E3S Web of Conferences **1**, 32002 (2013)
DOI: 10.1051/e3sconf/20130132002

Distribution and Potential Mobility of Selected Heavy Metals in a Fluvial Environment Under the Influence of Tanneries

M. L. K. Rodrigues[1,2] and M. L. L. Formoso[2]

[1] Fundação Estadual de Proteção Ambiental Henrique Luiz Roessler, Rua Aurélio Porto, 45 90620-090 Porto Alegre-RS (Brazil) metaisfepam@hotmail.com
[2] Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, 91509-900 Porto Alegre-RS (Brazil) milton.formoso@ufrgs.br

Abstract. In this study we evaluated the occurrence of heavy metals in a fluvial environment under the influence of tanneries – the Cadeia and Feitoria rivers basin (RS, south Brazil), highlighting the distribution and potential mobility of the selected elements. Every three months, over one year-period, selected heavy metals and ancillary parameters were analyzed in water and sediment samples taken at ten sites along the rivers. Water analyses followed APHA recommendations, and sediment analyses were based on methods from USEPA (SW846) and European Community (BCR sequential extraction). The determinations were performed by ICP/OES, except for Hg (CV/ETA). Statistical factor analysis was applied to water and sediment data sets, in order to obtain a synthesis of the environmental diagnosis. The results revealed that water quality decreased along the rivers, and mainly on the dry period (January), showing the influence of tannery plants vicinity and flow variations. Except for Fe, Al, and eventually Mn, heavy metal contents in water were in agreement with Brazilian standards. Concerning sediments, Al, Cu, Fe, Ni, Mn, Ti, and Zn concentrations appeared to reflect the base levels, while Cr and Hg were enriched in the deposits from the lower part of the basin. The partition of heavy metals among the sediment geochemical phases showed higher mobility of Mn along the sampling sites, followed by Cr in the lower reach of the basin, most affected by tanneries. Since Cr was predominantly associated to the oxidizable fraction, its potential mobilization from contaminated sediments would be associated to redox conditions. The detection of Hg in the tissue of a bottom-fish species indicated that the environmental conditions are apparently favoring the remobilization of this metal from contaminated sediments.

Keywords: Heavy metals, river water, sediment, sequential extraction, factor analysis, tanneries.

Introduction

Processing hides and skins is a traditional activity in the State of Rio Grande do Sul (RS), Brazil. During several decades, tanneries discharged liquid effluents into the streams, while solid wastes were disposed on the land, often on the bank of rivers or in flood-prone areas. Over the last years stringent laws and improved effluent control have helped reduce pollutant emissions. However, toxic compounds from the tanneries can remain in river sediments, and pose a potential risk to the aquatic environment and human health (Rodrigues and Formoso, 2006). In this study we investigated the occurrence of heavy metals (HMs) in the waters and sediments from Cadeia and Feitoria rivers (RS, Brazil), potentially affected by tannery activities, searching for estimating their distribution and potential availability to the surrounding environment.

Study Area

Cadeia and Feitoria Rivers belong to Caí river basin, a tributary of Guaíba Lake (Fig.1). The catchment area is 900 km^2, with altitudes varying from 800 m on the Brazilian Plateau to 10 m a.s.l. at the mouth. The local geology consists of Serra Geral Formation rocks (mainly basalts), sandstones of Botucatu Formation, and Tertiary sediments. The region concentrates agricultural activities in small properties, mainly dedicated to fruit and vegetables production. Despite some influence of agricultural and urban discharges, the leather and footwear manufacture represents the main anthropogenic activity contributing to a local increase of the environmental contamination by HMs (FEPAM/FINEP,

