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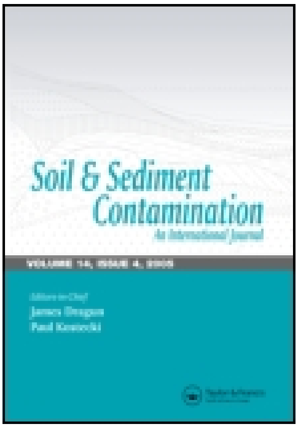

Soil and Sediment Contamination: An International Journal
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/bssc20

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Published online: 31 Jan 2012.

To cite this article: Alicia Rendina & Alicia Fabrizio de Iorio (2012) Heavy Metal Partitioning in Bottom Sediments of the Matanza-Riachuelo River and Main Tributary Streams, Soil and Sediment Contamination: An International Journal, 21:1, 62-81, DOI: 10.1080/15320383.2012.636776

To link to this article: http://dx.doi.org/10.1080/15320383.2012.636776

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Soil and Sediment Contamination, 21:62–81, 2012
Copyright © Taylor & Francis Group, LLC
ISSN: 1532-0383 print / 1549-7887 online
DOI: 10.1080/15320383.2012.636776

Heavy Metal Partitioning in Bottom Sediments of the Matanza-Riachuelo River and Main Tributary Streams

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This study provides geochemical partitioning, potential bioavailability, and enrichment of Cd, Cu, Pb, and Zn in bottom sediments collected from the Matanza-Riachuelo River and its main tributary streams. A modified Tessier sequential extraction procedure, complemented with acid volatile sulfide (AVS) and simultaneous extracted metals (SEM) measurements, was applied to determine the partitioning of metals into four fractions (metals bound to amorphous sulfide, carbonate, and exchangeable), bound to Fe/Mn oxides (reducible), bound to organic matter/sulfide (oxidizable) and residual. Spatial and vertical distributions of metals were studied. The core sediments show a decreasing concentration of metals with depth. In top sediments, non-residual Cu was mainly associated with oxidizable phase, whereas Pb, Cd, and Zn were mainly associated with amorphous sulfide. Pb exhibited the highest enrichment in all sites. The ratio AVS/SEM was greater than one at sediment sections close to the water column, indicating that metals extracted with hydrochloric acid were mainly associated with the amorphous sulfide. The strong influence of amorphous sulfide in the retention of Cd, Pb, and Zn in anoxic sediments of Matanza-Riachuelo river system suggests that dredging and aeration could lead to the remobilization of metals from sediments to the water column, hence making the metals more available to the biota.

Keywords Bottom sediments, heavy metals, acid volatile sulfide, sequential extraction, Matanza-Riachuelo River

1. Introduction

Most of the rivers and streams in urban areas of Buenos Aires Province contain a high load of urban and industrial wastes (Herkovits et al., 1996). The impacts produced by human activities on these watercourses result in the alteration of the natural balance of these water systems. Heavy metals are frequently detected in the environment, including both bed sediments and water columns, and they have gradually become a major concern worldwide. In Argentina, environmental concern is still incipient, as reflected in negligent practices by the population and in little federal monitoring of most polluting agents. Under this situation, the evaluation of the environmental impact originated by anthropic activities on sediments quality is now a high priority.

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It is well known that the mobility of hazardous metals depends strongly on their specific chemical forms or different binding forms, rather than on their total element concentrations. Accordingly, knowledge of metal partitioning among various geochemical phases of sediments is particularly interesting to assess the mobilization capacity, bioavailability, and potential toxicity (Li et al., 2000). Sequential extraction procedures (SEP) are often used to explore the binding fractions of metals in sediments, such as the SEP protocol elaborated by Tessier et al. (1979). According to the Tessier protocol, metals have been assumed into five fractions: exchangeable, bound to carbonate, bound to iron and manganese oxides (reducible fraction), bound to organic matter and sulfides (oxidizable fraction), and residual (metals within the crystal structure of primary and secondary minerals).

The metals extracted in the oxidizable fraction include metals associated to organic matter and pyrite (Huerta-Diaz and Morse, 1993; Ouddane et al., 2000). However, this traditional scheme does not allow identification of the metals bound to amorphous sulfides. During the application of SEP, the metals that originally presented amorphous sulfides are partially solubilized and then redistributed between other phases of the sediment (Hirner, 1992; Brumbaugh et al., 1994; Peltier et al., 2005), showing a lack of selectivity (Rao et al., 2008).

The amorphous sulfides present in sediments are quantified as acid volatile sulfides (AVS), which are operationally determined by the addition of cold hydrochloric acid to the sediment, by trapping, and then by analyzing the evolving sulfides (Allen et al., 1993).

It is important that the trace metals (e.g. Cu^{+2}, Cd^{+2}, Pb^{+2}, Zn^{+2}, Ni^{+2}, and Hg^{+2}) liberated during the evolution of sulfide in the AVS procedure (SEM, simultaneously extracted metals) are also determined (Di Toro et al., 1990). If a metal sulfide is not dissolved, then neither the AVS nor the SEM values will be increased. Measurement of AVS and SEM provides a means to evaluate the potential toxicity of trace metals in sediments (Allen et al., 1993; Yu et al., 2001; Liu et al., 2007). If the ratio of AVS to SEM, which is determined on the required molar basis, is greater than one, there will not be toxicity as all these trace metals would be expected to be present as their sulfides. If the ratio of AVS to SEM is less than one, there may be metal toxicity because the metals are likely to be bound as more bioavailable species (Allen et al., 1993).

The Matanza-Riachuelo River is one of the most polluted rivers in Latin America (Olson et al., 1998). Although the possibility and effectiveness of dredging to remove highly contaminated sediments of the Matanza-Riachuelo River in a lower basin area were analyzed through several river decontamination projects, the upper and middle basins have no modern data of the total content and partitioning of metals in river sediments.

The objective of this project is to provide a detailed study of the chemical forms, including metals bound to amorphous sulfide, potential bioavailability and enrichment of Cd, Cu, Pb, and Zn in anoxic sediment cores of the Matanza-Riachuelo River (Argentina) and its main tributary streams, in upper and middle basin areas. Second, chemical and physical characteristics such as organic matter, inorganic carbon, AVS, and grain size were determined in order to interpret the mechanisms involved in the association of heavy metals in the sediments.

2. Materials and Methods

2.1 Study Area

The Matanza-Riachuelo River is the main collector of a 2300 km^2 basin. This river drains directly into the de La Plata River, a huge binational estuary, which is the main source of drinkable water for the city of Buenos Aires and its outskirts (Magdaleno et al., 2008). The Matanza-Riachuelo River system is mainly composed of three tributary streams: Morales, Rodríguez, and Cañuelas. The climate of the Matanza-Riachuelo basin is humid sub-tropical. The maximum average temperatures are recorded in January (23.9°C) and the lowest average temperatures in July (10.4°C). Rainfall is around 1000 mm/year. The soils developed on loess-like sediments deposited throughout the late Pleistocene and the Holocene. The dominant soils of the alluvial plane (near watercourses) are frequently classified as Argiudolls, Natraqualfs, and Natraquolls (De Siervi et al., 2005).

The upper basin is mainly surrounded by agricultural and cattle breeding areas, while the middle and lower basin areas are highly urbanized and industrialized. A population of 5 million, as well as industrial activities, are concentrated in the lower basin. Pollutants that are dumped into the river or tributaries are generated by urban runoff, dump leachates, and by municipal and industrial wastewater effluents.

