

## Heavy Metals in Sediments of the Lower Paraíba do Sul River and Estuary, R.J., Brazil

M. M. Molisani,<sup>1</sup>M. S. M. B. Salomão,<sup>1</sup>A. R. C. Ovalle,<sup>1</sup>C. E. Rezende,<sup>1</sup>  
L. D. Lacerda,<sup>2</sup>C. E. V. Carvalho<sup>1</sup>

<sup>1</sup>Environmental Science Laboratory, CBB, North Fluminense State University, Av. Alberto Lamego, 2000, Horto, Campos dos Goytacazes, R.J., CEP: 28015-620, Brazil

<sup>2</sup>Geochemistry Department, Federal Fluminense University, Niterói, R.J. Brazil

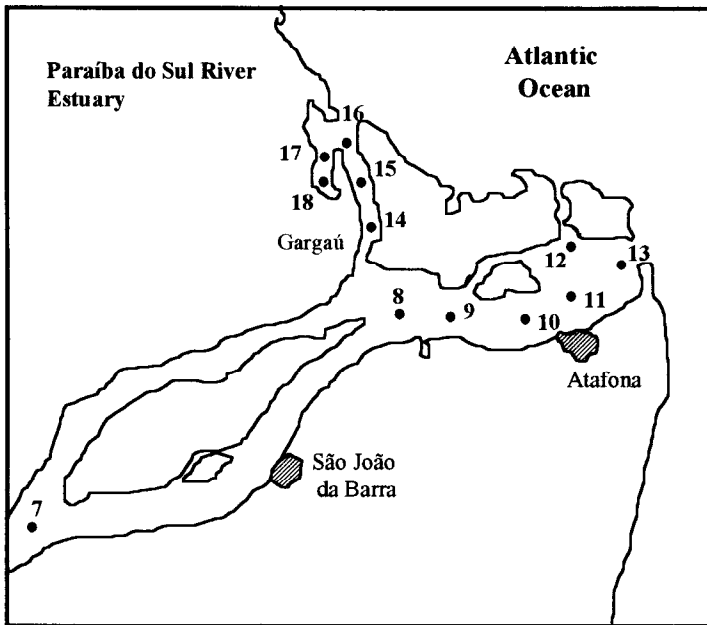
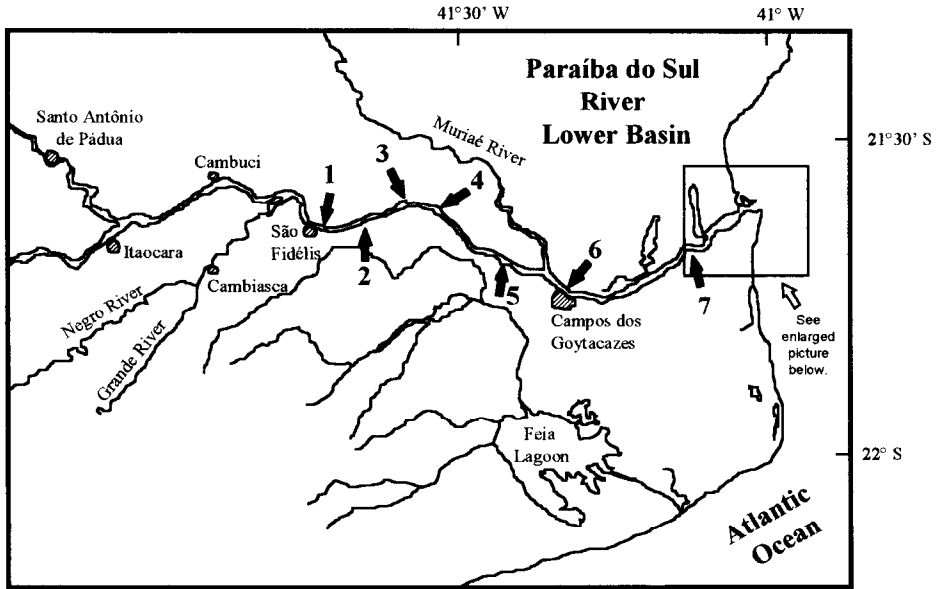
Received: 20 July 1999/Accepted: 9 September 1999

Heavy metals are introduced in aquatic environments by atmospheric deposition; intemperism and erosion of the geological matrix or through antropogenic sources (i.e. industrial effluents; mining wastes; etc). Their ecological importance is closely related to accumulation and toxicity, since these elements are not biodegradable (Nurberg, 1984).

