PARTITIONING OF METALS IN SEDIMENTS FROM THE LOWER PARAÍBA DO SUL RIVER, SE, BRAZIL

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RESUMO

Este estudo tem como objetivo fazer uma caracterização da distribuição de metais pesados na porção inferior do Rio Paraíba do Sul avaliando a possível dispersão destes elementos da porção média para a bacia inferior e estuário. Esta avaliação foi realizada através da determinação da concentração total e da especiação química de metais pesados em sedimentos de fundo do canal fluvial, áreas inundáveis marginais e região estuarina. Em geral as concentrações dos metais analisados na bacia inferior do Rio Paraíba do Sul foram inferiores as concentrações relatadas para a porção média do rio. Para metais como Cu, Cr, Fe e Ni a reduzida variação espacial das concentrações total e a especiação preferencialmente associada à estrutura cristalina de minerais sugerem que a distribuição destes elementos é determinada por fontes locais à bacia inferior como erosão de solos enquanto que a dispersão da bacia média do rio pode ser considerada de secundária. Por outro lado, a distribuição de metais como Cd, Pb e Zn tiveram um padrão de diminuição progressiva sugerindo uma diluição das concentrações ao longo da bacia inferior. Este padrão associado à especiação química que mostra uma predominância destes metais a fases sensíveis a aportes antrópicos sugere que a distribuição destes metais possa sofrer uma influencia da porção média do Rio Paraíba do Sul onde há uma intensa ocupação da bacia de drenagem do rio por fontes antrópicas de metais pesados.

ABSTRACT

This investigation aims to determine the extent of heavy metal dispersal from the heavily-industrialized middle river segment of the Paraíba do Sul River to the lower stretch of the river and estuary. This analysis was carried out in sediments from river channel, floodplain and estuary of the lower river basin by using total and slightly modified BCR sequential extraction procedures. Overall, the lower river basin shows smaller metal concentrations than industrialized river segment. For Cu, Cr, Ni the small spatial variation of total metal distribution and predominance of residual phase suggests reduced influence from middle river basin and distribution of such metals along the lower river basin controlled by local sources such as soil particles erosion. In contrast, the decay pattern observed as distance increased from the middle river basin for Cd, Pb, and Zn suggests that the metal dispersion from the middle river segment is reaching the lower stretch of the river. These metals are associated with reactive forms, which are environmentally significant with respect to chemical mobilization and ecotoxicology.

INTRODUCTION

Discussion in the literature has suggested that surface sediments integrate the environmental conditions occurring in the water column and thus play a major role in the storage of contaminants in fluvial systems (Bubb & Lester, 1994; Walling *et al.*, 2003). Therefore, sediment quality has been recognized as a valuable indicator of water pollution and the assessment of the metal content and distribution in surface sediments can provide information concerning human impact on fluvial systems. To improve the understanding of metal geochemical distribution in sediments, several analytical procedures have been designed. Such protocols are able to identify the main metal scavengers and to obtain information about the mobility and bioavailability of heavy metal content in freshwater (Förstner, 1993).

In the present study, total and sequential extraction procedures were used to evaluate the downstream heavy metal dispersal from the heavily industrialized river segment to the lower reaches and estuary of one of the most socially and economically important fluvial systems in Brazil. The Paraíba do Sul River is an example of a middle size fluvial environment impacted by intensive land use along its drainage basin on account of industrial and urban development. Many studies have examined the impact of these activities in water and sediment in the middle river basin, where heavy industrial activity is placed, suggesting a moderate to strong pollution scenario in terms of heavy metal distribution in water, soil, and sediments (Malm *et al*., 1989; Pfeiffer *et al*., 1986; Azcue *et al*., 1987; Mello, 1999; Governo do Estado do Rio de Janeiro, 1999). Even though the levels of some metals exceed the contamination threshold in the upper stretch of the Paraíba do Sul River, the decline of heavy industrial activities and land use changing to agricultural along downstream reaches, associated with the construction of dams would suggest not only a reduction of heavy metal dispersion along the lower stretch of the river, but also changes in the distribution and partitioning of heavy metals in the sediment.

The objective of this study is to investigate the heavy metal distribution and partitioning in river channel, floodplain, and estuarine sediments of the lower river Paraíba do Sul River by using both total and slightly modified BCR-three step procedures in order to detect the metal dispersion from an heavily industrialized river segment further afield via fluvial transport to the lower stretch of the river.

MATERIAL AND METHODS

Site description

The Paraíba do Sul River is approximately 1,145 km long and its drainage basin covers 55,400 km^2. The river crosses in an east-west direction along the most industrialized states of Brazil until flows into Atlantic Ocean (Figure 1). In the middle basin, many hydrological modifications have been implemented, such as reservoirs and water diversion scheme, to supply drinking water to around 10 million people. However, at the same time, large industrial complexes have been established along this region, including metallurgical, iron and steel production, paper, plastic, rubber and chemical manufactures, summing around 600 industries (Governo do Estado do Rio de Janeiro, 1999).