2.2 Sampling Sites and Sampling Collection

The following sampling sites of bottom sediment were chosen for this study (Figure 1): MOU on the Morales stream (upper basin), close to the headwaters; ROU on the Rodriguez stream (upper basin); MAU on the Matanza-Riachuelo River (upper basin), downstream of the Rodriguez stream. The main activities of the upper basin are cattle grazing, extensive agriculture, poultry and porcine production, and bovine feedlots. CAM, on the Cañuelas

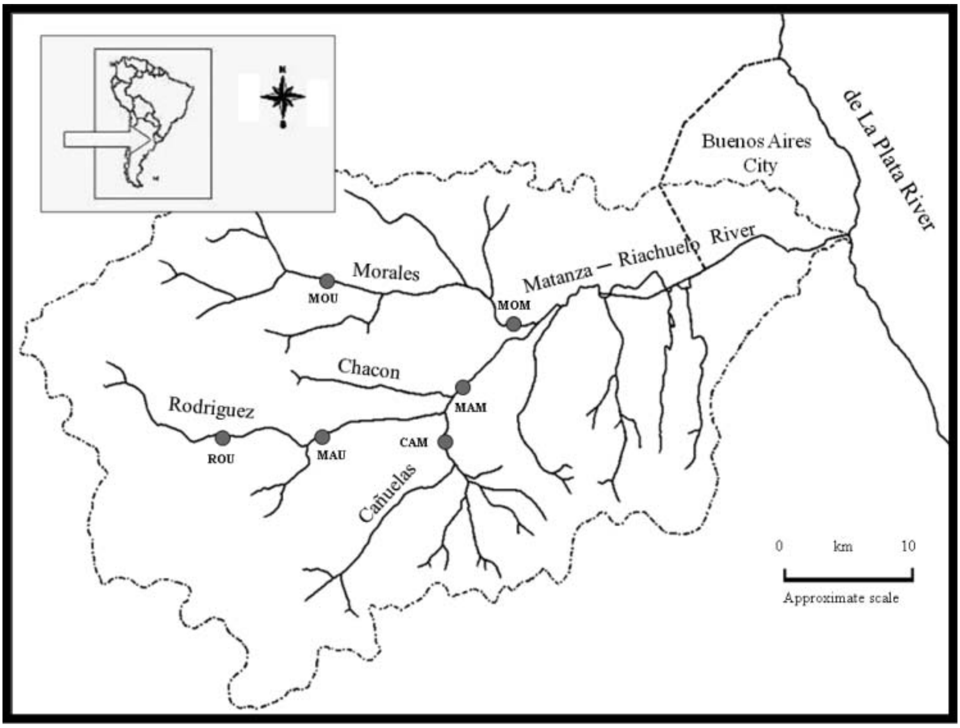

Figure 1. Study area in the upper and middle basin of Matanza-Riachuelo River. Solid symbols indicate sampling sites along the Matanza-Riachuelo River, Morales, Rodriguez, and Cañuelas streams.

stream (middle basin), represents the periphery of an industrialized and urbanized area. MOM, on the Morales stream (middle basin) located near the Matanza-Riachuelo River; and MAM, on the Matanza-Riachuelo River (middle basin) is located downstream (1km) from a meat industry and close to a solid waste dumpsite. The Matanza-Riachuelo River, between MAU and MAM and its tributary streams, has not been dredged or remediated. Therefore, sediment cores can provide a historical record of metal contamination within the watershed.

The sediments were collected approximately 2 m from the bank. Sampling was performed manually by pushing down as far as possible into the bed sediment the core tube, so the depth of sediment sampling was different for each location. The core tubes were sealed with plastic caps and placed in a cooler. Twelve core samples were collected from each of the six sites with core tubes of PVC (50 cm in length and 4 cm of inner diameter). In the laboratory, each sediment core was extruded from the core tube and then cut in a 2 cm section up to 4 cm in depth and in 4 cm sections, starting at 4 cm from that depth on. Sections from three cores were combined into each of four composite samples for each site and depth. Sediment samples were placed in polyethylene bags and stored at 4°C.

2.3 Sediment Analysis

The pH (1:5 sediment-water relation) was measured with a combined glass electrode connected to a pH-meter (Allison et al., 1985), cation exchange capacity (CEC) was determined after saturation with ammonium acetate (Allison et al., 1985), carbonate content was determined by back titrating the excess of 0.5M HCl added to sediment samples, with 0.5M NaOH (Allison and Moodie, 1965), and organic carbon was estimated by the Walkley-Black method (Walkley and Black, 1946) and converted to percent organic matter ($\%OM = 1.72 \times C$). Particle-size analysis (mechanical analysis) was done with a hydrometer (Gee and Bauder, 1986). Total iron (Fe) was determined by atomic absorption spectrometry after a wet mineralization with HNO_3-$HClO_4$-HF. Redox potentials (Eh) were measured with a platinum electrode and saturated calomel electrode (Orion N°96-78), and the data have been corrected relative to the standard normal hydrogen electrode. The water content of the sediment samples was determined by measuring weight loss after drying (105°C for 24 h). The water content was calculated as:

$$W = (W_w - W_d) \times 100/W_w$$

where W: water content (%), W_w: wet weight and W_d: dry weight (Allison et al., 1985).

Handling material was performed under strict anaerobic conditions in a nitrogen box to inhibit sediment oxidation. Extraction of both AVS and metals was performed within 24 h after sampling.

2.4 Fractionation Scheme

The sediment samples were submitted to a SEP procedure modified from Tessier et al. (1979), in which the first step consisted of the extraction with 1M cold hydrochloric acid that allowed identification of the metals bound to AVS. The SEP employed has been described in detail by Rendina (2002) and it is summarized in the flow charts presented in Figure 2. In order to obtain Fraction 1 (F1), 2–10 g of sediment was placed in a 500 mL round bottom flask containing 100 mL of distilled water. Each sample was purged for 10 min with nitrogen, before 20 mL of 1M HCL was introduced into the flask. Then, nitrogen

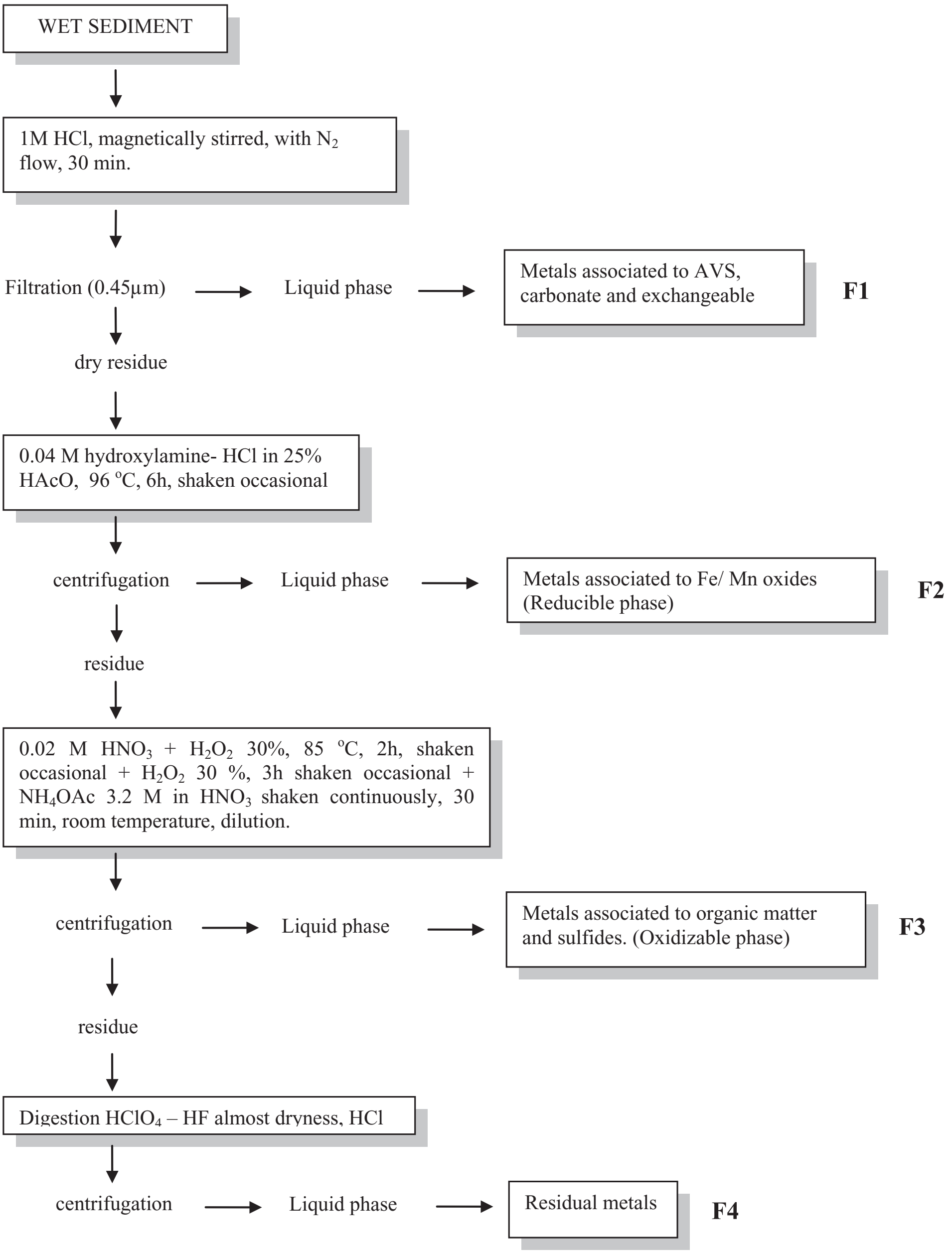

Figure 2. Flow chart of the sequential extraction scheme for determination of heavy metal binding forms in river sediments.

was bubbled through the sample for 30 min, while the sample was magnetically stirred. The concentration of each metal (in the extract from the reaction flask) was determined after filtering through Millipore 0.45 μm filter. Sulfides were determined as acid volatile sulfide (AVS), according to Allen et al. (1993). The SEM was calculated by summation of the concentrations of Cd, Cu, Ni, Pb, and Zn in the F1 fraction. The residue of F1 was washed with water. Then a 1g subsample was used to obtain F2 (metals bound to Fe/Mn oxides), F3 (metals bound to organic matter and sulfides), and F4 (residual), according to Tessier et al. (1979). In each fraction, metal concentration (mg/kg sediment) was calculated taking into account the total weight of residue of F1 fraction. The total concentration of each metal in the sediment was calculated by adding the concentrations of the metal in F1, F2, F3, and F4 fraction.

