

Particulate Heavy Metal Dynamics in a Tropical Estuary Under Distinct River Discharge and Tidal Regimes, Southeastern, Brazil.

G. M. Gonçalves and C. E. V. Carvalho

Laboratório de Ciências Ambientais, C.B.B.

Universidade Estadual do Norte Fluminense, Campos dos Goytacazes,

RJ, 28013-602, Brazil

carvalho@uenf.br



ABSTRACT

GONÇALVES, G.M. and CARVALHO, C. E. V., 2006. Particulate heavy metal dynamics in a Tropical Estuary Under Distinct River Discharge and Tidal Regimes, Southeastern, Brazil. *Journal of Coastal Research*, SI 39 (Proceedings of the 8th International Coastal Symposium), 1032 - 1035. Itajaí, SC, Brazil, ISSN 0749-0208.

The aim of the present study is to understand the particulate heavy metal behavior in distinct tidal regimes (neap and spring tides) and river discharges (dry and rainy season). The average heavy metal concentration observed in the present study are in accordance with previous works developed in the lower Paraíba do Sul Basin, as well as with the world average. The only exception was Zn that presented higher values in the present study. Aluminum and iron presented higher average concentrations during the high riverine discharge periods; the other studied metals (Mn and Zn) presented an opposite trend with higher concentrations during the low discharge period. The Al and Fe behavior is related to the increase in the surface runoff during the rainy season, due to the soils of the drainage basin being enriched in these elements. The behavior of the other studied metals are probably related to a different source (industrial and urban wastes) and the dilution effect caused by the raise of the river discharge and the input of a suspended particulate matter (from the lower drainage basin) impoverished in these elements. During the low discharge period the average metal concentrations were generally higher during the neap tide sampling, when compared with the spring tide sampling. In the high discharge period no statistical difference could be observed between the distinct tidal regimes, this trend is probably related to the stronger riverine influence inside the PSR Estuary during the higher discharge period.

ADDITIONAL INDEX WORDS: *Pollution, coastal areas, South America.*

INTRODUCTION

Suspended particulate matter is represented by a wide combination of inorganic material (i.e. clay minerals; Fe and Mn oxo-hydroxides) and organic matter (detritic or alive). These particles, due to their high surface area and also for the carrier nature of oxides, are the main heavy metals carriers in aquatic systems (JENNE, 1968; WARREN and ZIMMERMAN, 1993), playing an important role in the metal transport from the continents to coastal areas (SALOMONS and FORSTNER, 1984).

In estuaries metal concentration in suspended particulate matter is generally orders of magnitude higher than in the dissolved form (BALLS, 1989; COMBER, *et al.*, 1995) and so the fate of these elements are very close related to the SPM internal cycle. The composition and variability of the SPM in estuaries are affected by many complex geochemical processes (e.g. precipitation and flocculation, desorption-adsorption) and by physical processes (e.g. river flow, tidal energy, currents) (OWENS, *et al.*, 1997; HERUT and KRESS, 1997).

Estuaries are a transition zone between continental derived materials can act as a "geochemical reactor" changing the chemical forms (CHIFFOLEAU, *et al.*, 1994) of continental derived trace metals. The role of an estuarine system in the transformation and exportation of metals to coastal areas will depend upon several intrinsic characteristics of each estuary.

STUDY AREA

The Paraíba do Sul River (PSR) is a medium-sized river with 1,145 km long and a drainage basin of 55,400 km². It crosses three of the most important and developed states of Brazil (Minas Gerais; São Paulo and Rio de Janeiro). It is the main water supply for more than 11 million people only at Rio de Janeiro City, but it is also used as waste disposal for a very large number of industries along its course (Figure 1).

The Paraíba do Sul estuary is located at a coastal plain formed by the Paraíba do Sul River Delta in the north of the Rio de Janeiro State, near the City of São João da Barra (21° 36' S and 41° 05' W). The hydrological regime is relatively regular, following the standard tropical pluviometric distribution, with

higher discharges during summer (November to January) and lower discharges during winter (June to August). The average discharges during the rainy season range from 700 to 1,300 m³.s⁻¹ and during the dry period from 400 to 500 m³.s⁻¹. The tidal regime is semi-diurnal with micro tides (CARNEIRO, 1998).