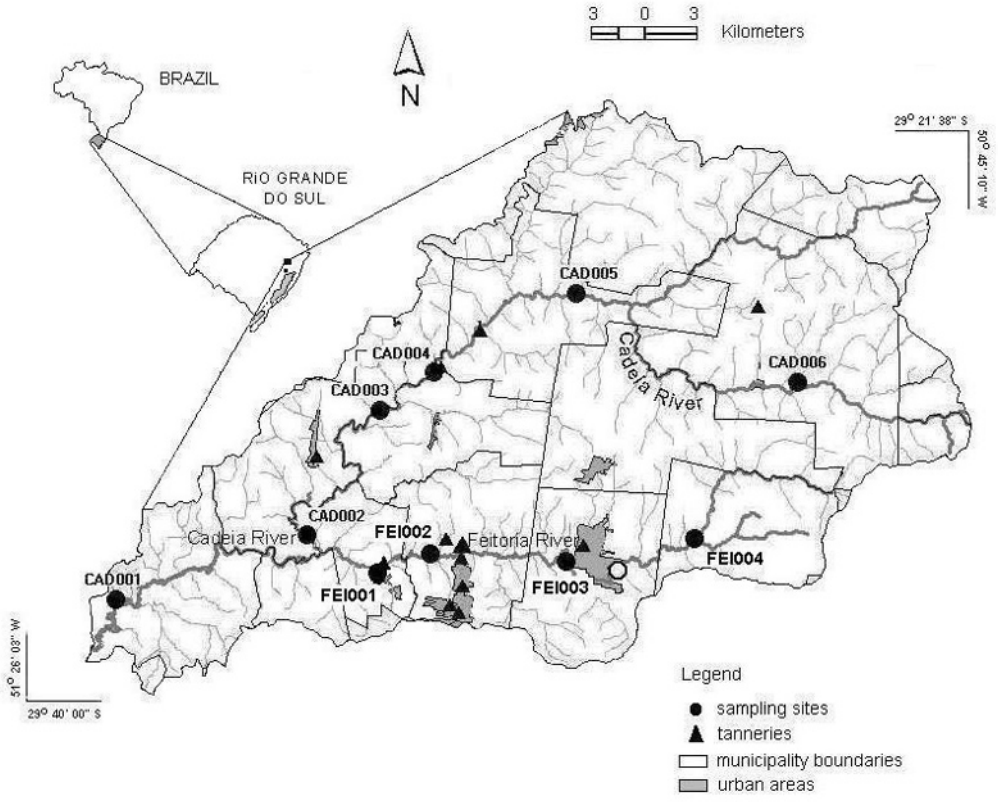

Fig.1 Location of Cadeia/Feitoria rivers basin and the sampling sites

Tab.1 Mean concentrations of heavy metals in the waters of Cadeia and Feitoria rivers (μg L^{-1})

River	Cd	Cu	Ni	Zn	Cr	Cr(VI)	Ti	Fe	Al	Mn	Hg
Feitoria	<0.2	2.3	1.2	11.8	14.6	<10	140	1440	1530	56	<0.2
Cadeia	<0.2	2.0	0.7	12.1	4.3	<10	160	1360	1310	34	<0.2

Tab.2 Mean concentrations of heavy metals in the sediments of Cadeia and Feitoria rivers

River	Cd*	Cu*	Ni*	Zn*	Cr*	Ti**	Fe**	Al**	Mn*	Hg*
Feitoria	<0.1	99.2	74.1	141	484	13.6	92.8	89.8	1480	0.203
Cadeia	<0.1	85.3	53.2	130	205	14.0	90.0	84.5	1670	0.124

*μg g^{-1}; **mg g^{-1}

2003). Thus, the area of study is particularly suitable for an environmental impact assessment of HMs originating from the activity of tanneries.

Materials and Methods

Ten sites were selected to collect water and sediment. Due to the distance from anthropogenic sources, points CAD006 and FEI004 were used as references, respectively for Cadeia and Feitoria rivers (Fig. 1). Every three months, between July 1999 and April 2000, selected HMs and ancillary parameters were analyzed in water (n=40) and sediment samples (n=40), in order to cover different hydrological conditions. Water analyses followed recommendations from APHA (1995), entailing dissolved (<0,45μm) and total metal contents. Sediment analyses were performed in the silt-clay fraction, using the method SW846-3052 (USEPA, 1996) and the BCR sequential scheme (Quevauviller et al., 1996). The determinations were performed by ICP/OES. Hg was analyzed by CV/ETA, after extraction according to method SW846-3051. Statistical factor analysis was

applied to water and sediment data sets, in order to obtain a synthesis of the information. The use of factor analysis generated statistical indexes (factor scores) representing the contamination degree of waters and sediments evaluated (Rodrigues and Raya-Rodríguez, 2003; Rodrigues and Formoso, 2006abc).

Results and Discussion

Table 1 summarizes the results obtained for the evaluation of HMs in water samples. The contents were generally in agreement with Brazilian standards, except for Fe, Al, and eventually Mn. Concerning mean dissolved percentage of HMs in water samples, the following rank was found: Ti(8%) < Ni(17%) < Fe(28%) < Al(29%) < Cr(39%) < Mn(51%) < Cu(53%) < Zn(54%). Ti, Ni, Fe, and Al showed a higher tendency to retention within the limits of the basin, while Zn, Cu, and Mn had the greatest potential for export by the waters in the downstream direction. With an intermediary dissolved fraction, Cr also showed a considerable potential of availability in sites under the influence of tannery plants (FEI002 and FEI001).