The lower river basin comprises 90 Km along the broad coastal lowlands (elevations ~ 10 m) and depositional delta (Figure 1). This stretch of the river is almost entirely agricultural; however, this region has been substantially modified to improve urban development and agricultural fields for cattle breeding and sugar cane plantation. Significant industrial plants are not observed in the studied area, however, domestic sewage and small industrial activities may be a potential source of heavy metals to the river (Governo do Estado do Rio de Janeiro, 1999). The Paraíba do Sul Delta consists of two principal channels (Figure 1), which transport the fluvial discharge seaward, flaked by low-lying inter-channels, mangroves swamps, tidal flats, and beach ridges. The morphology of the delta is determined by the interactions between fluvial deposition and the effects of tides, waves, and currents in dispersing sediments parallel to the coastal line (Costa, 1994). The occupation of adjacent area of the Paraíba do Sul Delta is characterized by low intensity of industrial and domestic activities.

Sampling

In the dry season (July, 1999), under low discharge conditions, surface sediments (above 5 cm of bed material) were randomly sampled within 26 reaches scattered throughout the lower river basin. These included 13 samples from the river channel, 6 samples along the adjacent floodplain, and 7 samples seaward along the two principal estuarine channels (Figure 1). Selected sampling sites represent the range of variability along this stretch of the river, clustering agricultural and urbanized portion of the watershed at fixed distance intervals, measured by using Global Positioning System (GPS) technology. Each of the sediment samples were composed by 10 sub-samples, which were pooled and homogenized and a single sample performed.

Analytical Procedures

All samples were collected with a Teflon grabber and frozen prior to analysis. While in laboratory, the sediment samples were sieved to obtained the grain-size distribution and < 63µm-size fraction was used for metal analysis.

