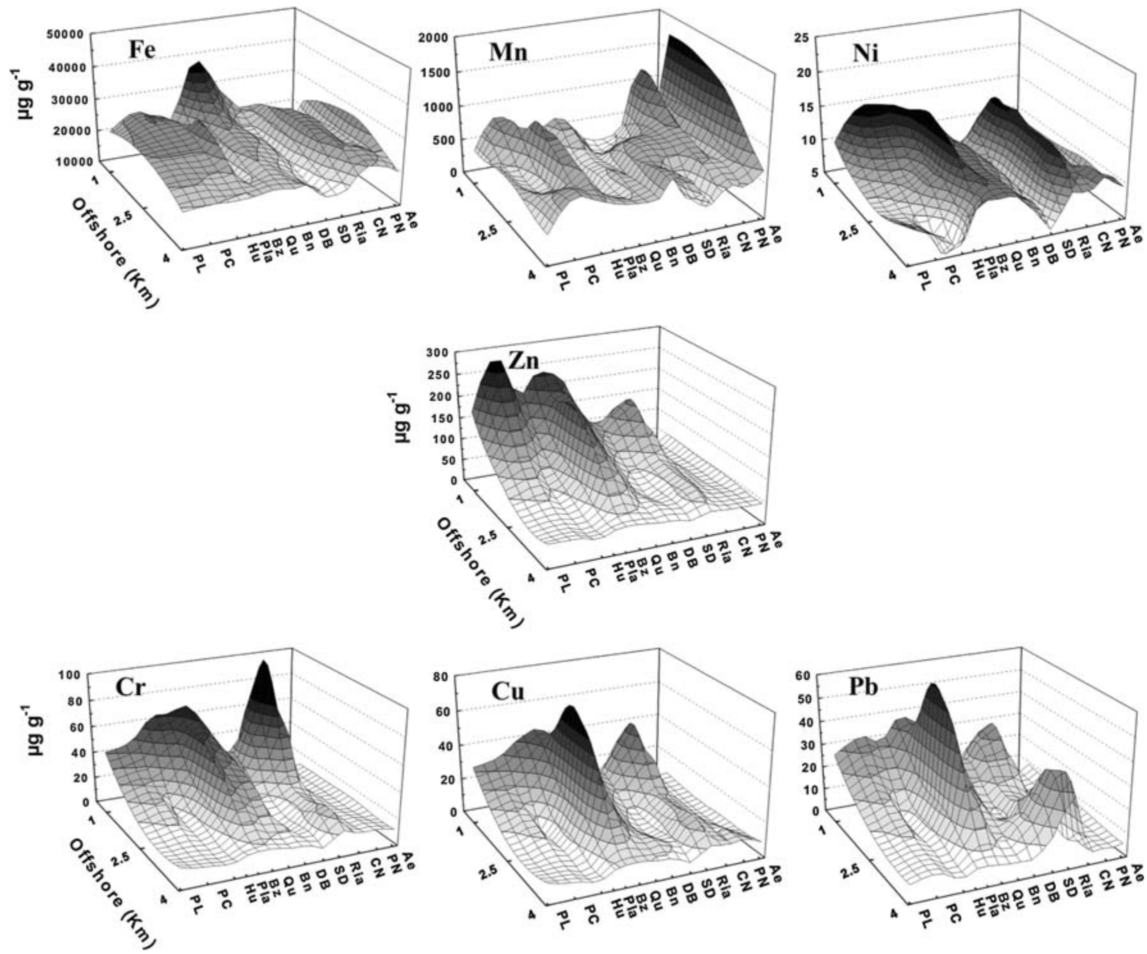

Fig. 2 Surface interpolation of trace metal concentrations (μg g^{-1}) in Río de la Plata sediments