Sediment samples were analyzed in triplicate. The average values of the variation coefficients, which were obtained (lesser than 8%), can be considered adequate for environmental analysis.

A standard reference material CRM 320 (river sediment) was used to verify the accuracy of metal determination in the sequential extraction analysis. The recovery rates for heavy metals in the standard reference material ranged from 88 to107%.

Metal concentrations in all the extracts were measured by atomic absorption spectrometry with air/acetylene flame (Perkin Elmer Model AAnalyst 200), using external standards prepared from stock solution of the metals (1,000 mg/kg, Merck). The results of the analysis of the wet samples are reported as dry weight of sediment.

2.5 Results Analysis

Data were analyzed using one way analysis of variance (ANOVA). The Bartlett's test was used to verify the homogeneity of variances, and means were compared using the Tukey range test at the 0.05 level of significance.

3. Results and Discussion

3.1 Routine Sediment Characterization

Sediment textures from MOU, ROU, and MAU sites (upper basin) were loam and the sediment textures from CAM, MOM. and MAM sites (middle basin) were clay loam. The small slope of the middle basin implies that the depositional processes are mainly gravity-controlled. The grain size composition of the sediments of all sites did not show depth differences; therefore, down-core variations in metal concentrations reflect historical variations in metals input (Mecray et al., 2001). Other characteristics of sediments at different sites and depths are shown in Figure 3. Anoxic conditions of sediments prevailed at all depths (Eh less than 100 mV), except at the site ROU, where the sediments showed suboxic condition (Eh greater than 100 mV) at depth greater than 8 cm.

The total Fe concentrations in the sediment profiles did not vary greatly (3.0 ± 0.3%), implying that there is little additional Fe input in the study area and that Fe in the sediments is from lithogenous origin. This result parallels that of Villar et al. (1998) in bottom sediments from Parana River and the River Plate Estuary.

The organic matter (OM) distribution showed a maximum in the upper sediments (0–2 cm, section closest to sediment-water interface) with a decrease with depth for all sites. The high OM contents in MAM and MOM sites (6.3% and 5.3%, respectively) probably are attributed to impact by garbage dumps, cold-storage chambers, and sewage sludge.

The sediments were neutral to slightly alkaline in reaction (7.4 to 8.7 unit of pH). The values of $CaCO_3$ ranged between 3.2 and 10.7%. The high pH and content of carbonate in the top sediments of the MAM site can be attributed to the active process of anaerobic

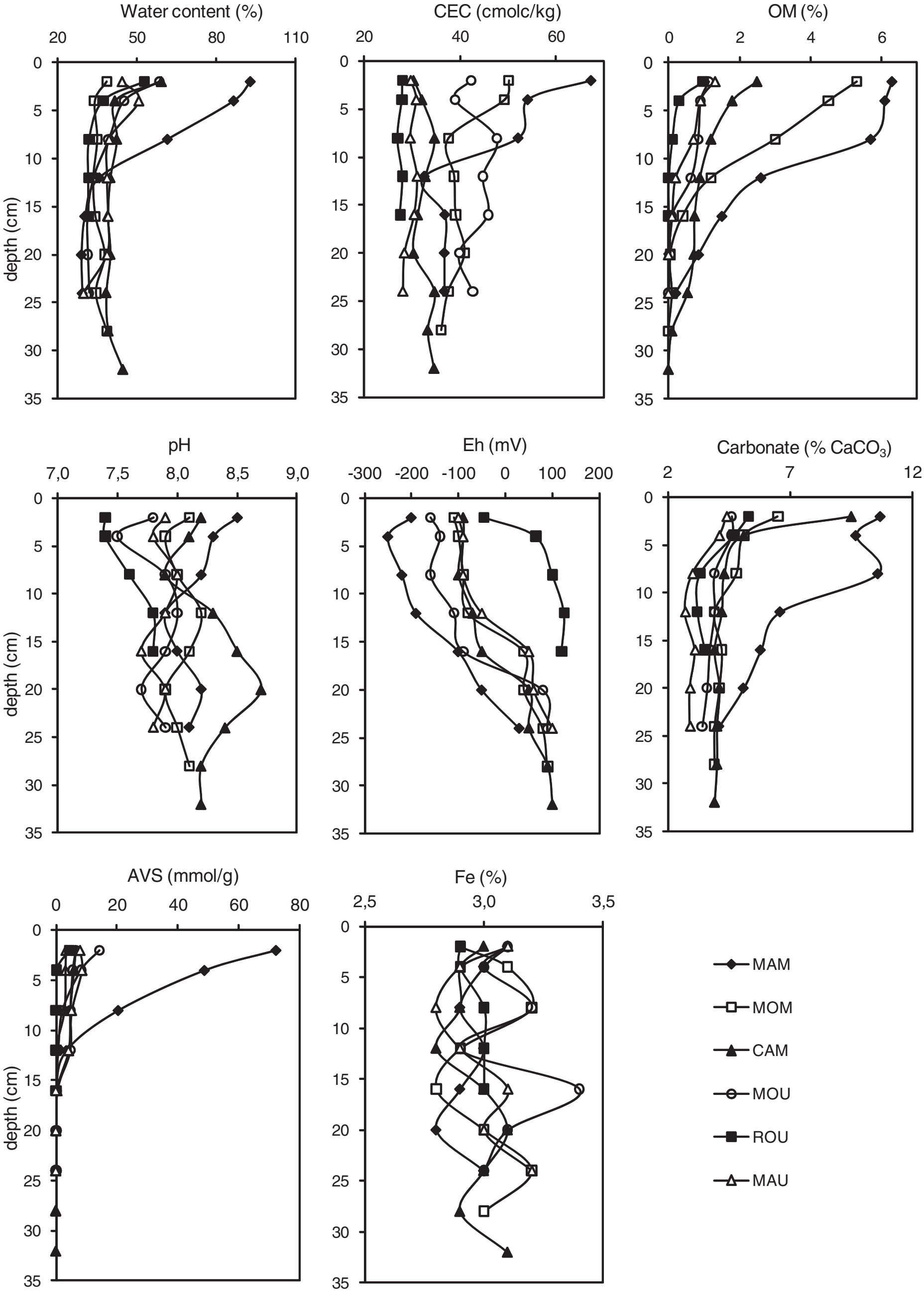

Figure 3. Chemical characteristics of sediments at different sites and depths.

degradation of the organic matter from waste generated in the industrial processing of meat. The CEC values ranged between 27.0 and 67.3 $cmol_c$/kg, MAM and MOM presented high CEC in the top sediments in coincidence with the greatest contributions of organic waste.

Table 1

Mean concentration of total metals (mg/kg) in top sediments (0–2 cm) from Matanza River (MA), Morales stream (MO), Rodriguez stream (RO), and Cañuelas stream (CA); (U) Upper basin, (M) Middle basin

Site	Land use	Cd	Cu	Pb	Zn
MAM	peri-urban/industrial	4.9 a	37.9 a	130 a	261 a
MOM	peri-urban/industrial	2.6 bc	32.2 b	57.7 b	114 b
CAM	peri-urban	2.3 cd	29.6 bc	64.0 b	94.6 bc
MOU	Farming/cattle grazing	1.7 d	26.0 bc	48.1 c	86.7 c
ROU	Farming/cattle grazing	1.9 d	25.3 c	46.3 c	79.0 c
MAU	Farming/cattle grazing	1.3 d	24.7 c	41.9 d	95.6 bc

Different letters within a column denote significant differences between sites ($p < 0.05$).