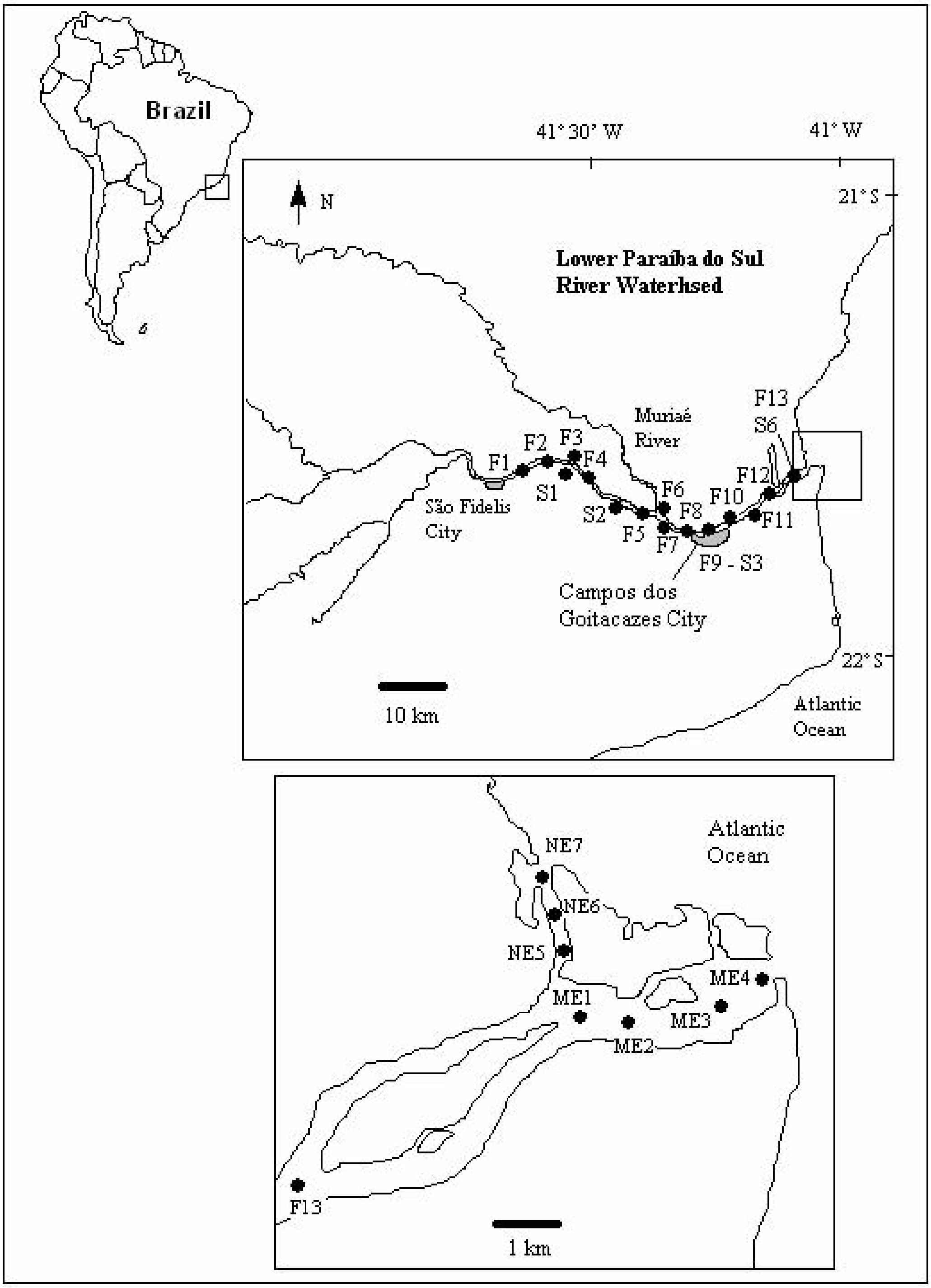

Figure 1 - Map showing the location of the study area and the sampling sites across the river channel (F), floodplain (S) and estuarine (ME-main channel in the estuary; NE- narrow channel) of the lower Paraíba do River.

Aliquots (0.5 g) were completely dissolved using acid mixture (10 mL) of HNO_3 and HF (1:1) for 12 hours at 100 °C. Extracts were analyzed to obtain the total concentration of Fe, Mn, Zn, Cr, Cu, Ni, Pb and Cd in bed sediments.

Basically, the sequential extraction procedure has been used to differentiate chemical forms of sediment-bound metals, operationally defined by the action of an extractor, which solubilised a specific component and its associated metals. The three-step sequential extraction procedure was applied to the procedure proposed by the Community Bureau of Reference (BCR) and described in detail elsewhere (Quevauviller *et al.*, 1994). In addition to proposed BCR steps, this study includes step (4), which extracts metals bound to the residual, crystalline phase.

1. Exchangeable – weakly bound to substrate: 1.0 g sediment sample was extracted at room temperature for 16 h (overnight) with 40 mL of 0.11 mol/L acetic acid solution in a centrifuge tube with continuous agitation.

2. Reducible – bound to Fe-Mn oxides: The residue obtained from step (1) was leached for 16 h at room temperature (overnight) with 40 mL of 0.1 mol/L hydroxylamine hydrochloride solution, acidified with HNO_3 to pH 2, in a centrifuge tube with continuous agitation.

3. Oxidable – bound to organic matter and sulphides: To the residue in step (2), 10 mL of 8.8 mol/L H_2O_2 was added and the pH adjusted to 2 with HNO_3. The mixture was digested at room temperature for 1 h and digested again for another 1 h at 85°C. A second 10 mL aliquot of 8.8 mol/L H_2O_2 (pH 2) was added and the digestion was continued for 1 h at 85°C. After cooling, 50 mL of 1 mol/L ammonium acetate, adjusted to pH 2 with HNO_3, was added and the mixture was agitated for 16 h at ambient temperature.

4. Residual – crystal lattice of primary and secondary minerals: The residue obtained from step (3) was digested with HF - HNO_3 mixture as per the procedure followed for the analysis of total metal concentration.

Supernatants of each step were also analyzed for Fe, Mn, Zn, Cr, Cu, Ni, Pb and Cd. All these elements were determined by ICP – AES (Varian Liberty 200). Triplicates and analytical blanks were used in all analysis. The precision of the analytical procedure, expressed as the relative standard deviation of the replicates was better than 10%. Certified multi-element standard sediment (NIST 2704 Buffalo River), supplied by the National Institute of Standards and Technology (USA) was extracted simultaneously with samples to determine the efficiency of the total metal extraction procedure. The recovery of the leaching procedure was generally in the range 90% of the certified heavy metal concentration observed on the standard sediment. The comparison between total concentrations with the sum of all metal phases was used to determine sequential extraction accuracy and in all tests the values remained around 15%.

RESULTS AND DISCUSSION

Particle-size analysis

The samples collected in the river channel and along the wider channel in the estuary consisted of sand sediments in which the fine fraction (<63 mm) represents less than 34 and 11% respectively (Table 1). On the other hand, silt/clay-size particles are markedly more abundant in samples from the floodplain sites and along the narrower channel in the estuary. The amounts of sand and silt/clay sediments stored within each sampled area (river channel, floodplain, and estuary) were not found to be highly variable with CVs of ca. 20%. The grain-size analysis shows that the floodplain and the narrow channel in the estuary retain most of the fine sediments transported along the lower river

Table 1 - Grain size distribution of the bed sediments in lower Paraíba do Sul River Basin.

	Sand (%) 2 mm-63 m	Silt-Clay (%) < 63 m
River channel	66	34
Floodplain	36	64
Estuary (main channel)	89	11
Estuary (narrow channel)	15	85

basin. Thus as silt/clay particles are important geochemical support for heavy metals in the Paraíba do Sul River (Salomão *et al.*, 2001; Carvalho *et al.*, 2002), these areas have a major importance on storage of metals carried along the lower Paraíba do Sul River.