Previous work performed at the middle reaches of the PSR, as well as in some of its tributaries (Paraibuna, Pomba Muriaé and Rivers, Figure. 1), indicated that those rivers are contaminated by heavy metals. The main sources of these pollutants are the industrial activity, urban wastes particularly as major sources of Zn, Pb, Cu, Cr, (TORRES 1992; MALM 1986 and AZCUE, 1987) and gold mining activities, a significant source of Hg to the PSR lower basin, up to the late 1980's (LACERDA *et al.*, 1993 and SOUZA, 1994).

Although several studies dealt with heavy metal distribution, behaviour and fate in the Paraíba do Sul River (MALM, 1986; TORRES, 1992; CARVALHO *et al.*, 1999; MOLISANI, *et al.*, 1999; SALOMÃO, *et al.*, 2001; CARVALHO, *et al.*, 2002) no studies evaluate the role of the PSR estuary in the transformation and transport of these pollutants to the coastal environments. The objective of the present study is to understand the particulate heavy metal behavior in distinct tidal regimes (neap and spring tides) and river discharges (dry and rainy season).

METHODS

Four tidal cycles, one during neap tide and another during spring tide at October 19 and 25, 2000 (dry season) and February 17 and 24, 2001 (rainy season) were analysed. In each survey water samples were taken (surface and bottom), physico-chemical parameters were measured (pH, conductivity, temperature, dissolved oxygen) every hour. Current velocity and direction with an acoustic doppler current profiler was also recorded, as well as water level and vertical profiles of salinity and temperature.

Water samples were collected by a "Van Dorn" sampler and stored in polyethylene flasks, which were kept in ice during the transport for the laboratory. In the laboratory the samples were filtered in duplicate (Millipore cellulose acetate 0.45 µm of pore diameter), and oven-dried (80°C/48h).

