Journal of Radioanalytical and Nuclear Chemistry, Vol. 269, No.3 (2006) 707–709

Metal concentrations in surface sediments of Paraíba do Sul River (Brazil)

M. O. Pereira,[1] C. Calza,[1] M. J. Anjos,[1,2]* R. T. Lopes,[1] F. G. Araújo[3]

[1] *Nuclear Instrumentation Laboratory, COPPE/UFRJ, P.O. Box 68509, Rio de Janeiro, Brazil*
[2] *Physics Institute, UERJ, Rio de Janeiro Brazil*
[3] *Fish Ecology Laboratory, UFRRJ, Rio de Janeiro, Brazil*

(Received April 6, 2006)

The Paraíba do Sul River is located in a strategic region between the most important urban and industrial centers of Brazil. In the last years, an increase in the water pollution has been reported, caused by the untreated domestic sewerage of the inhabitants, effluents discharged by various industries, mining activities and sand extraction from the riverbed. This work used total reflection X-ray fluorescence with synchrotron radiation (SRTXRF) to determine metals in the bioavailable and residual fractions from the surface sediments. The metals identified were Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Ba and Pb.

Introduction

The pollution of aquatic ecosystems became matter of concern in the last years, not only for economic reasons, but also for the potential risk to the human health because of the consumption of contaminated water and fishes. Metals are introduced into the aquatic systems as a result of the weathering of rocks and soils, for example, from volcanic eruptions, through periodic precipitation contaminated with airborne pollutants and also from several human activities including mining operations and metallurgical activities, fuel emissions, agricultural proceedings, and industrialization (accidental leaks and discharges of industrial effluents) domestic sewerage, dumping wastes and others.[1,2]

The Paraíba do Sul is a medium-sized river located in a region between the two most important urban and industrial centers of Brazil, Rio de Janeiro and São Paulo, with 1145 km in length and a drainage basin of 55400 km^2. Formed by the junction of the Paraibuna and Paraitinga rivers, it arises in Serra da Bocaina (São Paulo state) and flows to the Atlantic Ocean until its mouth in Atafona (Rio de Janeiro state), as seen in Fig. 1. The increase of water pollution has been caused by the untreated domestic sewerage of the inhabitants, effluents discharged by various industries (including metallurgical, chemical, sugar cane industry), mining activities and sand extraction from the riverbed. Consequently, a decline in the diversity and abundance of the fish species has been observed.[3]

Sediments constitute the most important reservoir or sink of metals and other pollutants in the aquatic environment. Fishes with bottom dwelling habits are indirect exposed to contaminated sediments when feed on benthic invertebrates such as chironomids and tubificid worms, which ingest particulate matter. Direct exposure via the sediment can take place by resuspension of the contaminated particulate matter into the water column by both natural and anthropogenic disturbances, which can result in metal remobilization.[4,5] The evaluation of total metal concentrations only provides information of metal enrichment of the sediment, but not direct information on the biological effects of the metals, since effects will only occur if metals are or become available for biota. Metal bioavailability is related to binding phases in sediment, which have a tendency to reduce not only metal bioavailability but also mobility and, therefore, their toxicity. Metal binding processes can be affected by pH, alkalinity, hardness, redox potential, organic content, as well as other chemical characteristics of the river.[6,7]

This work used the total reflection X-ray fluorescence with synchrotron radiation (SRTXRF) technique to determine metal levels in the bioavailable and residual fractions from the surface sediment, in sampling points along the Paraíba do Sul River basin. In the bioavailable fraction the metals, weakly bound to the sediment geological matrix, which present risk to human health, and the metals in the residual fraction that constitute the geological structure of sediment were determined.