Total metal concentration and downstream patterns of distribution

The total heavy metal sediment analysis from the lower Paraíba do Sul River displayed the range as (in mg kg^{-1} and Fe, %): Cd, 0.1-2.4;

Table 2 - Distribution, mean, standard deviation (SD) and coefficient of variation (CV, %) of the total metal concentration in bed sediments of river channel (F), floodplain (S), wider (ME) and narrower (NE) channels in the estuary of the lower Paraíba do Sul River (Fe %; others mg kg^{-1} dry weight).

	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn
F1	2.4	96	47	4.4	860	38	40	184
F2	2.3	108	47	4.4	796	40	45	186
F3	2.4	118	48	6.0	1,820	43	19	198
F4	1.9	105	47	4.9	1,182	38	21	174
F5	1.5	90	51	4.5	792	45	30	171
F6	0.1	100	49	5.0	1,020	48	9	126
F7	0.5	90	47	3.7	600	42	41	130
F8	0.6	90	46	3.9	680	47	35	132
F9	1.4	114	46	4.9	1,320	44	17	180
F10	1.5	100	47	6.6	1,200	42	34	150
F11	1.2	92	50	3.8	508	40	34	150
F12	1.2	104	53	3.3	800	50	33	159
F13	1.3	109	54	6.0	1,080	50	42	180
Mean	1.4	101	49	5.0	974	44	31	163
SD	0.7	9.4	2.6	1.0	352	4.2	11	24
CV	52	9	5	21	36	10	36	15
ME1	1.3	117	60	3.9	1,131	44	42	174
ME2	1	102	55	3.8	867	50	37	168
ME3	0.6	90	35	4.1	372	37	30	132
ME4	0.5	90	40	3.9	340	37	17	120
NE5	0.6	102	57	4.8	700	49	39	138
NE6	0.7	107	52	4.6	376	49	15	162
NE7	1.8	114	58	4.9	336	53	9	198
Mean	0.9	103	51	4.0	589	46	27	156
SD	0.5	11	10	0.5	317	6	13	27
CV	51	10	19	11	54	14	49	17
S1	1.2	102	59	3.1	336	40	23	156
S2	1.2	84	48	3.9	528	39	34	144
S3	0.6	105	53	4.5	660	46	25	162
S4	1.2	102	51	5.4	880	46	12	173
S5	1.5	102	54	5.0	810	48	47	174
S6	0.6	94	43	4.4	627	44	42	138
Mean	1.1	98	51	4.0	640	44	31	158
SD	0.4	7.9	5	1.0	196	4	13	15
CV	35	8	11	19	31	8	43	9

Cr, 84-118; Mn, 336-1,820; Fe, 3.1-6.6; Ni, 37-53; Cu, 35-60; Pb, 9-47; Zn, 120-198 (Table 2). Although, the sampling design comprised of distinct sites (river channel, floodplain, estuary), the spatial variation of Cr, Fe, Cu, Ni, and Zn concentrations were found to be a smaller degree variable, with the coefficient of variation (CV) varying from 9% to 20%. In contrast, Cd, Mn, Pb levels displayed greater variation along the river basin with CVs ranging from 39 to 72%. In general, the mean metal concentration in the sediments from river channel, floodplain, and estuary were found to be fairly similar (Table 2).

Downstream metal distribution in the river channel for the 90-km study reaches were examined by plotting the concentration of such metals against the distance downstream (Figure 2). Generally, the Cu, Cr, and Ni concentrations

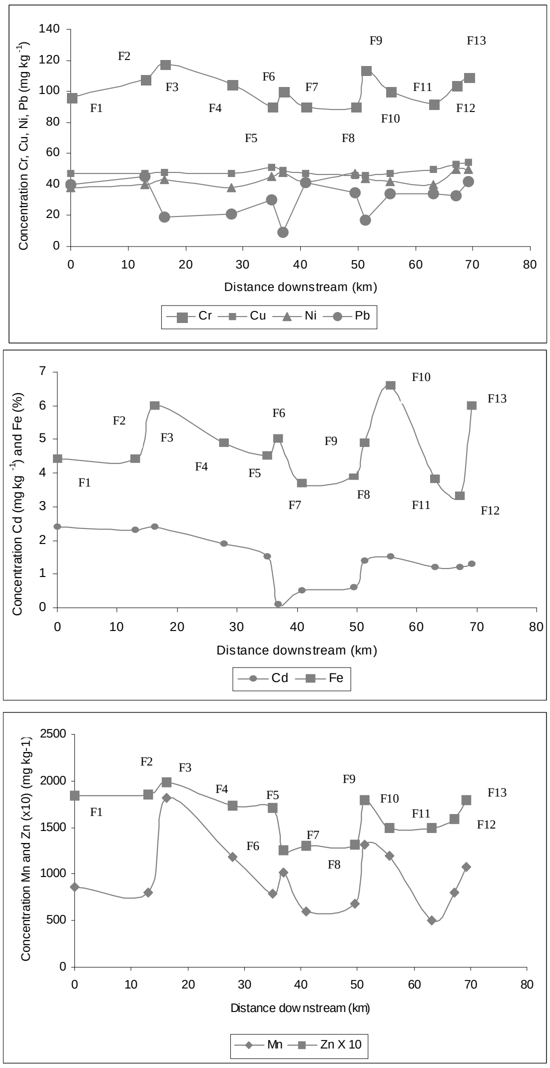

Figure 2 - Downstream distribution of the total metal concentrations in river channel sediments along the study area.