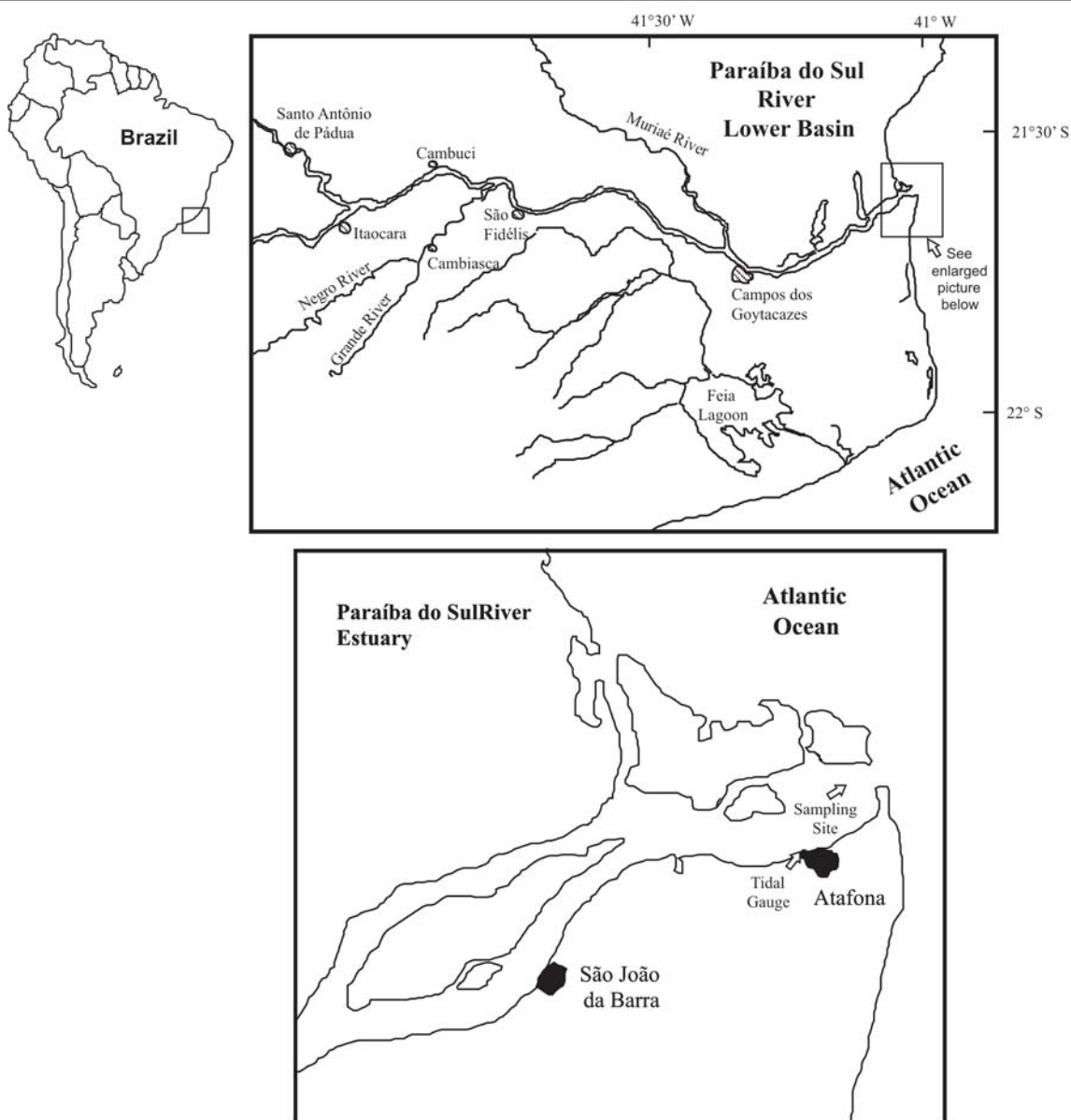


Figure 1. Sampling site location

The filters digestion methodology followed a modified version of the procedure used by WATTS and SMITH (1994). The filters were placed in Teflon bombs, with concentrated acids (HNO₃ + HF) in oven (100°C / 12h), after the digestion of the sample, the acid was evaporated to almost dryness, and redissolved with HNO₃ 0,5N (20 ml). The extracts were then analyzed by atomic emission spectrophotometry with induced coupled plasma (ICP/AES, Varian, Liberty II).

RESULTS AND DISCUSSION

Surface samples presented higher average heavy metal concentrations when compared with bottom samples for all the studied metals (Fe; Al; Mn and Zn), the only exception was the third sampling when an opposite trend was observed. Aluminum was the most abundant element followed by Fe, Mn and Zn (Table 1).

Aluminum and iron presented its higher average concentrations in the February sampling (rainy season) when the river presented higher river discharge, an opposite trend was observed for manganese that presented higher concentrations in the October sampling (dry season) when the river discharge was lower. This behavior had already been described by CARVALHO *et al.* (1999) for the lower Paraíba do Sul River drainage basin. According to the above mention author the higher Al and Fe

concentrations observed during the high discharge periods are probably due to the strong association of these metals with surface runoff, their origin are the regional soils rich in iron oxides. The opposite trend observed for Mn and Zn is probably reflecting the importance of the industrial and urban effluents as a secondary source of this element. Its behavior is probably associated with the dilution effect caused by the input of a suspended matter from surface runoff poor in this element during the rainy season.

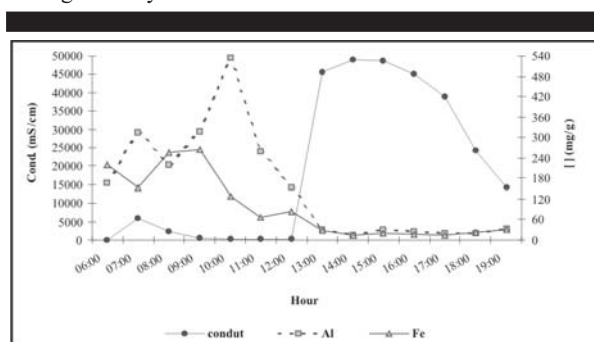


Figure 2. Aluminum, iron (mg.g⁻¹) concentrations in suspended particulate matter and electric conductivity (µS/cm) distribution along time in bottom samples from February 24th.