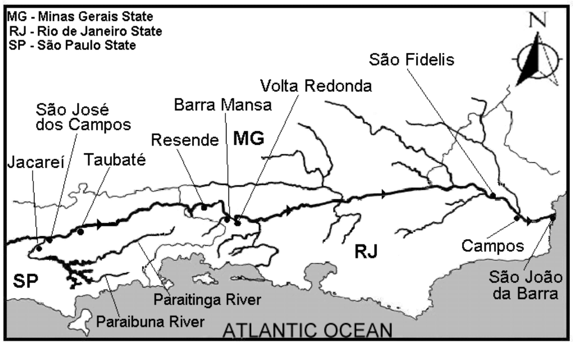

Fig. 1. Paraíba do Sul River basin and sampling site locations

---

* E-mail: marcelin@lin.ufrj.br

0236–5731/USD 20.00

Akadémiai Kiadó, Budapest
Springer, Dordrecht

Experimental

The samples were collected in four distinct areas of the Paraíba do Sul River, beginning at the riverhead until the mouth, from November 2002 to April 2003. Sediment samples were dried at 60 °C during 24 hours, homogenized and sieved using a 200 mesh sieve, to perform the bioavailable fraction analysis. Portions of 2.5 g of sieved sediment were digested with 7.5 ml of 0.1N HCl, during 16 hours, at room temperature. Afterwards, the solution was filtered. For the residual fraction analysis, dried sediment was sieved, using a 375 mesh (45 µm) sieve. 200 mg were digested with 2 ml of aqua regia during 16 hours at room temperature. The solution was heated to 80 °C for 2 hours, and at room temperature (25 °C) was diluted to 5 ml with Milli-Q water. Aliquots (450 µl) of resultant solutions, from bioavailable and residual fractions, were extracted with a micropipette and added to 50 µl of a selenium standard solution. Finally, 10 µl of each final solution were deposited on the sample carriers of Lucite, and the droplets were dried using an infrared lamp. The analysis by SRTXRF was performed at XRF beamline of the Brazilian Synchrotron Light Laboratory (LNLS), using a white beam for the excitation and a Si(Li) semiconductor detector with resolution of 165 eV. All samples were excited for 100 seconds. Accuracy of the SRTXRF technique and adequacy of the sample preparation method were tested with a reference material, MURST-ISS-A1 (Antarctic Sediment) that presented certified values for sediment residual fraction.

Results and discussion

The elements identified were Ti, Cr, Mn, Fe, Cu, Zn, Rb, Sr, Ba and Pb. The minimum detection limits (MDL) range from 4 $ng \cdot g^{-1}$ for Cu to 10 $ng \cdot g^{-1}$ for Sr. The accuracy and validity of the measurements were determined by analysis of a reference material (MURST-ISS-A1). The results varied from 3.4% (iron) to 9.9% (lead), agreeing well with the certified values.

This work used an international criterion for sediment contamination[8] to analyze the results of the residual fraction. According to this criterion, the classification of contamination effects involves three levels: Lowest Effect Level (LEL) for concentrations around a minimum settled limit; Moderated Effect Level (MEL) for concentrations between the maximum LEL limit and the minimum SEL limit; and Severe Effect Level (SEL) for concentrations higher than the maximum MEL limit. Sediment is contaminated if any criterion was exceeded. In the case of all criteria were exceeded, the contamination level is considered as severe. If only LEL was exceeded, the contamination level is moderated. Table 1 shows the metal concentrations in the sampling regions compared to the LEL and SEL settled limits.

Analyzing the results, it was observed that in the riverhead all metals showed moderate effects, excepting Mn that presented severely impacted effect in the region of Bocaina River. This result was expected due to the characteristics of the analyzed area, including low demographic density and absence of large industries.

In the middle upper flow, the concentrations of Mn and Zn exhibited severe effect in the region of São José dos Campos (São Paulo state). This region shows large industrial complexes and urban concentrations that contribute with daily discharges of untreated domestic sewerage of the inhabitants and industrial effluents in the river basin.

With the exception of Fe, which presented severe effect in the region of Volta Redonda (Rio de Janeiro state), all metals showed moderated effect in the middle lower flow. The region of Volta Redonda also shows a heavily industrialized area, mainly chemical and metallurgical industries, and a high urban concentration established alongside of the river. Finally, in the lower flow the concentrations of Fe and Mn showed severe effects in the region of Pomba River. High concentration levels of Fe were expected because of its natural occurrence in the Paraíba do Sul River Basin. In addiction, an enrichment of this metal can be seen downstream from the most heavily industrialized area, mainly in the region of Volta Redonda. The regions of São José dos Campos and Volta Redonda exhibited the highest metal concentration levels in this work. High levels were also observed in a study with muscle, gonads and gills of fishes, in the same sampling points, along the Paraíba do Sul River basin.[9] These results are due to daily discharges of untreated domestic and industrial effluents in these regions. However, the fish tissues showed very high Cr concentrations and, in this work, Cr was found only in the residual fraction of the sediment with concentration levels below the settled limits.

In Table 2, the metal concentrations found in sediments were compared to some values reported in the literature.

Table 1. Average (mean ± SD) and range values for metal concentrations (in $\mu g \cdot g^{-1}$, except for Fe in %) in the study areas compared to Lowest Effect Level (LEL) and Severe Effect Level (SEL) limits

Metal	LEL	SEL	Riverhead[a]	Middle higher[b]	Middle lower[c]	Lower[d]
Cr	26	110	27 ± 2 14 – 40	26 ± 2 15 – 37	39 ± 2 11 – 57	46 ± 3 35 – 79
Mn	460	1100	664 ± 18 14—2374	849 ± 18 355 – 1718	506 ± 19 33 – 794	692 ± 23 75 – 1324
Fe, %	2	4	2.6 ± 0.1 1.3—3.7	2.3 ± 0.1 1.3 – 3.3	3.2 ± 0.1 2.0 – 4.2	3.4 ± 0.1 2.4 – 4.3
Zn	120	270	88 ± 2 44—204	124 ± 6 55 – 423	101 ± 2 79 – 140	113 ± 3 54 – 264
Cu	16	110	21 ± 1 1—58	3 ± 1 1 – 8	10 ± 1 4.7 – 18.2	10 ± 1 4.4 – 20.0
Pb	31	110	51 ± 3 20—90	36 ± 2 7 – 99	26 ± 3 22 – 29	25 ± 1 11 – 80