3.2 Acid Volatile Sulfide

The AVS values in top sediments (Figure 3) ranged from 3.4 to 72.3 μmol S^{2-}/g. The MAM site presented the highest AVS content, low Eh value (-200 mV), and high OM content (6.3%). The drastic changes in the characteristics of Matanza-Riachuelo River sediments between MAU and MAM are attributed to the anthropogenic impact produced by the inflowing waters of Chacon stream (Figure 1), which receives sewage from automotive and meat industries. The AVS content in the sediments of all sites decreased drastically below 8 to 12 cm depth. In the deepest sections where the sediments are consolidated (low water content), the AVS concentration was close to or less than the limit of detection of the determination method (0.01 μmol S^{2-}/g sediment). The highest AVS concentration in the top sediments regarding the deep sections would indicate a very low oxygen transfer from overlying water into top sediment, favoring the AVS formation and inhibiting its oxidation.

3.3 Total Metal Concentrations in Top Sediments and Vertical Distribution

The concentration of heavy metals in the top sediments (0–2cm) ranged as follow: Cd (1.3 - 4.9 mg/kg), Cu (24.7-37.9 mg /kg), Pb (41.9-130 mg /kg), and Zn (79.0-261 mg /kg) (Table 1). The concentration of Cd, Pb, and Zn in MAM was significantly higher than the other sites.

The Cd in agricultural and cattle-grazing sites (MOU, ROU, and MAU) showed the lowest values (1.7, 1.9, and 1.3 mg/kg, respectively). The MAM and MOM sites had Cd, Cu, Pb, and Zn concentrations significantly higher than MAU and MOU sites. The soils of the agricultural and cattle-grazing areas of Buenos Aires Province have naturally low concentration of heavy metals (Cd 0.77 mg/kg, Cu 29.7 mg/kg, Pb 33.9 mg/kg, and Zn 84.1 mg/kg in average). They have a short history of phosphate fertilizer application and light accumulations of heavy metals due to fertilization (Lavado et al., 1998). This suggests that the metal concentrations increased in the middle basin due to urban and industrial activities. However, the Pb and Zn levels in MOM (Pb 57.7 mg /kg, Zn 114 mg /kg) and MAM (Pb 130 mg /kg, Zn 261 mg /kg) were lower than those found by Magdaleno et al. (2008) in top sediments of the river (Pb 239 mg /kg and Zn 584 mg /kg), near the mouth of the Matanza-Riachuelo River, where the river carries an impressive load of industrial waste.

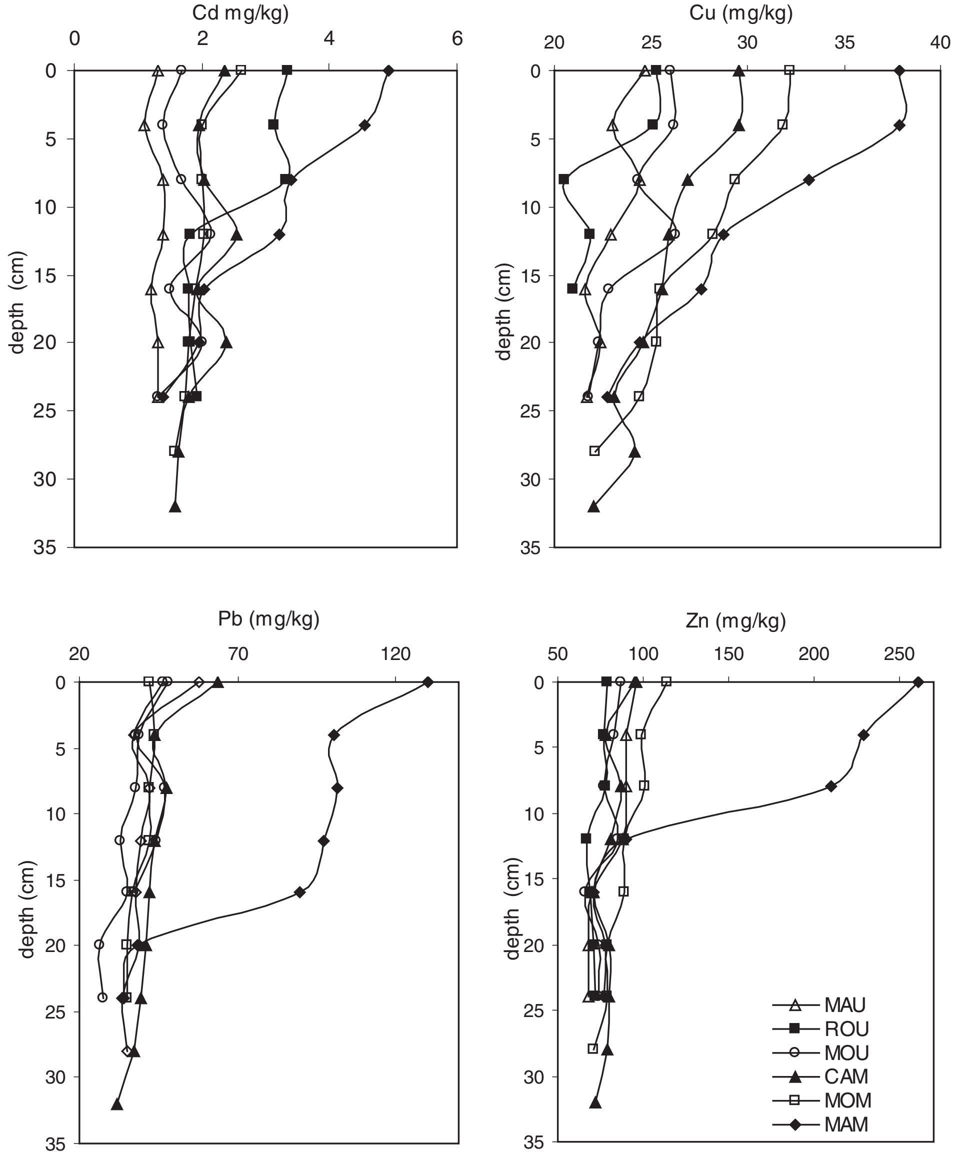

Figure 4. Vertical distributions of Cd, Cu, Pb, and Zn in sediment cores.

The metal concentrations in sediments of all sites consistently decreased with depth (Figure 4). Depth variations of metals concentrations at MAM site are characterized by a pronounced concentration reduction below 8 to 16 cm of depth. Although geochemical profiles of sediments can provide a history of chronological metal loading, diagenetic metal remobilization can redistribute metals within the sediment profile. The gradient from anoxic conditions at the sediment-water interface (Eh = −200 mV) to less anoxic conditions below 12 cm of depth (Eh = −100 mV) at MAM site suggests that the redox conditions control the retention of metals. The metals remain almost constant down to the bottom of the sediment core. The mean concentration (of the six sites) of Cd, Cu, Pb, and Zn in the

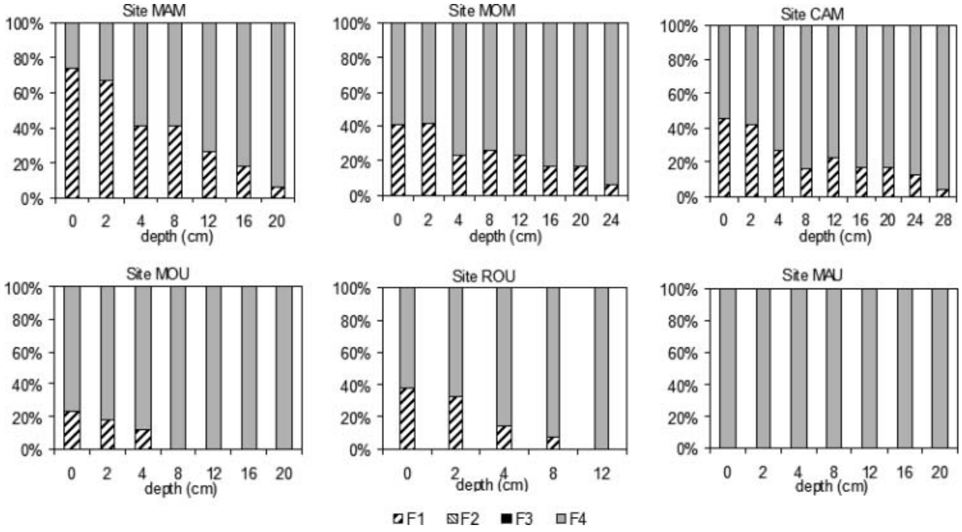

Figure 5. Partitioning of Cd among the different sediment fractions, at different sites and depths, expressed as percentage (%) of sum of fractions (F1: amorphous sulfide, carbonate and exchangeable; F2: Fe/Mn oxides; F3: organic matter/sulfide and F4: residual).

deepest section of the profile ranged between 1.3-1.6 mg/kg, 21.0-22.7 mg/kg, 27.4-37.4 mg/kg, and 67.9-77.0 mg/kg, respectively.