Table 1. Average heavy metal concentration in suspended particulate matter (mg.g^{-1}).

Date	Depth	Al	Fe	Mn	Zn
19/10/00	Surface	103.4	53.6	2.33	0.25
	Bottom	81.3	49.3	1.56	0.01
25/10/00	Surface	82.1	42.6	1.26	0.63
	Bottom	60.8	42.2	0.94	0.25
17/02/01	Surface	115.7	78.9	1.02	n.d.
	Bottom	168.9	111.7	1.34	n.d.
24/02/01	Surface	174.0	100.1	0.85	n.d.
	Bottom	152.8	94.5	0.70	n.d.

An inverse relation was observed between electric conductivity and heavy metal concentration for both sampling depths in all sampling periods (Figure 2). The only exception was the February 17th sampling (neap tide during rainy season) where no temporal variation in conductivity was observed, suggesting the predominance of riverine derived waters. This trend was already expected and are mainly due to: 1) dilution of the heavy metal enriched riverine waters by depleted coastal waters; 2) riverine particulate matter deposition due to the loss of the river transport capacity and 3) desorption and adsorption processes due to changes in physicochemical parameters (SALOMONS and FÖRSTNER, 1984).

The average heavy metal concentration observed in the present study are in accordance with previous works developed in the lower Paraíba do Sul Drainage Basin (CARVALHO *et al.*, 1999; SALOMÃO, 1999), as well as with the world average (MARTIN and MEYBECK, 1979) (Table 2).

CONCLUSION

Seasonal differences on heavy metal concentrations in suspended particulate matter were observed, with the same trend previously observed for the lower Paraíba do Sul River Basin. Differences on the average metal concentration between dry and rainy season for neap tides for all the studied metals were observed. There were also differences on the average metal concentration between neap and spring tides for all the studied metals only at the dry season. The only exception was the February 17th sampling (neap tide during rainy season) where no temporal variation in conductivity and heavy metal distribution was observed, suggesting the predominance of riverine derived waters.

ACKNOWLEDGEMENTS

The authors would like to thank FENORTE, FAPERJ (CEVC Proc.n° E26-170.368/1999; ALSME26-150.566/2000) and CNPq (TMTM Proc.n° 103415/00-9) for the financial. The authors also would like to thank M.Sc. Wanderson Primo de Souza for helping during the samplings.

LITERATURE CITED

- AZCUE, J.M.P., 1987. Possíveis vias de acesso de metais pesados provenientes do sistema hídrico Rio Paraíba do Sul-Rio Guandú, RJ, até o homem. Brazil: Rio de Janeiro Federal University. Master's thesis, 179 p.
- AZCUE, J.M.P., 1987. Possíveis vias de acesso de metais pesados provenientes do sistema hídrico Rio Paraíba do Sul-Rio Guandú, RJ, até o homem. Brazil: Rio de Janeiro Federal University. Master's thesis, 179 p.
- BALLS, P.W., 1989. The partitioning of trace metals between dissolved and particulate phases in European coastal waters. A compilation of field data and comparison with laboratory studies. Netherlands Journal of Sea Research, Issue No. 23, pp. 7 - 14.

Table 2. Average heavy metal concentration in the present study compared with other studies ($\mu\text{g.g}^{-1}$).

	Al	Fe	Mn	Zn
PSR River (a)	-	75,451	2,473	249
PSR River (b)	74,000	47,000	1,120	135
PSR Estuary (c)	117,189	71,615	1,250	143
Global average (d)	91,000	48,000	1,050	350

(a) CARVALHO *et al.* (1999); (b) SALOMÃO (1999); (c) present study; (d) MARTIN and MEYBECK (1979).