The Paraíba do Sul River receives both industrial and domestic wastes, mostly without any treatment. According to previous studies performed in the mid - point portion of the river, as well as, in some of its tributaries (Paraibuna, Pomba and Muriaé Rivers), contamination by heavy metals has been reported. The main source of these pollutants are industrial effluents and urban wastes (Torres, 1992; Malm, 1986; Azcue, 1987) and gold mining activities in some tributaries (Pomba and Muriaé Rivers) (Souza, 1994). Although these pollution sources were identified, heavy metal concentrations observed in the continental shelf near the mouth of Paraíba do Sul River, showed little or no antropogenic influence, and could be considered without metal contamination (Carvalho, 1992; Lacerda *et al*, 1993). Therefore, the lower section of the Paraíba do Sul River may act as an efficient trap for heavy metals, decreasing their concentration in the coastal waters.

The Paraíba do Sul River has a drainage area of approximately 55.400 km<sup>2</sup> and it is 1.145 km long, crossing the most industrialized states of Brazil: São Paulo and Rio de Janeiro. In the northern region of Rio de Janeiro State the river crosses 120 km between Itaocara and São João da Barra Cities, at the coast. The main tributaries of this region are the Pomba, Muriaé and Dois Rios Rivers. In the Itaocara region, the geology is dominated by gneisses with a ripple relief. Below São Fidelis city the geology became dominated by fluvial quaternary deposits with a plane relief. The soil use is dominated by sugarcane plantations, agriculture, animal farming and urbanization (figure 1).

The Paraíba do Sul Estuary can be classified as an homogenous fresh water estuary during most months (medium and high water flow), but during the winter time, when the lowest water flow is observed (dry season), it is possible to observe the presence of a salt edge during flood tide. The estuary presents two main channels, the largest one is close Atafona City and the smaller in Gargaú (figure 1) where mangrove areas occur (8 km<sup>2</sup>, RADAMBRASIL, 1983).



**Figure 1.** Sampling sites location along the river and the estuary of the Paraiba do Sul River. Dashed areas are the main cities located at the river and estuary drainage.

The present study investigates the heavy metal distribution in bottom sediment of the Lower Paraíba do Sul River and Estuary, in order to characterize the behavior of these elements and locate possible accumulation zones.

## MATERIALS AND METHODS

The bottom sediment sample were collected during the dry season between July and August 1995. A total of 17 sampling sites were sampled (figure 1): seven points along Lower Paraíba do Sul River itself (between São Fidelis and São João da Barra cities); six points at the main channel of the estuary; three points at the secondary channel (Gargaú) and two stations in a mangrove tidal creek near Gargaú. In each station five surface sediment subsamples were collected and homogenized in order to better represent the sampling site (composite samples). All the samples were collected with the help of a plastic trowel and stored in plastic bags.

In order to obtain the grain size distribution, the bottom sediments were wet sieved in 2mm, 1mm, 212  $\mu$  125  $\mu$  and < 63 $\mu$  fractions. After sieving the fractions were oven dried (40°C) and weighed. The < 63 $\mu$ m fraction was separated to be used for heavy metal determinations.

The total heavy metal extraction used was a modification of the method used by Watts & Smith (1994). The sediments (< 63 $\mu$  fraction) were digested with hot concentrated acids (HF + HNO<sub>3</sub>, 1:1) in Teflon bombs at 100° C for 24 hours. After the total dissolution of the sample, the acid was evaporated to almost dryness, and the residue redissolved with HCl 0.5 M (30 ml).