3.4 Partitioning of Metals in Top Sediments

Cadmium. In all sites, the only non-residual form of Cd (Figure 5) was from the leaching with hydrochloric acid (F1). Although this extracting agent can release metals of the sulfide phase (AVS), exchangeable and carbonates phase, the ratio AVS/SEM greater than 1 (Table 2) suggests that the metals are mainly associated with the amorphous sulfide in top sediments. Under anoxic conditions the Cd may be strongly bound as CdS in the sediments; nevertheless, recent research has shown that the Cd precipitated as sulfide can be quickly released as a result of aeration of sediments and can increase the bioavailability of metal for benthic organism (Wang et al., 2010).

The absence of Cd in F2 and in F3 is in parallel to the data of Abrameto et al. (2000) in sediments of the Negro River (Argentina). The low stability of the Cd-humic complexes and the low degree of association with pyrite (Cooper and Morse, 1998) would explain the absence of Cd in the organic matter/sulfide fraction (F3). On the other hand, the low affinity of this metal by the amorphous oxides of Fe and Mn does not facilitate the adsorption of Cd in F2.

MAM showed a high percentage (74%) of non-residual Cd (Figure 5), denoting an appreciable anthropogenic accumulation of this element. In contrast, the other sites showed a percentage of non-residual Cd less than 45%.

Copper. The Cu distribution among non-residual fractions (F1, F2, and F3) in all sites (Figure 6) followed the order: F3 > F1 ≥ F2. In the F3, Cu can either be coupled to active sites of organic molecules (OH of carboxylic and phenolic groups of organic substances) or precipitate/occluded in pyrite. Studies on preferential adsorption (Rashid, 1985) indicate

Table 2

Acid volatile sulfide: AVS (μmol/g), simultaneously extracted metals: SEM (μmol/g), and molar ratio AVS/SEM in sediments at different sites and depths

	MAM			MOM			CAM			MOU			ROU			MAU		
Depth (cm)	AVS	SEM	AVS/ SEM	AVS	SEM	AVS/ SEM	AVS	SEM	AVS/ SEM	AVS	SEM	AVS/ SEM	AVS	SEM	AVS/ SEM	AVS	SEM	AVS/ SEM
0–2	72.3	2.67	27.1	3.36	0.81	4.1	6.40	0.54	11.7	14.3	0.56	25.6	4.3	0.37	11.8	7.98	0.55	14.5
2–4	48.8	2.47	19.8	3.2	0.59	5.4	5.80	0.40	14.6	8.18	0.28	29.4	0.09	0.26	0.3	8.59	0.53	16.1
4–8	20.5	2.13	9.6	2.9	0.58	4.9	4.60	0.34	13.7	2.18	0.22	10.1	0.01	0.17	0.06	5.20	0.49	10.7
8–12	3.47	0.70	4.9	0.08	0.66	0.1	4.20	0.29	14.3	0.84	0.19	4.4	nd	0.15		4.16	0.44	9.4
12–16	0.13	0.19	0.7	0.07	0.42	0.2	0.41	0.21	1.9	0.05	0.14	0.3	nd	0.13		0.01	0.20	0.05
16–20	0.05	0.17	0.3	0.07	0.34	0.2	0.05	0.23	0.2	0.02	0.12	0.2				nd	0.14	
20–24	nd	0.14		0.05	0.28	0.2	nd	0.19		nd	0.12					nd	0.13	
24–28				0.01	0.13	0.1	nd	0.22										
28–32							nd	0.17										

SEM: was calculated as the sum of the concentrations of Cd, Cu, Ni, Pb, and Zn solubilized with cold hydrochloric acid.

nd: not detected (AVS values less than the limit of detection 0.01 μmol S^{2-}/g).

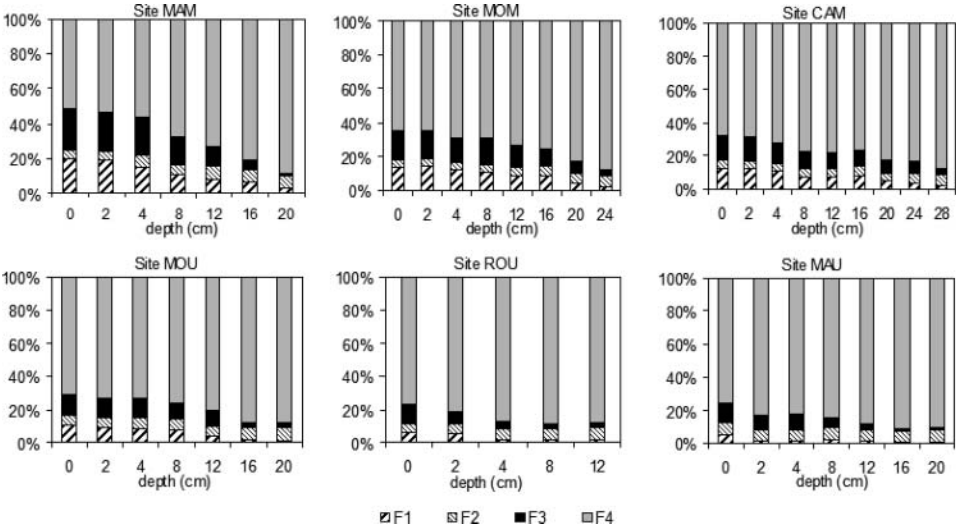

Figure 6. Partitioning of Cu among the different sediment fractions, at different sites and depths, expressed as percentage (%) of sum of fractions (F1: amorphous sulfide, carbonate and exchangeable; F2: Fe/Mn oxides; F3: organic matter/sulfide and F4: residual).

that among the transition metals assayed, Cu competed more strongly for the bonding sites of the humic material. Metals in organic fraction are not considered to be very mobile or available due to their association to humic substances of high molecular weight. Although the organic matter dominates the Cu distribution in top sediments, substantial amounts of Cu were present in the F1 fraction (23 and 41% of non-residual forms). MAM and MOM presented the highest Cu content in F1 fraction in coincidence with the high AVS contents (Figure 3).

MAM, MOM, and CAM showed (Figure 6) the lowest percentages of Cu in the residual (F4) fraction (51, 65, and 67% of total Cu, respectively), in coincidence with the greatest contribution of organic waste of urban and industrial origin, whereas the highest percentages of Cu in F4 were found in MOU, ROU, and MAU (71, 77, and 75%, respectively). In the upper basin of the Reconquista River (rural area of Buenos Aires province), the residual Cu fraction of river sediments presented very similar percentages (71% in average) to those of this study (Rendina et al., 2001), showing the predominantly lithogenous origin of this element in both rural areas.