- CARVALHO, C.E.V.; OVALLE, A.R.C.; REZENDE, C.E.; MOLISANI, M.M.; SALOMÃO, M.S.M.B. and LACERDA, L.D., 1999. Seasonal variation of particulate heavy metals in the lower Paraíba do Sul River, R.J., Brazil. *Environmental Geology*, 37 (4): 297-302.
- CARVALHO, C.E.V.; SALOMÃO, M.S.M.B.; MOLISANI, M.M.; REZENDE, C.E. and LACERDA, L.D., 2002. Contribution of a Medium-Sized Tropical River to the Particulate Heavy Metal Load for the South Atlantic Ocean. *The Science of the Total Environment*, 284(1-3): 85-93.
- CARNEIRO, M.E.R., 1998. Origem, transporte e destino da matéria orgânica no estuário do rio Paraíba do Sul. Brazil: Federal University of Niterói, Ph.D. thesis, 210p.
- CHIFFOLEAU, J.F.; COSSA, D.; AUGER, D. and TRUQUET, I., 1994. Trace metal distribution, partitioning and fluxes in the Seine estuary (France) in low discharge regime. *Marine Chemistry*, 47:145-158.
- COMBER, S.D.W.; GUNN, A.M. and WHALLEY, C., 1995. Comparison of the partitioning of trace metals in the Humber and Mersey Estuaries. *Marine Pollution Bulletin*, 30:851-860.
- HERUT, B. and KRESS, N., 1997. Particulate metals contamination in the Kishon river estuary, Israel. *Marine Pollution Bulletin*, 34(9): 706-711.
- JENNE, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soil and water: the significant role of hydrous Mn- and Fe-oxides. *American Chemistry Society Advanced Chemistry Series* 73, 337-387.
- LACERDA, L.D.; CARVALHO, C.E.V.; REZENDE, C.E. and PFEIFFER, W.C. 1993. Mercury in Sediments from the Paraíba do Sul Continental Shelf, SE-Brazil. *Marine Pollution Bulletin*, vol. 26 (4): 220-222.
- 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. Brazil, Rio de Janeiro Federal University. Master's thesis, 127 p.
- MARTIN, J.M. and MEYBECK, M., 1979. Elemental mass-balance of material carried by major world rivers. *Marine Chemistry*, 7: 173-206.
- MOLISANI, M.M.; OVALLE, A.R.C.; REZENDE, C.E.; SALOMÃO, M.S.M.B.; LACERDA, L.D. and CARVALHO, C.E.V., 1999. Heavy Metals Distribution in Sediments of the Lower Paraíba do Sul River and Estuary - R.J., Brazil. *Bulletin of Environmental Contamination and Toxicology*, 63 (5): 682-690.
- OWENS, R.E.; BALLS, P.W. and PRICE, N.B., 1997. Physicochemical processes and their effects on the composition of suspended particulate material in estuaries: Implications for monitoring and modeling. *Marine Pollution Bulletin*, 34(1):51-60.
- SALOMÃO, M.S.M.B., 1999. Dinâmica de metais pesados nas frações particulada e dissolvida na porção inferior do Rio Paraíba do Sul, RJ. MSc Thesis, Universidade Estadual do Norte Fluminense, Horto, Campos dos Goytacazes, RJ, Brazil.
- SALOMÃO, M.S.M.B.; MOLISANI, M.M.; OVALLE, A.R.C.; REZENDE, C.E.; LACERDA, L.D. and CARVALHO, C.E.V., 2001. Particulate Heavy Metals Transport in The Lower Paraíba do Sul River Basin, SE, Brazil. *Hydrological Processes*, 15(4): 587-593.

- SALOMONS, W. and FÖRSTNER, U., 1984. Metals in the Hydrocycle. Springer Verlag, 349p
- SOUZA, C.M.M., 1994. Avaliação ambiental dos riscos do mercúrio, em áreas de garimpo no Brasil. Ph.D.Thesis, IBCCF, UFRJ. 127p.
- TORRES, J.P.M., 1992. Ocorrência e distribuição de metais pesados no Rio Paraíba, Juiz de Fora, M.G. M.Sc. Thesis, IBCCF, UFRJ. 114p.
- WAREN, L.A. and ZIMMERMAN, A.P., 1993. Trace metal/SPM associations in a fluvial system: physical and chemical influences. In *Particulate matter and aquatic contaminants*, ed. Rao, S.S. Lewis Publishers, 425 p.
- WATTS, S.E.J. and SMITH, B.J., 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.