remained relatively constant along river channel sites. In contrast, Cd, Zn, and Pb displayed a decay pattern as distance from the middle basin increases (37 km downstream), with the lowest concentrations exhibited at site F6. After site F6, the increase of Cd, Zn, and Pb concentration coincides with land use change from agricultural to urban areas. Distribution patterns of Mn and Fe are similar with significant positive correlation (r = 0.79, P < 0.05), however no distinct trend can be established.

An examination of total concentration shows that the bed sediment from the lower river basin has less metal content than middle basin (Table 3). The low metal content in sediments from the lower river basin is in agreement with Carvalho *et al.* (2002), Salomão *et al.* (2001) and Molisani *et al* (1999) who have already described suspended matter and bottom sediment along this stretch of the river showing low or no heavy metal contamination. After data comparison, the Cd concentrations in the lower river basin seem to be influenced to a certain extent by the Pomba River. The Paraíba do Sul tributary is located downstream from the industrial river segment which shows similar Cd concentration to the bed sediments from lower basin (Table 3). Some industrial plants located along the watershed of this tributary, as related by Torres (1992), might be an important source of Cd-rich particles to the lower Paraíba do Sul River basin. Salomão *et al.* (2000) described suspended sediments with similar Cd concentration at upstream sampling stations of the lower river basin demonstrating that Cd is intimately associated with fine-grained sediments frequently transported as suspended load from the middle river basin.

The low spatial variation of Cr, Cu, and Ni suggests that the reduction of the total metal concentration still occurred within the middle river basin indicating that higher-metal content sediments from middle basin have not extensively dispersed down through lower river basin. On the other hand, lower amounts of Pb, Cd, and Zn in bed sediments of lower river basin are attributed to the reduction of downstream concentration along the 37-km reach of the river, although increased concentration was observed in the urban river segment. The concentration reduction with increasing distance along the 37-

Table 3 - Total metal concentration in bed sediments at different segments of Paraíba do Sul River until continental shelf under its influence; all values in mg kg $^{-1}$; except for Fe, %.

	Cu	Cr	Zn	Ni	Mn	Fe	Pb	Cd
Middle river basin [1]	105	265	327	62	757	6.1	94	0.6
Paraibuna River[2] (Tributary - middle basin)	36	109	285	61	881	5.6	44	2.2
lower river basin - this Study	49	101	163	44	479	5.0	31	1.4
Continental Shelf [3]	29	84	147	36	876	6.2	-	-
[1] Malm *et al.*, 1988; [2] Torres, 1992; [3] Carvalho, 1992								

km agricultural reach of the lower Paraíba do Sul River suggests the dilution effect of upstream concentrations by lower metal-content sediment from the lower river basin as well as the absence of metal source significance along this stretch of the river. In addition, this distribution suggests that the middle river sediment particles are reaching the lower river Paraíba do Sul River. Although the downstream field variance for metal concentration in this study is much lower compared to the order of magnitude variance observed in sites influenced by mining activities (Taylor & Kesterton, 2002), the between-sites metal variability observed along the Paraíba do Sul River (Figure 2) is similar to other rivers impacted by industrial and domestic sewage (Singh *et al*., 2003).

In general, the pattern of downstream metal distribution on floodplain sediments demonstrated no marked variations (Table 2). In the case of estuarine metal distribution, a seaward decreasing trend was observed for metal concentrations in the main estuarine channel (Table 2), presumably as a consequence of the absence of a pollution source in the estuary and as a result of marine and fluvial sediment mixing. Marine sediments with low metal concentration would dilute the metal load associated with riverine sediments. This pattern is generally consistent with the observations of Carvalho (1992), who noted a seaward decrease in the total metal concentration with lower values in continental shelf bottom sediments under Paraíba do Sul River influence (Table 3). In the narrow channel, only Pb and Mn concentrations appeared to reflect a seaward reduction pattern, while Zn and Cd displayed an inverse distribution with seaward increasing concentrations (Table 2).

Metal speciation

The downstream distribution of the chemical forms of heavy metal in some sampling sites along the lower Paraíba do Sul River are shown in Figure 3 and 4. The speciation was performed in sediments from sampling sites randomly chosen to characterize the agricultural (0-37 km) and urban (37-70 km) river segments, adjacent floodplain and the two main branches of the estuary. The results are examined in terms of percentage for the total metal concentration. The spatial distribution of chemical forms show that the increasing distance from the middle river basin and the land use change along downstream river segments did not alter the metal speciation significantly in the lower river basin, mostly the proportion between the labile (exchangeable, reducible, and oxidable) and residual phases.