Lead. The percentage of Pb in non-residual forms in the top sediments (Figure 7) followed the order: F1 > F2 > F3. The Pb in F2 and F3 ranged between 7 to 27% and 5–14% of total Pb, respectively. Despite the reported affinity of Pb to organic matter (Gonzalez et al., 2000), the Pb bound to F3 presented the lower percentages in all sediment samples. The percentage of this fraction did not exceed 14% of total Pb in top sediment. This indicates that organic matter is not the primary factor impacting the behavior of this metal in the study area, even in sediments with high organic matter content. Lead in F1 represented between 29 and 73% of the total Pb, suggesting that the metal is mainly associated with the amorphous sulfide. Gonzalez et al. (2000), applying the Tessier procedure, found that more than 50% of the Pb was bound to organic matter fraction and/or crystalline sulfide. On the other hand, Griffin et al. (1989), who worked in sediments of the Chesapeake Bay, showed that a great

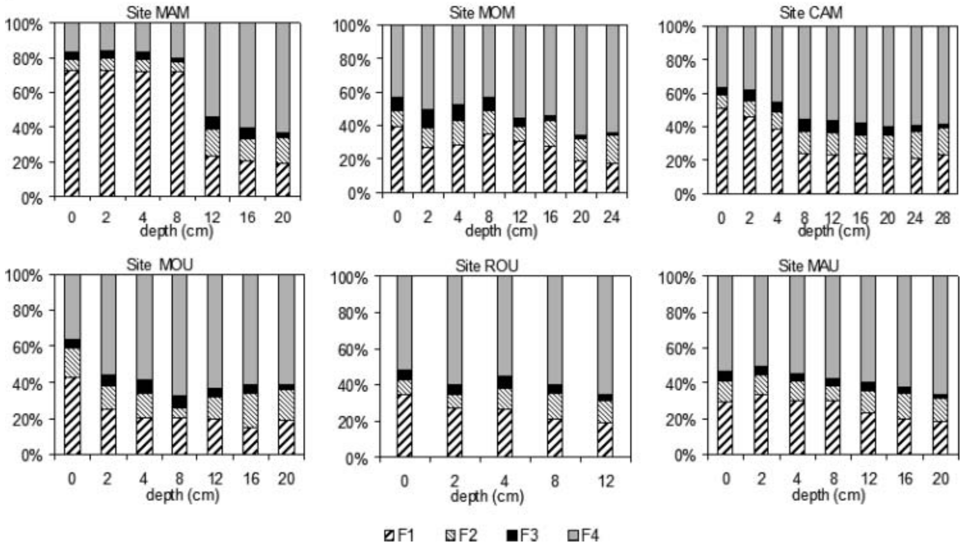

Figure 7. Partitioning of Pb among the different sediment fractions, at different sites and depths, expressed as percentage (%) of sum of fractions (F1: amorphous sulfide, carbonate and exchangeable; F2: Fe/Mn oxides; F3: organic matter/sulfide and F4: residual).

proportion of the Pb is found in the fraction extracted by DTPA (organically adsorbed and complexed), but it is bound to neither crystalline sulfide nor amorphous sulfide (AVS). Nevertheless, a discussion of these results is not only difficult due to the various methodologies applied to establish the relative importance of each geochemical phase in the retention of metals, but it is also complicated owing to the different physical and chemical conditions (e.g. Eh, pH) of the analyzed sediments.

The MAM presented the highest percentage of Pb in non-residual forms (82.7% of total Pb); in the other sites, the percentages ranged between 46.3 to 63.6%. The significant Pb concentrations in non-residual fractions suggest that they may be from anthropogenic sources.

Zinc. The Zn distribution among non-residual fractions of the top sediments (Figure 8) obeyed the following order: F1 > F2 > F3. The Zn concentration in F1 ranged between 48 and 75% of non-residual Zn. The F2 fraction represented between 20.4 and 37.8% and F3 represented between 2.3 and 8.2% of the total Zn. The association of Zn with the Fe and Mn oxides of sediments (Li et al., 2000) has been widely recognized, showing that the Zn adsorption onto the oxides has high stability constants. However, in reduced sediments the production of high levels of AVS determines that only some oxides could compete with the binding capability of AVS, shifting the equilibrium of Zn towards the formation of ZnS amorphous.

The high percentage of non-residual Zn (76% of total Zn) found in MAM contrasted with the percentage of the other sites (31–46%). This may be due to the effect of effluents inflows from metallurgic and automotive industry through Chacon Stream (Figure 1). In addition to industrial activities, leachates from a waste dumpsite located near the main course at MAM may constitute a huge pollution potential. In Argentina, these areas accept demolition materials as well as industrial, commercial, and domestic solid wastes

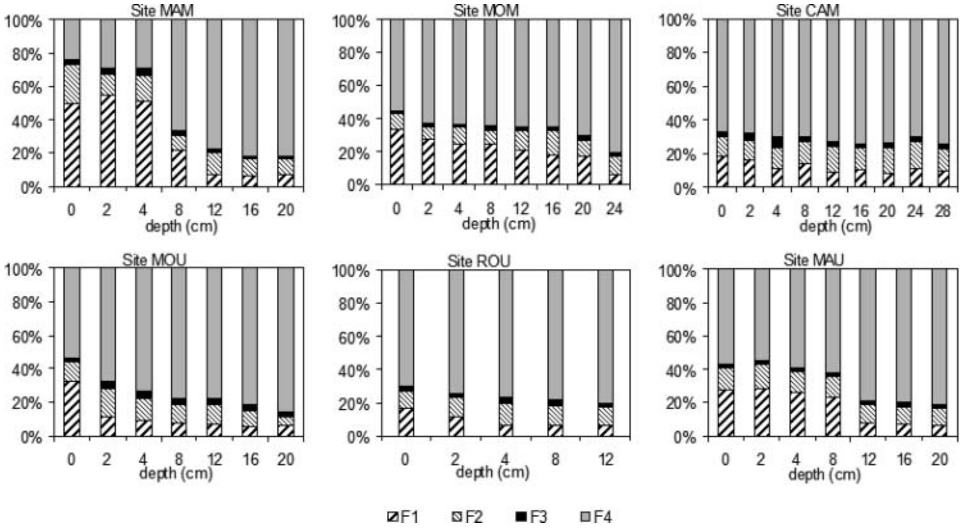

Figure 8. Partitioning of Zn among the different sediment fractions, at different sites and depths, expressed as percentage (%) of sum of fractions (F1: amorphous sulfide, carbonate and exchangeable; F2: Fe/Mn oxides; F3: organic matter/sulfide and F4: residual).

(Magdaleno et al., 2008). The co-disposal of industrial and domestic wastes in clandestine dumpsites increases the toxic chemical risk for the environment (Schrab et al., 1993).

3.5 Vertical Distribution of Metals

The percentages of Cd, Cu, Pb, and Zn in non-residual forms (F1+F2+F3) become smaller with increasing sediment depth (Figures 5–8), representing in the deepest sections on average 2.8, 11.5, 37.5, and 19.4%, respectively. Cu and Zn distribution among non-residual fractions changed with depth. The metals proportion decreased in F1 and F3 fractions and increased in F2 with depth. The distribution of metals among different geochemical phases does not depend only on the affinity between the metal and phase geochemistry. The solid-phase distribution of metals can change if the physical-chemical characteristics of the sediment (i.e. pH, Eh) are modified. The geochemical environment of sediment determines the presence and abundance of the different phases. In our study, the sediments showed a general decrease in OM and AVS concentrations, and less anoxic conditions with increasing depth. These conditions do not favor the reductive dissolution of Fe and Mn oxides, and therefore the Cu and Zn bound themselves preferably to amorphous oxides.

On the other hand, Pb has a different behavior. The non-residual Pb fractions in the whole profile were mainly associated to F1. The very low concentration of AVS in depth indicates that the metals extracted in F1 correspond to exchangeable forms and/or adsorbed on carbonates. Considering what was mentioned above, our results show that more than 37% of the total Pb in the deepest sections of cores is present in labile forms. In contrast, the percentages of Cd, Cu, and Zn were substantially lower (0.0–6.3%, 1.4–2.7%, and 5.9–10.4%, respectively), which indicates a low risk of mobilization of these metals.

3.6 Enrichment Factors and Background Concentrations of Metals

In the present study, an enrichment factor was used (EF) based on sediment metal concentrations available in this study. The EF was defined as the ratio of the total heavy metal concentrations and the metal concentration in the residual phase:

$$\mathrm{EF} = ([\mathrm{Me}]_{\mathrm{F1}} + [\mathrm{Me}]_{\mathrm{F2}} + [\mathrm{Me}]_{\mathrm{F3}} + [\mathrm{Me}]_{\mathrm{F4}})/[\mathrm{Me}]_{\mathrm{F4}}$$

This enrichment factor indicates how much the sediment is enriched relative to metal concentration in the residual fraction (mainly of lithogenous origin). EF values that equal one suggest no enrichment, and EF values that are substantially greater than one suggest anthropogenic input of metals.

The EF of Cd, Cu, Pb, and Zn in top and lower sections (maximum depth sampled in each site) of cores are shown in Table 3.

The top sediments of all the sites are enriched in Cd, Cu, Pb, and Zn (EF greater than 1), except for Cd in MAU site. The EF values for Cd (3.8), Cu (1.9), Pb (5.8), and Zn (4.1) in top sediments of MAM are greater than the other sites. The EF values of Cd, Cu, Pb, and Zn in MAM represent an anthropogenic enrichment (relative to the residual metal concentrations) of 280, 90, 480, and 310%, respectively.