same do not hold for Cr which is impoverished in the Río de la Plata (0.0004 vs. 0.0011) and Mn which is diagenetically enriched in North sites relative to the crust (0.05 vs. 0.02). These results reflect the variability of local environmental conditions and support the criticism raised for EF based only on crustal information (Reimann and de Caritat 2005). All anthropogenic metals show a significant enrichment at 1 km from the shore and in some 2.5 km stations (the sewer and two sites upstream), and specially in the settling material which plot at the top of all regressions, whereas 4 km sediments plot close to background sites. The metal-Fe regressions estimated for background North sites also hold for most 2.5 km stations (excepted in the sewer area) but with slopes 1.6–2.7 times higher denoting an anthropogenic influence (Fig. 3), but are completely lost in polluted 1–2.5 km sites. These results provide further evidence of the utility of the metal-Fe relationships in detecting anthropogenic impact which rapidly distort the natural element proportions. According to the local abundance of metals, the cutoff values of crust derived enrichment factors differs markedly ranging from ~1 to 1.5 for Cr to 2–3 for Zn, Cu and Pb. The EF_{crust} in the settling material decrease from Cu (11) > Zn (7.3) > Pb (5.8) > Cr (3.2), comparable to the trend in polluted 1 and 2.5 km sediments (Zn: 4.3 ± 1.5–Cu: 3.2 ± 1.8 > Pb: 2.4 ± 1.2 > Cr: 1.9 ± 0.6), implying that Zn and Cu are the most impacted metals in this environment. Although the settling material appears slightly enriched in Ni (EF_{crust}: 2.1), anthropogenic sources do not significantly contribute to its sedimentary levels which are low compared to the crust (6–16 vs. 19 μg g^{-1}; EF_{crust}: 0.7 ± 0.2). Mn reflect the enrichment in the North sector which show twice as higher EF_{crust} relative to most polluted sediments (2.5 ± 1.1 vs. 1.2 ± 0.4).

The comparison with local background sites provides a different scenario. Effectively, Pb and Cr have more anomalous values than Cu (Fig. 3). This is captured by the EF_{bkd} which for polluted 1–2.5 km sediments are almost equally high for all metals but with a reversed impact scheme compared to EF_{crust} (Pb: 3.4 ± 1.4–Cr:

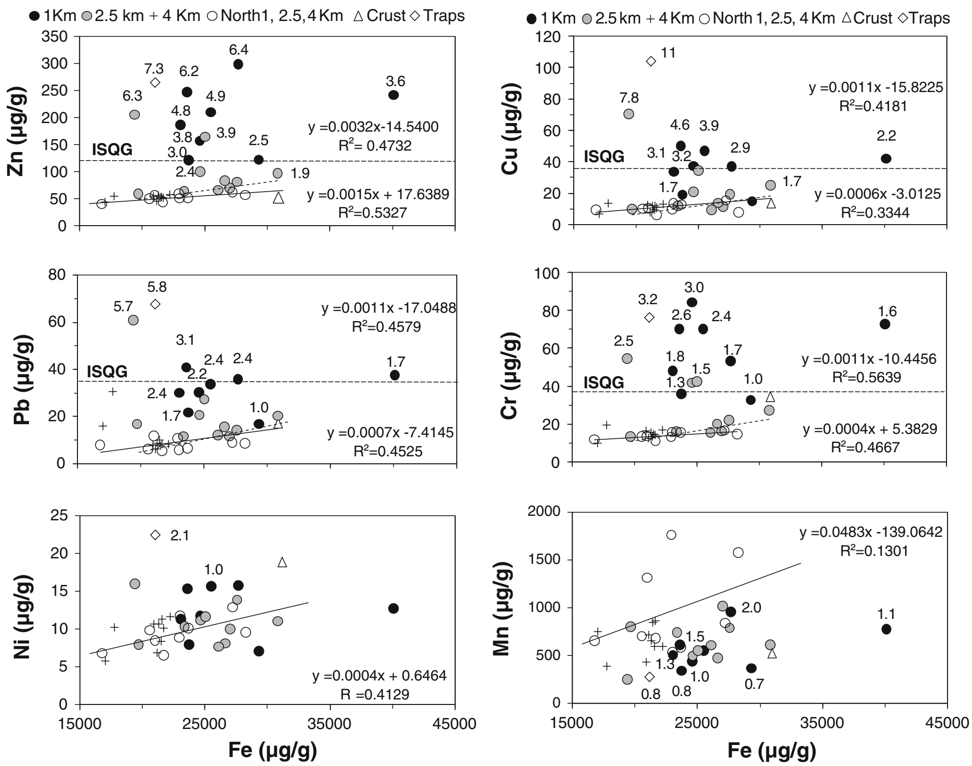

Fig. 3 Metal-Fe relationships discriminating 1, 2.5 and 4 km sampling sites. The average settling material and crust metal concentration as well as the Canadian Interim Sediment Quality Guidelines (ISQG) are shown in the figure. The regressions were calculated for background North 1, 2.5 and 4 km sites (*solid line*) and for 2.5 km stations not grossly affected by the sewer (*dotted line*)