The weakly-bound heavy metal fraction was determined in the sediment (< 63 $\mu$ ) following the described by Boniforti *et al* (1988). Two grams of sediment were mixed with 10 ml of HCl 0.5 M in a polietilene centrifuge flask and left shaking for 24 hours at room temperature. After this procedure, the flasks were centrifuged at 3000 rpm for 20 minutes, and the extract was analyzed by a conventional flame absorption spectrophotometer.

**Table 1.** Recovery percentage of the total metal concentration in the two standard materials (n = 3).

Standard Material	Cu	Cr	Zn	Mn	Fe
River Sediment* (NIST - 2704)	103 %	90%	91%	87%	86%
Estuarine Sediment* (NIST - 1646a)	95%	85%	105%	91%	90%

The coefficient of variation for triplicates of the same sample was generally less than 10 %, in the case of higher values another replicate was analyzed in order to check the obtained values. Two standard reference materials were analyzed in triplicate for all the studied metals in order to estimate the accuracy of the method used. The first one was a riverine sediment (Standard Material 2704) and the second one was an estuarine sediment (Standard Material 1646a) both supplied by the National Institute

of Standards & Technology (USA). Concentrations differed less than 5% for Cu and Zn and between 5 to 10% for Cr and from 10 to 15% for Mn and Fe relative to reference concentrations for all the studied metals (table 1).

## RESULTS AND DISCUSSION

The bottom sediment grain size distribution during the period of low discharge (table 2) showed the classical behavior for fluvial and estuarine zones previously described by several authors (Salomons and Förstner, 1984; Mudroch, 1986). The larger particles (212 $\mu$  -1mm), were mainly settled in the fluvial portion during this period. The smaller size particles are transported until they reach the estuarine zone where they are partially trapped (Kremiling, 1988) by distinct processes like flocculation (Gibbs, 1973); sedimentation caused by the decrease of river transport capacity and/or mechanic retention by mangrove roots, as in the PSR estuary.

**Table 2.** Average grain size distribution (%) at all sampling sites from the three different areas of the lower Paraíba do Sul River and estuary.

Grain size fractions	River (stations 1 to 7)	Estuary (stations 8 to 16)	Tidal Creek (stations 17 to 18)
< 63 $\mu$	3	17	50
63 - 125 $\mu$	5	10	6
125 - 215 $\mu$	5	15	4
212 $\mu$ - 1 mm	68	49	35
1 - 2 mm	14	7	4
> 2 mm	5	2	1

In general, all the studied metals presented similar behavior, with the exception of Cr. Higher concentrations were observed in the fluvial portion, where the main heavy metals sources are located, decreasing their concentrations toward the estuary, where the rich metal fluvial sediments are mixed with poor metal marine sediments. Chromium showed an increase in total concentrations toward the estuary (table 3). Weakly bound concentrations (table 4) were fairly constant along the river-estuary complex. Only Mn showed a marked decrease in weakly bound concentrations at the tidal creek. Here, other processes like desorption and adsorption can also take place in estuarine areas, causing changes in the heavy metal distribution in the sediments (Salomons and Förstner, 1984).

The total copper concentrations ranged from 38 to 91  $\mu\text{g.g}^{-1}$ , with small spatial variation (table 3). The highest Cu values were observed near the cities of Campos and São João da Barra (sampling sites 6 and 11, respectively). These higher concentrations are probably indicating the antropogenic influence caused by the input of untreated domestic sewage, as this element has a preferential association with organic matter (Hirner *et al*, 1990). The total Zn concentrations showed the highest values in the fluvial portion (244  $\mu\text{g.g}^{-1}$ ), with a sharp decrease toward the sea (126  $\mu\text{g.g}^{-1}$ ). This may indicate a strong dilution effect by marine sediments depleted from this metal in the estuary (table 3). This distribution is also observed for Cu and Zn in the weakly-bound fraction (table

4). In some sampling stations it was possible to observe some antropogenic influence, like Cu in station 6, near the city of Campos and station 11, near the city of São João da Barra, probably due to the domestic sewage input. Although the low concentrations observed for the weakly bound fraction of all metals is indicated, these elements do not offer risk to the environment or to human health.