The Pb presented the highest EF of the four analyzed metals both in rural as well as in peri-urban and industrial environments. The Pb atmospheric pathway is one of the main explanations of Pb dispersion into the rural environments. Lead may be found in small particles and aerosols (Komárek et al., 2008), which might fall on the earth's surface very far from their emission source. The brick manufacture is widely distributed both in rural and in peri-urban areas of the Matanza-Riachuelo basin. Fly ash generated in the combustion of coal, oils, tires, and other wastes is a potential source of metals, dioxins, and other pollutants generally released into the atmosphere.

The lower sections of the cores that are characterized by constant low metal concentration and $\mathrm{EF} \cong 1$ would belong to the concentration of the pre-anthropogenic metal (background) in the sediments. The EF of Cd and Cu were close to one (1.0–1.1) in the deepest sections of the sediments for all sites, for which the total concentrations of Cd and Cu (1.6–1.3 mg/kg and 21.7–22.7 mg/kg, respectively) would be the indicators of the natural levels of the studied area. However, the EF values of Pb ranged between 1.5 and 1.9. These results indicate that Pb derived from anthropogenic sources increased 50–70% (as compared to residual Pb concentration) in the deepest section, even in the farming and cattle grazing sites.

The high enrichment of Pb in the whole profile recorded in this study is in good agreement with data reported by other authors (Lacey et al., 2001; Martin, 2000). On the other hand, the EF of Zn in the deepest section of the sediments showed a similar accumulation in all sites (1.2–1.3).

It is possible to infer from the obtained results that the depths sampled do not approach pre-anthropogenic sediments, therefore the values of the total concentrations of Pb and Zn in the deepest sections sampled are not indicators of their natural levels.

3.7 Potential Bioavailability of Metals in Sediments

Research has established that the molar ratio of AVS and SEM (which usually contains Cd, Cu, Pb, Zn, and Ni) is able to predict the availability of various heavy metals for different organisms (Di Toro et al., 1990; Allen et al., 1993; US EPA, 2004); if the molar ratio of

Table 3

Enrichment factors (EF) of metals at top (0–2 cm) and deepest section of cores at different sites; values in parenthesis correspond to anthropogenic contributions (%) of each metal in the sediments relative to metal concentration in the residual fraction

	EF-Cd		EF-Cu		EF-Pb		EF-Zn	
Sites	top	deep	top	deep	top	deep	top	deep
MAM	3.8 a (280)	1.1 a (10)	1.9 a (90)	1.1 a (10)	5.8 a (480)	1.5 a (50)	4.1 a (310)	1.2 a (20)
MOM	1.7 b (70)	1.1 a (10)	1.5 b (50)	1.1 a (10)	2.3 c (130)	1.5 a (50)	1.8 b (80)	1.2 a (20)
CAM	1.8 b (80)	1.0 a (—)	1.5 b (50)	1.1 a (10)	2.7 b (170)	1.7 a (70)	1.5 c (50)	1.3 a (30)
MOU	1.3 bc (30)	1.0 a (—)	1.4 b (40)	1.1 a (10)	2.7 b (170)	1.6 a (60)	1.8 b (80)	1.2 a (20)
ROU	1.6 b (60)	1.0 a (—)	1.3 c (30)	1.1 a (10)	1.9 d (90)	1.5 a (50)	1.4 c (40)	1.2 a (20)
MAU	1.0 c (—)	1.0 a (—)	1.3 c (30)	1.1 a (10)	1.9 d (90)	1.5 a (50)	1.7 b (70)	1.2 a (20)

Different letters within a column denote significant differences between sites ($p < 0.05$).

AVS to SEM exceeds one, the heavy metals can effectively react with sulfide to make them unavailable to biota (Liber et al., 1996).

The concentration of the metals (Cd, Cu, Pb, Zn, and Ni) solubilized during the acidification step (SEM) in top sediments of all sites (Table 2) was less than those of AVS (AVS/SEM greater than one); the metals would not present adverse effects on benthic organisms.

Because this study was performed in early spring, the water and sediment temperatures are comparatively low in relation to summer temperature. It is speculated that during the summer season (higher temperatures) an increase of AVS concentration is to be expected when the sulfate reduction rates increase, as was observed by Leonard et al. (1993) and Mackey and Mackay (1996); therefore the molar relation between AVS and SEM would continue being greater than one.

In the MAM, MOU, and MAU sites, the AVS/SEM ratios (Table 2) were greater than one up to 12 cm depth. By contrast, at ROU site the ratio AVS/SEM was less than one at depths greater than 2 cm. This result is consistent with less anoxic condition of ROU sediments (low AVS) with respect to other sites (Figure 3).

In core sections where the AVS/SEM ratios were greater than one, the literature suggests that the metals extracted with hydrochloric acid are mainly associated with the AVS phase (Di Toro et al., 1990). The metals in exchangeable and carbonate forms (phases that are solubilized with HCl) are expected to be important only for sediments with AVS/SEM less than one. This situation is present in the deep sections of the sediments where AVS was not detected or its concentration was very low. At these sediment sections, the extracted metals in F1 would come only from the exchangeable fraction, carbonates, and/or oxides of low stability (Berry et al., 1996). Although these forms are more bioavailable, the absence of organic matter in these core sections (Figure 3) indicates that the biological activity is low.

4. Conclusions

In the areas where the land use is mainly agriculture and cattle grazing, the concentration of total metals in top sediments was low. Conversely, in those areas where the land uses are both peri-urban and industrial, the concentration of total metals in sediments is greater.

The chemical sequential extraction used in this study showed that Cd, Pb, and Zn in the top sediments were mainly associated with the AVS phase, for which the amorphous sulfide phase should be included when the partitioning of these metals is performed in anoxic sediments. On the other hand, the Cu was mainly associated with oxidizable fraction. The differences in the sediment composition from the upper basin to the middle basin of the streams and the Matanza-Riachuelo River do not change the distribution pattern of heavy metals among the non-residual fractions of the top sediments.

Due to the decrease of AVS and organic matter with depth, Cu and Zn showed a vertical variation in the distribution of its non-residual forms. Cu and Zn bound to reducible fraction increased with increasing sediment depth. In contrast, Cd and Pb were mainly associated to forms leached with cool hydrochloric acid, which in the sediment sections without the presence of AVS would be exchangeable and carbonate.

The enrichment factors of Cd, Cu, Pb, and Zn showed a reduction from the closest section to the interphase water-sediment towards depth. The Pb exhibited the highest enrichment factors in rural as well as in peri-urban and industrial sites. Investigations should be approached on the pollution of this metal at more limited scales in order to determine local sources of pollution.

The ratio values of AVS to SEM were greater than one in top sediments, indicating that the metals would not be bioavailable to benthic organisms. However, due to the dredging and aeration that are currently being proposed for cleaning up the system, the results of this study warn of the risk of remobilization of metals from the sulfide phase to the water column and its effects on biota.

Acknowledgement

The authors acknowledge the financial support of the National Agency of Science and Technology (ANPCyT) and Buenos Aires University in the frame of projects PICT 15028 and UBACyT G011-G055.

References

Abrameto, M., Gil, M. I., Freije, R. H., and Marcovecchio, J. 2000. Fe, Mn, Ni and Cd geochemical partitioning in sediments from the Negro River, Argentina. In: Nriagu, J.O. (Ed.), *Heavy Metals in the Environment*, Contrib. N°1391, University of Michigan, School of Public Health, Ann Arbor, MI (CD-ROM).

Allen, H. E., Fu, D., and Deng, B. 1993. Analysis of acid-volatile sulfide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments. *Environ. Toxicol. Chem.* **12**, 1441–1453.

Allison, L. E., and Moodie, C. D. 1965. Carbonate. In: Black, C.A. (Ed.), *Methods of Soil Analysis. Part 2: Chemical and Microbiological Properties*, Am. Soc. Agron., Madison, WI, pp. 1379–1396.

Allison, L. E., Brown, J. W., Hayward, H. E., and Richards, L. A. 1985. *Diagnóstico y Rehabilitación de Suelos Salinos y Sódicos*. Mexico: Limusa.

Berry, W., Hansen, D. J., Mahony, J. D., Robson, D. L., Di Toro, D. M., Shipley, B. P., Rogers, B., Corbin, J. M., and Boothman, W. S. 1996. Predicting the toxicity of metal-spiked laboratory sediments using acid-volatile sulfide and interstitial water concentrations. *Environ. Toxicol. Chem.* **15**, 2067–2079.