$3.3 \pm 1.1 >$ Cu: 3.0 ± 1.7–Zn: 2.9 ± 1.0), whereas Ni EF_{bkd} remain low (1.1 ± 0.4). This provides further evidence on the necessity of studying local background areas to more accurately evaluate the anthropogenic impact. The ISQG evaluation provides an intermediate prioritization scheme of anthropogenic influence. For the whole data base of 36 sediments samples, 4–9 normally exceeded the threshold effect level (TEL), decreasing from Cr ($n = 9 > 37.3\ \mu g\ g^{-1}$), Zn ($n = 8 > 123\ \mu g\ g^{-1}$), Cu ($n = 6 > 35.7\ \mu g\ g^{-1}$) and Pb ($n = 4 > 35\ \mu g\ g^{-1}$). All these sites are located in the Central and South area, basically 1 km stations and 2.5 km sediments influenced by the sewer discharge. None of the samples located at 4 km exceed the guideline indicating a natural trace metal composition. Río de la Plata trace metal sediment concentrations are all below the Canadian probable effect level (PEL; Zn: 315; Cr: 90; Cu: 197; Pb: 91.3 $\mu g\ g^{-1}$), indicating that in spite of the significant human impact adverse effects are expected not to occur frequently.

Acknowledgments Financial support was provided by the National Research Council (CONICET) and the Research Commission from Buenos Aires State (CIC).

References

Abessa DMS, Carr RS, Rachid BRF, Sousa ECPM, Hortelani MA, Sarkis JE (2005) Influence of a Brazilian sewage outfall on the toxicity and contamination of adjacent sediments. Mar Pollut Bull 50:875–885

Bilos C, Colombo JC, Rodriguez Presa MJ (1998) Trace metals in Suspended particles, sediments and asiatic clams (*Corbicula fluminea*) of the Río de la Plata Estuary, Argentina. Environ Pollut 99:1–11

Blaser P, Zimmermann S, Luster J, Shotyk W (2000) Critical examination of trace element enrichments and depletions in soils: As, Cr, Cu, NI, Pb, and Zn in Swiss forest soils. Sci Total Environ 249:257–280

Bothner MH, Casso MA, Rendigs RR, Lamothe PJ (2002) The effect of the new Masachusetts Bay sewage outfall on the concentrations of metals and bacterial spores in nearby bottom and suspended sediments. Mar Pollut Bull 44:1063–1070

CCME (Canadian Council of Ministers of the Environments) (2001) Canadian sediment quality guidelines for the protection of aquatic life: Summary tables. In: Canadian environmental quality guidelines, 1999, Canadian Council of Ministers of the Environments, Winnipeg

Chapman PM, Paine MD, Arthur AD, Taylor LA (1996) A triad study of sediment quality associated with a major, relatively untreated marine sewage discharge. Mar Pollut Bull 32:47–64

Colombo JC, Cappelletti N, Barreda A, Migoya MC, Skorupka CN (2005) Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina. Chemosphere 61:1345–1357

Colombo JC, Cappelletti N, Speranza E, Migoya MC, Lasci J, Skorupka CN (2007) Vertical fluxes and organic composition of settling material from the sewage impacted Buenos Aires coastal area, Argentina. Org Geochem 38:1941–1952

Framiñan MB, Etala MP, Acha EM, Guerrero RA, Lasta CA, Brown OB (1998) Physical characteristics and proceses of the Río de la Plata estuary. In: Piccolo MC, Pino-Quivira M, Perillo GME (eds) Estuaries of South America, their geomorphology and dynamics. Springer, Berlin, pp 161–194

Matthai C, Birch GF (2000) Trace metals and organochlorines in sediments near a major ocean outfall on a high energy continental margin (Sydney, Australia). Environ Pollut 110:411–423

Reimann C, de Caritat P (2005) Distinguishing between natural and anthropogenic sources for elements in the environment: regional geochemical surveys versus enrichment factors. Sci Total Environ 337:91–107

Salomons W, Förstner U (1984) Metals in the hydrocycle. Springer-Verlag, Berlin

Soto-Jiménez M, Páez-Osuna F, Morales-Hernández F (2001) Selected trace metals in oysters (*Crassostrea iridescens*) and sediments from the discharge zone of the submarine sewage outfall in Mazatlán Bay (southeast Gulf of California): chemical fractions and bioaccumulation factors. Environ Pollut 114:357–370

Wedepohl KH (1995) The composition of the continental crust. Geochim Cosmochim Acta 59:1217–1232