Basically, the mean partitioning shows most Cd is observed to be in the exchangeable (70% of total concentration), reducible (15%) and residual (14%) fractions, thus non-lithogenous fraction (sum of the exchangeable, reducible, and oxidable fractions) accounts for more than 80% of the total sediment Cd concentrations. The same trend can be described for Mn which was found to be present in a greater extend in non-lithogenous fractions (85%), represented by exchangeable (60%), reducible (20%), and oxidable (5%) fractions. The spatial distribution of the chemical forms shows a downstream decrease of exchangeable Cd and a simultaneous increase of residual fraction in the river channel sediments. An inverse pattern was found in floodplain sediments where a downstream increase of exchangeable Cd was observed that culminates a Cd entirely at the sampling site S6 shown in the exchangeable

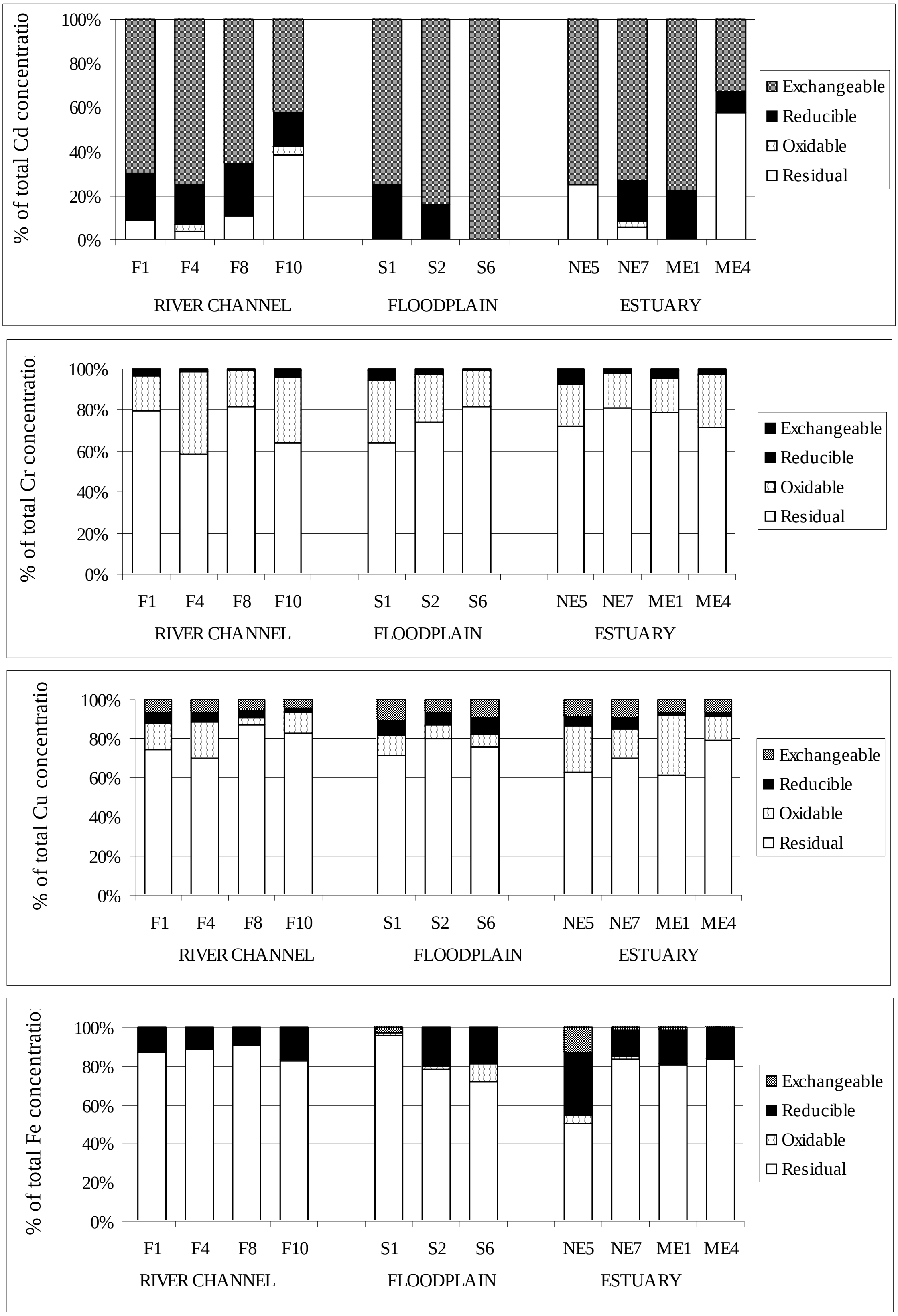

Figure 3 - Cd, Cu, Cr, and Fe speciation (% of total concentration) in surface sediments in the river channel, floodplain, and estuarine sampling sites of the lower basin of the Paraíba do Sul River.