**Table 3.** Total heavy metal distribution in bottom sediments of the Lower Paraíba do Sul River and estuary (n = 5 per station).

River	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe %
1	84	90	222	1029	10,4
2	65	93	202	1178	11,2
3	75	94	244	1005	11,6
4	64	87	195	871	10,8
5	69	97	240	729	11,4
6	91	85	215	792	10,6
7	67	95	239	933	10,7
Average	73	91	222	933	10.9
SD	10	4	18	141	0.4
Main Estuary	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe %
8	54	114	212	1021	11,4
9	59	75	185	879	9,0
10	62	77	166	881	8,8
11	87	100	197	880	9,5
12	59	88	190	860	9,2
13	54	87	202	850	9,6
Average	63	90	192	895	9.5
SD	11	13	15	57	0.9
Secondary Estuary	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe %
14	44	83	198	800	10,1
15	47	196	126	836	10,2
16	45	143	179	762	10,4
Average	45	140	167	799	10.3
SD	1	46	30	30	0.1
Tidal Creek	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe %
17	54	101	152	388	9,7
18	51	130	173	455	10,6
Average	52	115	162	421	101
SD	1	15	10	33	0.4

The total chromium distribution did not present a clear spatial variation in the fluvial portion, although in the estuary Cr concentrations were higher (up to 130  $\mu\text{g.g}^{-1}$ ) compared to lower river values (90  $\mu\text{g.g}^{-1}$ ). This increase is probably due to association of this metal with the dissolved organic matter, that generally controls its concentration and transport along the lower portion of the river. Gibbs (1973) observed in the Amazon and Yukon Rivers that organic particulate

matter and organic soluble compounds are the main Cr carrier along these rivers, after residues of the crystalline structure of minerals. With the increase in salinity, mainly observed in the smaller channel of the estuary, the Cr associated with the organic compounds is probably flocculating being deposited on bottom sediments, increasing the sediment concentration. Campbell & Yeats (1984) have already observed the same pattern of behavior for this metal in St. Lawrence Estuary. The weakly bound fraction presented the same trend strengthening the above mentioned processes.

**Table 4.** Weakly bound heavy metals concentration in bottom sediments of the lower Paraíba do Sul river and estuary (n = 5 per station).

River	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$
1	9	6	9	159	1554
2	9	7	10	135	1525
3	8	6	9	130	1747
4	9	7	9	159	1895
5	11	7	8	88	1776
6	20	6	7	72	1710
7	9	6	4	83	1236
Average	10	6	8	118	1634
SD	4	0.5	2	34	201
Main Estuary	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$
8	7	8	8	113	1545
9	8	7	6	104	1465
10	14	7	4	99	1201
11	19	9	7	114	1651
12	9	8	5	102	1418
13	8	10	6	61	1412
Average	11	8	6	99	1448
SD	4	1	1	18	138
Secondary Estuary	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$
14	7	9	6	104	1587
15	7	11	6	90	1615
16	5	4	3	84	1269
Average	6	8	5	93	1490
SD	1	3	1	8	156
Tidal Creek	Cu $\mu\text{g.g}^{-1}$	Cr $\mu\text{g.g}^{-1}$	Zn $\mu\text{g.g}^{-1}$	Mn $\mu\text{g.g}^{-1}$	Fe $\mu\text{g.g}^{-1}$
17	10	10	5	43	1210
18	14	10	6	55	1393
Average	12	10	6	33	1301
SD	2	0	0.5	6	91

The total manganese distribution showed the largest spatial variation ranging from 388 to 1,178  $\mu\text{g.g}^{-1}$ . The lowest concentrations (388  $\mu\text{g.g}^{-1}$ ) were observed in the mangrove area and are probably due to the highly anoxic condition of

these sediments. This anoxic conditions cause the dissolution of manganese oxides, the major form of Mn transported through the river. This release reduced  $Mn^{2+}$  into pore waters, which then migrate from the sediments to the water column decreasing the Mn sediment concentration (Salomons & Förstner, 1984, table 3). The weakly bound fraction followed the same pattern described above with a decrease toward the ocean and smallest values in tidal creek of mangrove area (table 4).