The sampling areas include the following regions:

[a] Paraibuna, Paraitinga and Bocaina Rivers;

[b] São José dos Campos, Taubaté, Jacareí and Guaratinguetá;

[c] Barra Mansa, Volta Redonda and Além Paraíba;

[d] São Fidélis, São João da Barra, Campos, Italva and Pomba River.

Table 2. Metal concentrations (in $\mu g \cdot g^{-1}$, except for Fe in %) found in this work compared to the literature

Reference	Cr	Mn	Fe, %	Cu	Zn	Pb
10	15 – 270	–	–	14 – 69	37 – 122	9 – 60
11	63 – 84	0.02 – 0.11	1.8 – 6.2	15 – 29	63 – 147	–
12	75 – 196	388 – 1178	8.7 – 13	38 – 91	126 – 244	–
13	18.2 – 54.2	–	–	13.3 – 45.5	53.4 – 417.6	12.4 – 43.1
14	18.3 – 85.4	–	–	26.8 – 69.6	238 – 1220	169 – 1529
15	118 – 233	355 – 1159	4.5 – 5.2	45.2 – 179.9	127 – 519	39.3 – 71.8
16	18 – 126	305 – 1276	1.9 – 9.1	11 – 347	70 – 591	42 – 371
This work	11 – 79	14 – 2374	1.3 – 4.3	1 – 58	44 – 423	7 – 99

Conclusions

Comparing the results of sediment analysis to the international criterion, most metals exhibited moderated effect levels. However, there are sampling points where the metal concentrations reached severe effect levels: Mn at the Bocaina River; Mn and Zn at the region of São José dos Campos; Fe at Volta Redonda; Fe and Mn at the Pomba River. The highest levels were found at the regions of São José dos Campos and Volta Redonda, probably because of daily discharges of untreated industrial and domestic effluents.

*

This work was developed partially at Brazilian National Synchrotron Light Laboratory (LNLS) and had the financial support of CNPq.

References

1. M. H. Al-Yousuf, M. S. El-Shahawi, S. M. Al-Ghais, Sci. Total Environ., 256 (2000) 87.
2. M. Prudente, E. Y. Kim, S. Tanabe, R. Tatsukawa, Mar. Pollut. Bull., 34 (1997) 671.
3. R. G. S. Lima Junior, F. G. Araújo, M. F. Maia, A. S. S. B. Pinto, Environ. Res., 89 (2002) 171.
4. P. S. M. Carvalho, E. Zanardi, S. V. Buratini, M. C. Lamparelli, M. C. Martins, Water Res., 32 (1998) 193.
5. L. Bervoets, R. Blust, R. Verheyen, Ecotoxicol. Environ. Saf., 48 (2001) 117.
6. K. C. Cheung, B. H. T. Poon, C. Y. Lan, M. H. Wong, Chemosphere, 52 (2003) 1431.
7. R. Moraes, P. Gerhard, L. Andersson, J. Sturve, S. Rauch, S. Molander, Hum. Ecol. Risk Assess., 9 (2003) 149.
8. R. R. Long, L. G. Morgan, in: NOAA Technical Memorandum No. 5, OMA52, NOAA National Ocean Service, Seattle, Washington, 1990.
9. C. Calza, M. J. Anjos, C. R. F. Castro, R. C. Barroso, F. G. Araújo, R. T. Lopes, Radiat. Phys. Chem., 71 (2004) 787.
10. W. C. Pfeiffer, M. Fiszman, O. Malm, Sci. Total Environ., 58 (1986) 73.
11. C. E. V. Carvalho, Heavy Metals Environ., 9 (1993) 4.
12. M. M. Molisani, M. S. M. B. Salomão, A. R. C. Ovalle, C. E. Rezende, L. D. Lacerda, C. E. V. Carvalho, Bull. Environ. Contam. Toxicol., 63 (1999) 682.
13. S. Minissi, D. Caccese, F. Passafiume, A. Grella, E. Ciccotti, M. Rizzoni, Genet. Toxicol. Environ., 420 (1998) 77.
14. H. Y. Zhou, R. Y. H. Cheung, K. M. Chan, M. H. Wong, Water Res., 32 (1998) 3331.
15. D. Vignati, M. Pardos, J. Diserens, G. Ugazio, R. Thomas, J. Dominik, Water Res., 37 (2003) 2847.
16. E. De Miguel, S. Charlesworth, A. Ordónez, E. Seijas, Sci. Total Environ., 340 (2005) 137.