fraction. It can imply a possible relationship between speciation and sediment grain size sorting. In the outer sampling site of the main branch of the estuary, the percentage in the exchangeable fraction drops considerably, and increases the residual fraction. The speciation pattern found for Cd is not atypical; high percentages of total Cd concentrations have been

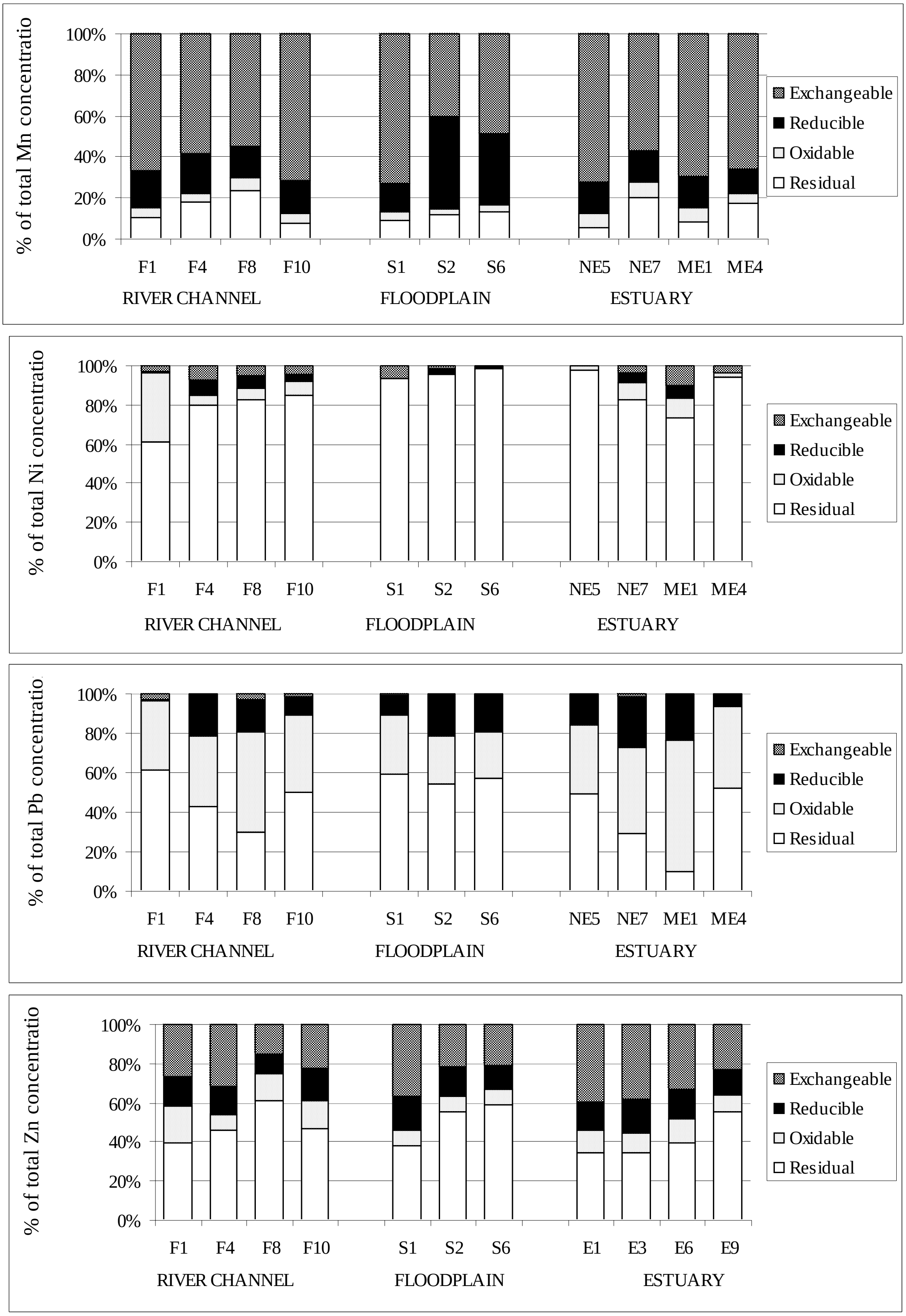

Figure 4 - Mn, Ni, Pb, and Zn speciation (% of total concentration) in surface sediments in the river channel, floodplain, and estuarine sampling sites of the lower basin of the Paraíba do Sul River.

found in exchangeable fraction by other studies (Morillo *et al*. 2002; Surija & Branica, 1995).

Despite the fact that the residual phase of Pb and Zn seems to be dominant these metals mostly occur in non-lithogenous fractions (55 and 54%, respectively) (Figure 4). However, these metals show a very different phase distribution between the samples from the river channel. In downstream sampling sites the residual Zn increases while for Pb the residual phase decreases with a simultaneous increase of oxidable fraction, indicating the association between Pb and organic matter along the river channel sediments. In the main branch of the estuary both metals show higher residual phase in outer sampling site.