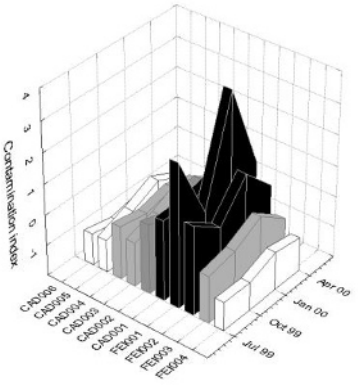

Fig.2 Spatial and temporal variation of factor 1 scores (contamination indexes) obtained for the water data set, and linked to tanneries influence

The application of factor analysis to the water data set summarized the information in two components, loaded with 50% and 15% of total variance, respectively. Cr and Mn, besides Na, Ca, K, Suspended and Dissolved Solids, Dissolved Oxygen, and Conductivity were the well-correlated variables with the first factor (correlations > 0.8), indicating the influence of tanneries. The correspondent factor scores showed a water quality decrease from headwaters up to mouth along the streams, with highest values at the lower reach of Feitoria river, where tanneries are concentrated. Water contamination was associated to flow variations, and a poorer quality was observed during dry period (January) (Fig.2). The second component, in which Fe, Al, and Suspended Solids were the relevant variables, was possibly linked to natural events. In this case, higher factor scores were found during the period of increased water flow (October), which caused re-suspension and entrainment of solid material to the rivers bed (Fig.3).

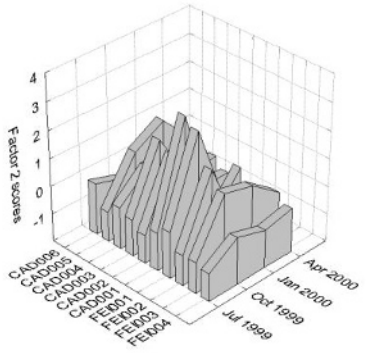

Fig.3 Spatial and temporal variation of factor 2 scores obtained for the water data set, and associated to natural contributions

Concerning sediments (Tab. 2), the concentrations of Al, Cu, Fe, Ni, Mn, Ti, and Zn probably reflected the local base levels, in opposition to Cr and Hg, enriched in the deposits from the lower part of the basin. The structuring of sediment data set by factor analysis indicated that the first factor should be retained for interpretation. Loaded with 28% of total variance, it was well-correlated with the variables Cr, Hg and S. The correspondent factor scores demonstrated a well-defined geographical distribution of these contaminants, highlighting the influence of tanneries installed near points FEI002 and FEI001 (Figs. 1 and 4).

The mean potential availability of HMs in relation to the total content in sediments was assessed by adding up the results for the three mobile phases of the BCR sequential scheme. The following hierarchical order was found: Ti(1%) < Al(5%) < Ni(6%) < Fe(10%) < Cu(20%) < Zn(28%) < Cr(49%) < Mn(76%). Therefore, the partition of HMs among the geochemical phases of sediment highlighted the higher tendency of Mn mobility along the basin, followed by Cr in the area most affected by tanneries (predominantly associated to the oxidizable fraction). The high percentage of Ti, Al, Ni, and Fe in the residual phase showed that these elements have a low environmental mobility and are poorly affected by human activity in the study area. Other studies also report a high potential of availability for Mn, even when a natural origin is predominant (Rodrigues and Raya-Rodríguez, 2003). The remarkable occurrence of Cr in the oxidizable sediment phase is a fingerprint for tanneries impact, and indicates that most of the metal is temporarily retained in sediments, probably as the less toxic Cr(III).

The accumulation of Cr and Hg in sediments from the lower course of Feitoria river would be facilitated by a decreasing flow rate and by a lower dilution capacity in this part of the basin. Increased contents of mud, organic