Total iron concentrations presented small spatial variation throughout the river, with values ranging from 10.5 to 11.5 %. The large amount of Fe present in these sediments makes it difficult to visualize any significant change in concentrations due to mixing processes. For the weakly bound fraction, Fe behaves like Mn, with highest concentrations ( $1,776 \mu\text{g.g}^{-1}$ ) at the river stations, and the lowest ( $1,210 \mu\text{g.g}^{-1}$ ) at the tidal creek and in the main channel ( $1,201 \mu\text{g.g}^{-1}$ ). Dissolution of Fe oxides and mobilization of reduced  $Fe^{2+}$ , as in the case of Mn, explain these results.

Table 5 compares the obtained results with global averages, polluted rivers, the medium portion of PSR and the adjacent continental shelf. Comparing our results with polluted rivers like the Rhine, Cu, Zn and Cr presented smaller concentrations, strengthening the hypothesis of low contamination. The high values observed for Fe are due to the geological matrix of the area that is enriched in iron oxides (10 to 15%, RADAMBRASIL, 1983). Our results also presented smallest concentrations for Cu, Zn and Cr when compared to the results of the medium PSR (Malm, 1986), probably indicating that these elements are being diluted in the lower portion by unpolluted sediments, and/or these rich metal particles are being trapped in preferential deposition sites along the river (Salomão *et al*, submitted).

**Table 5.** Comparison of the average total heavy metal concentrations found in sediments of the Paraíba do Sul River (PSR) with other areas.

	Cu ( $\mu\text{g.g}^{-1}$ )	Cr ( $\mu\text{g.g}^{-1}$ )	Zn ( $\mu\text{g.g}^{-1}$ )	Mn ( $\mu\text{g.g}^{-1}$ )	Fe (%)
Crust <sup>1</sup>	50	100	75	950	4,1
Average Shale <sup>1</sup>	45	90	95	850	4,7
Rhine River <sup>2</sup>	376	397	1096	750	3,7
PSR upper basin <sup>3</sup>	105	265	327	757	6,1
PSR lower basin <sup>4</sup>	74	91	222	951	11.1
PSR estuary and tidal creek <sup>4</sup>	53	115	174	705	10
PSR continental shelf <sup>5</sup>	29	84	147	876	6,2

1- Salomons & Förstner, 1984; 2 - Förstner & Wittmann, 1983; 3 - Malm, 1986; 4 - Present study; 5 - Carvalho (1992).

The weakly bound fraction of all analyzed metals were also smaller than in the medium PSR. According to Azcue (1987) the PSR medium portion (PSR - Guandú River System), receives high antropogenic influence, presenting the following weakly bound percentage: Cu: 70% ; Cr: 45% ; Zn: 70% ; Mn: 70% ; Fe: 20%, and our results showed only: Cu: 17% ; Cr: 7% ; Zn: 3% ; Mn: 11% ;

Fe: 1.5%. Although the methodologies used in both studies were different, this behavior strengthens the low contamination of the sediments of this region and also the low risk for the environment and human health. However, they suggest that a significant amount of heavy metals are being trapped in the river.

The results showed that, with exception of Cr, all metals presented the same distribution pattern, with higher concentrations in the fluvial portion, decreasing toward the estuary of the river. Comparing the obtained values with the upper basin of the PSR, under higher antropogenic influence, a decrease of some metals concentration was observed, mainly in the weakly bound fraction. This and the absence of large metal pollution sources, results in the observed decrease of heavy metals concentration in the lower basin and estuary, and also explains the lower heavy metals concentrations found by Carvalho (1992) in the adjacent continental shelf sediments.