Other metals found mostly in residual fraction are Cr, Cu, Fe, and Ni, which constitutes 74, 76, 82, and 87%, respectively, of the total concentration (Figure 3and 4). Although the residual fraction seems to be the most dominant, oxidable fraction is a noticeable phase for Cr (23%) and Cu (12%) speciation, while the reducible fraction comprises of 15% of the total Fe concentration. Despite the fact that Pb and Zn speciation mostly occurs in non-lithogenous fractions (53 and 52%, respectively), residual phase seems to be dominant, although oxidable (37%) and exchangeable (27%) are noticeable phases for Pb and Zn speciation, respectively.

Basically, the metal speciation in river channel, floodplain, and estuarine sediments shows similar distribution of chemical fractions of Cu, Zn, Fe, and Cr. Exchangeable Cd was found in greater values (86%) in floodplain than river channel (60%) and estuarine (63%) sediments. The same pattern can be described for reducible Mn, which was found to be present in higher proportions in floodplain sediments (33%) than river channel (15%) and estuary (16%). In contrast, oxidable Pb shows lesser concentration in floodplain sediments (26%) than river channel (40%) and estuarine sediment (47%).

It is now generally accepted that determining the total metal concentration is usually insufficient in order to fully assess implications of metal distribution in sediments (Ma & Rao, 1997). Sequential extraction partitioning was also used to complement the information obtained from the total metal concentration. Assessment of the speciation conducted on the downstream sediment samples shows the predominance of residual phase for Cr, Cu, Fe, Ni. These metals are bound to sediments in such a manner that they can be considered to be environmentally inert and thus can be taken as a measure of contribution by natural sources. Thus the assessment of total content of Cr, Cu, Fe, and Ni in sediments associated to their speciation allows us to conclude that concentrations of these metals are thought to have resulted from local sediment input with lower metal content while the influence from the middle river basin may be considered insignificant as well as industrial and urban activities along the lower river basin. Given the partitioning of these metals in chemically inactive form, it may be considered environmentally insignificant with respect to ecotoxicology and chemical mobilization within the lower Paraíba do Sul River basin.

On the contrary, metals such as Cd, Zn, and Pb were found mainly in the non-residual phases (exchangeable, reducible, and oxidable) along the lower river basin suggest that potential exist for the mobilization and thus a portion of these metals may became bioavailable accordingly to the environmental conditions. At the same time, the predominance of non-residual fraction of those metals suggests that changes in sediment-water characteristics such as redox, salinity and pH status might influence the partitioning of metals between water column, pore water and sediment in response of diagenetic reactions (Delaune and Smith, 1985; Shaw et al., 1990). Thus the effect of diagenetic processes should also be considering an important controlling factor of metal accumulation and distribution in sediments across the Lower Paraíba do Sul River watershed. Although the total metal distribution displayed distinct patterns along the lower river basin, the extent of total metal changing along the river channel and floodplain sites did not alter significantly the metal speciation, mostly relative to the labile and residual phase ratio. This geochemical scenario prevails along the lower Paraíba do Sul River up to the estuary, which also shows predominance of non-lithogenous fractions of Cd, Zn, Pb, and Mn (Figure 3 and 4). The dominance of the non-lithogenous phase of metals under influence of salinity in the estuarine zone might enhance their remobilization from sediments and thus increasing the time exposure for the uptake of biota. Salomons *et al*. (1988) showed that Cd is an example of metal sensitivity to desorption from suspended sediments due to salinity gradients. The influence of saltwater intrusion was observed until site ME1 (Figure 1) in dry season (Carneiro *et al.*, 1995), and thus predominance of the exchangeable Cd in estuarine sediments from Paraíba do Sul River suggests that the exchange of this element between the sediment and water column might take place easily.

CONCLUSION

Downstream metal distribution along the lower Paraíba do Sul River suggested that higher-metal content sediments from the middle basin have not extensively dispersed down metals such as Cr, Cu, Ni, and Fe to the lower river segment. However for Cd, Zn, and Pb the spatial distribution displayed a dilution pattern occurred yet within the lower river basin suggest that to a small extent the middle river basin sediment particles are reaching the studied area and dispersing these metals downstream. Although the absence of important anthropogenic sources reduce such concentrations along the lower river basin, increased concentration was observed in the urban river segment showing the importance of the large city of this stretch of the river as a source of Cd, Zn, and Pb to the river. The floodplain area and narrow branch of the estuary appear to be the zone, where major fine grain-size sediment accumulates along the lower river basin and thus important compartments for sediment-bound metal deposition. The sediments of lower river basin displayed a reduction of total metal concentration compared to the middle river basin, although sediments are potentially reactive on account of non-residual Cd, Zn, and Pb prevailing along the lower river basin and estuary.

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