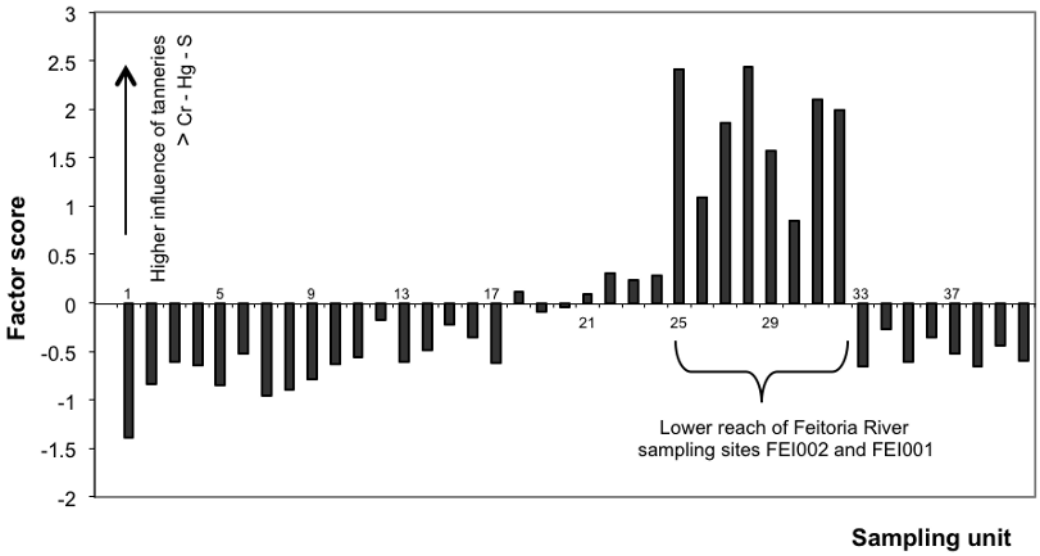

Fig.4 Spatial and temporal variation of factor 1 scores obtained for the sediment data set and linked to the influence of tannery plants

carbon and sulfur suggest that the river section most affected by the neighborhood of tanneries is also the most vulnerable for fine grain deposition and metal accumulation in the study area. Since Cr was predominantly associated to the oxidizable fraction, its mobilization from sediments would depend from changes in redox conditions. On the other hand, the detection of Hg in the tissue of a bottom-fish (*Rineloricaria*, point FEI001, n=22, µ=222 µg kg^{-1}), reported by Rodrigues and Formoso (2006c), suggested that part of Hg accumulated in sediments is suffering remobilization under local environmental conditions. Cr was not detected in the fish tissue, but its considerable enrichment in sediments from the lower part of the basin indicated a potential of occurring hazardous effects on aquatic organisms.

Conclusions

The evaluation of waters and sediments from Cadeia and Feitoria rivers indicated that HMs originate from natural and anthropogenic contributions, mainly represented by weathering of basalt rocks and tannery activities. Water quality decreased along the rivers, especially on dry period, showing influence of tannery plants vicinity and flow variations. Although HM contents in water were generally in agreement with Brazilian standards, an important enrichment of Cr and Hg was found in sediments from the lower part of the basin, where tanneries are concentrated. Since Cr was predominantly associated to the oxidizable fraction of sediments, its potential mobilization from contaminated deposits would be associated to redox conditions. The detection of Hg in the tissue of a bottom-fish species indicated that local environmental characteristics are apparently favoring the Hg remobilization from the contaminated sediments.

Acknowledgements

The authors thank MSc. Lilian Ferraro (FEPAM), scholarship student Camila Cerveira (PROBIC/FEPAM), and Dr. Vera Vargas for the support provided as coordinator of EcoRISCO project. (CNPq/FEPAM).

References

APHA. Standard Methods for the Examination of Water and Wastewater. 19.ed. Washington DC: APHA, 1995.

FEPAM/FINEP, VARGAS, V.M.F. (coord.). Estratégias ecotoxicológicas de avaliação de risco. Porto Alegre: FEPAM, 2003. Eco-Risco Saúde Project Report.

Quevauviller, Ph., Rauret, G., López-Sánchez, J.F. et al. The certification of the EDTA-extractable contents (mass fractions) of Cd, Cr, Ni, Pb and Zn in sediment following a three-step sequential extraction procedure. Louxembourg: Office for Communities, BCR Information, 1996. 59p.

Rodrigues, M.L.K., Formoso, M.L.L. Pesquisas em Geociências. 33(2), 55-70 (2006a).

Rodrigues, M.L.K., Formoso, M.L.L. Water, Air & Soil Pollution. 169, 167-184 (2006b)

Rodrigues, M.L.K., Formoso, M.L.L. Water, Air & Soil Pollution. 176, 307-327 (2006c).

Rodrigues, M.L.K.; Raya-Rodríguez, M.T.

Statistical factor analysis of heavy metal pollution in the Caí river basin sediments (Brazil). In: II International Symposium on Contaminated Sediments, 2003, Québec. Transactions. Québec: Locat, J.; Galvez-Cloutier, R.; Chaney, R.C.; Demars, K. (eds.), 2003. p.394-399.

USEPA. Method 3051. Microwave assisted acid digestion of sediments, sludges, soils and oils. In: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods - SW-846. Washington, DC: US EPA, 1995.

USEPA. Method 3052: Microwave assisted acid digestion of siliceous and organically based sediments. In: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods - SW-846. Washington, DC: US EPA, 1996.