*Acknowledgments.* We thank our technicians, Arizoli A.R. Gobo, Cristina B. Siqueira and Rodrigo R. Tugores for help in the laboratory, and our technician Antonio C.O. Pessanha for his help during the sampling. We also thank FENORTE and FAPERJ for financial support.

## REFERENCES

- Azure JMP (1987) Possíveis vias de acesso de metais pesados provenientes do sistema hídrico Rio Paraíba do Sul - Rio Guandú, RJ, até o homem. M.Sc. Thesis, IBCCF, UFRJ, p 179
- Boniforti R, Bacciola D, Niccolai I, Ruggiero R (1988) Selective extraction as an estimate o bioavailability of As, Cd, Co, Cr, Fe, Mn, Ni, Pb and Zn in marine sediments collected from the Central Adriatic Sea. *Environ Tech Let* 9: 117-126
- Campbell JA, Yeats PA (1984) Dissolved chromium in the St. Lawrence estuary. *Est Coast Shelf Sci* 19: 513-522.
- Carvalho CEV (1992) Distribuição de metais pesados na plataforma continental Nordeste e Sudeste do Brasil. M.Sc. Thesis, Depto de Geoquímica, UFF, p 91
- Föstner U, Wittmann,GTW (1983) Metal pollution in aquatic environment. Springer-Verlag, Berlin, p 486
- Gibbs RJ (1973) Mechanisms of trace metals transport in rivers. *Science* 180: 71-73
- Hirner AV, Kristotakis K, Tobschall HJ (1990) Metal - organic association in sediments - I. Comparison of unpolluted recent and ancient sediments and sediments affected by antropogenic pollution. *Appl Geochem* 5: 491-505
- Kremiling K (1988) Metal cycles in coastal environments. In: *Metals in Coastal Environments of Latin America*. Seeliger U, Lacerda LD, Patchineelam SR (eds) Springer-Verlag, New York, 198-214
- Lacerda LD, Carvalho CEV, Rezende CE, Pfeiffer WC (1993) Mercury in sediments from the Paraíba do Sul River Continental Shelf, S.E. Brazil. *Mar Poll Bull* 23:107-116



- Malm O (1986) Estudo da poluição ambiental por metais pesados no sistema Rio Paraíba do Sul-Rio Guandú (RPS-RG) através da metodologia de abordagem pelos parâmetros críticos. M.Sc. Thesis, IBCCF, UFRJ, p 127
- Mudroch A, Duncan GA (1986) Distribution of metals in different size fractions of sediments from the Niagara River. *J Great Lakes Res* 12:117-126.
- Nurberg HW (1984) The voltammetric approach in the trace metals chemistry of natural waters and atmospheric precipitation. *Anal Chim acta* 164:1-21
- Projeto Radambrasil (1983) Folhas SF.23/24 Rio de Janeiro/Vitória; geologia, geomorfologia, pedologia, vegetação e uso potencial da terra. Rio de Janeiro, p 780
- Salomons W, Föstner U (1984) Metals in the hydrocycle. Springer - Verlag, Berlin, p 349
- Torres JPM (1992) Ocorrência e distribuição de metais pesados no Rio Paraíba, Juiz de Fora, M.G. M.Sc. Thesis, IBCCF, UFRJ, 114
- Salomão MSMB, Molisani MM, Ovalle ARC, Rezende CE, Lacerda LD, Carvalho CEV (submitted) Particulate heavy metal dynamic and mass balance in the lower Paraíba do Sul River Watershed, RJ, BRAZIL. *Hydrol Process*
- Souza CMM (1994) Avaliação ambiental dos riscos do mercúrio, em áreas de garimpo no Brasil. Ph.D. Thesis, IBCCF, UFRJ, p 127
- Watts SEJ, Smith, BJ (1994) The contribution of highway runoff to river sediment and implications for the impounding of urban estuaries, a case study of Belfast. *The Science of Total Environment* 146/147: 507-514