Brumbaugh, W. G., Ingersoll, C. G., Kemble, N. E., May, T. W., and Zajicek, J. L. 1994. Chemical characterization of sediments and pore water from the upper Clark Fork River and Milltown reservoir Montana. *Environ. Toxicol. Chem.* **13**, 1971–1983.

Cooper, D. C., and Morse, J. W. 1998. Extractability of metal sulfide minerals in acid solution: Application to environmental studies of trace metal contamination within anoxic sediments. *Environ. Sci. Technol.* **32**, 1076–1078.

De Siervi, M., Iorio, A., and Chagas, C. I. 2005. Heavy metals in sediments and runoff waters in soils of the Matanza River Basin, Argentina. *Comm. Soil Sci. Plant Anal.* **36**(17 and 18), 2303–2314.

Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Hicks, M. B., Mayr, S. M., and Redmond, M. S. 1990. Toxicity of cadmium in sediments: The role of acid volatile sulfide. *Environ. Toxicol. Chem.* **9**, 1487–1502.

Gee, G. W., and Bauder, J. W. 1986. Particle size analysis. In: Klute, A. (Ed.), *Methods of Soil Analysis, Part 1. Physical and Mineralogical Methods*, Agronomy Monograph No. 9, American Society of Agronomy, Madison, WI, pp. 383–411.

Gonzalez, E., Rodríguez, M. T., Jiménez Sánchez, J. C., Fernández Espinosa, A. J., and Barragán De La Rosa, F. J. 2000. Assessment of metals in sediments in a tributary of Guadalquivir River (Spain): Heavy metals partitioning and relation between the water and sediment system. *Water Air Soil Poll.* **121**, 11–29.

Griffin, T. M., Rabenhorst, M. C., and Fanning, D. S. 1989. Iron and trace metals in some tidal marsh soils of the Chesapeake Bay. *Soil Sci. Soc. Am. J.* **53**, 1010–1019.

Herkovits, J., Perez-Coll, C. S., and Herkovits, F. D. 1996. Ecotoxicity in the Reconquista River, Province of Buenos Aires, Argentina: A preliminary study. *Environ. Health Persp.* **104**, 186–189.

Hirner, A. V. 1992. Trace element speciation in soils and sediments using sequential chemical extraction methods. *J. Anal. Chem.* **46**, 77–85.

Huerta-Diaz, M. A., and Morse, J. W. 1993. Pyritization of trace metals in anoxic marine sediments. *Geochim. Cosmochim. Ac.* **56**, 2681–2702.

Komárek, M., Ettler, V., and Mihaljevic, M. 2008. Lead isotopes in environmental sciences: A review. *Environ. Int.* **34**, 562–577.

Lacey, E. M., King, J. W., Quinn, J. G., Mecray, E. L., Appleby, P. G., and Hunt, A. S. 2001. Sediment quality in Burlington Harbor, Lake Champlain, USA. *Water Air Soil Poll.* **126**, 97–120.

Lavado, R. S., Rodriguez, M. B., Scheiner, J. D., Taboada, M. A., Rubio, G., Alvarez, R., Alconada, M., and Zubillaga, M. S. 1998. Heavy metals in soils of Argentina: Comparison between urban and agricultural soils. *Commun. Soil Sci. Plant Anal.* **29**, 1913–1917.

Leonard, E. N., Mattson, V. R., Benoit, D. A., Ankley, G. T., and Hoke, R. A. 1993. Seasonal variation of acid-volatile sulfide concentrations from three northeastern Minnesota lakes. *Arch. Environ. Con. Tox.* **271**, 87–95.

Li, X., Shen, Z., Onyx, W. H., Wai, W. H., and Li, Y. 2000. Chemical partitioning of heavy metal contaminants in sediments of the Pearl River Estuary. *Chem. Spec. Bioavailab.* **12**(1), 17–25.

Liber, K., Call, D. J., Markee, T. P., Schmude, K. L., Balcer, M. D., Whiteman, F. W., and Ankley, G. T. 1996. Effects of acid-volatile sulfide the experiments on zinc bioavailability and toxicity to benthic macroinvertebrates: A spiked-sediment field experiment. *Environ. Toxicol. Chem.* **15**, 2113–2125.

Liu, J., Yan, C., Macnair, M. R., Hu, J., and Li, Y. 2007. Vertical distribution of acid-volatile sulfide and simultaneously extracted metals in mangrove sediments from the Jiulong River Estuary, Fujian, China. *Environ. Sci. Pollut. R.* **14**(5), 345–349.

Mackey, A. P., and Mackay, S. 1996. Spatial distribution of acid-volatile sulphide concentration and metal bioavailability in mangrove sediments from the Brisbane River, Australia. *Environ. Pollut.* **93**, 205–209.

Magdaleno, A., Mendelson, A., Iorio, A., Rendina, A., and Moretton, J. 2008. Genotoxicity of leachates from highly polluted lowland river sediments destined for disposal in landfill. *Waste Manag.* **28**, 2134–2139.

Martin, C. W. 2000. Heavy metal trends in floodplain sediments and valley fill, River Lahn, Germany. *Catena.* **39**, 53–68.

Mecray, E. L., King, J. W., Appleby, P. G., and Hunt, A. S. 2001. Historical trace accumulation in sediments of an urbanized region of the Lake Champlain watershed, Burlington, Vermont. *Water Air Soil Poll.* **125**, 201–230.

Olson, D., Dinerstein, E., Canevari, P., Davidson, I., Castro, G., Morisset, V., Abell, R., and Toledo, E. 1998. *Freshwater Biodiversity of Latin America and the Caribbean: A Conservation Assessment*, Biodiversity Support Program, Washington, DC.

Ouddane, B., Billon, G., Boughriet, A., and Wartel, M. 2000. Artifact in the speciation of sulfides in anoxic estuarine sediments. *ESPR–Environ. Sci. Pollut. R.* Abstracts 7th FECS Conference.

Peltier, E., Dahl, A. L., and Gaillard, J. F. 2005. Metal speciation in anoxic sediments: When sulfides can be construed as oxides. *Environ. Sci. Technol.* **39**(1), 311–316.

Rao, C. R. M., Sahuquillo, A., and Lopez-Sanchez, J. F. 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. *Water Air Soil Poll.* **189**, 291–333.

Rashid, M. A. 1985. *Geochemistry of Marine Humic Compounds*, Springer-Verlag, New York.

Rendina, A. 2002. Distribución geoquímica de metales pesados en sedimentos del Río Matanza y principales arroyos afluentes. Thesis Magister Science, EPG–Facultad de Agronomía, UBA, Buenos Aires, Argentina.

Rendina, A., Arreghini, S., De Cabo, L., Bargiela, M., and de Iorio, A. F. 2001. Geochemical distribution and mobility factors of Zn and Cu in sediments of the Reconquista River, Argentina. *Revista Internacional de Contaminación Ambiental.* **4** (17), 187–192.

Schrab, G. E., Brown, K. W., and Donnelly, K. C. 1993. Acute and genetic toxicity of municipal landfill leachate. *Water Air Soil Poll.* **69**, 99–452.

Tessier, A., Campbell, P. G. C., and Vison, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **51**, 844–851.

US EPA (United States Environmental Protection Agency). 2004. *The Incidence and Severity of Sediment Contamination in Surface Waters of the United States (National Sediment Quality Survey)*, EPA 823-R-04-007, 2nd ed., U.S. Environmental Protection Agency, Office of Water, Washington, DC.

Villar, C., Tudino, M., Bonetto, C., de Cabo, L., Stripeikis, J., d'Huicque, L., and Troccoli, O. 1998. *Verh. Internat. Verein. Limnol.* **26**, 963–966.

Walkley, A., and Black, C. A. 1946. Total carbon, organic carbon, and organic matter. In: Sparks, D.L. (Ed.), *Methods of Soil Analysis Part 3, Chemical Methods*, Soil Science Society of American Journal, Madison, WI, pp. 1367–1378.

Wang, S., Jia, Y., Wang, S., Wang, X., Wang, H., Zhao, Z., and Liu, B. 2010. Fractionation of heavy metals in shallow marine sediments from Jinzhou Bay, China. *J. Environ. Sci.* **22** (1), 23–31.

Yu, K. C., Tsai, L. J., Chen, S. H., and Ho, S. T. 2001. Chemical binding of heavy metals in anoxic river sediments. *Water Res.* **35**(17), 4086–4094.