

Metal contamination and fractionation in sediments from the lower basin of the Vale do Ribeira (SE, Brazil)

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Abstract The sediment quality of Ribeira de Iguape River is affected by former Pb extraction mining. Some studies affirm the restoration status of the basin, however, mobility of metals and its associated risk is still questioned. This study integrates the metal concentrations in the lower part of the basin with different contamination source to determine the existence of risks associated with the mobile fractions of the geochemical matrix. Despite concentrations of metals were low and the environmental risk factor values were negative, our results indicated that As, Mn, Pb, and V were present in the most labile forms. The multivariate analysis conducted using metal concentrations, environmental risk factor values and speciation suggested that any risk would be associated with the labile fractions of the

analyzed elements, especially for Pb. The station from Registro was stressed by Co, Pb and Zn; with Pb under the reactive fraction that could be associated with high mobility and potential bioavailability.

Keywords Iguape River · Metal monitoring · Environmental risk assessment · Sequential extraction

Introduction

The Vale do Ribeira is located on the Southeast of Brazil, between Paraná and São Paulo states; it takes place in very preserved region, which is considered the Atlantic rainforest reserve of the biosphere and connects to the World Natural Heritage site of the Cananéia-Iguape Estuarine Complex. Its fluvial network was historically affected by former mining activities of lead extraction, especially the Ribeira de Iguape River (RIR). Although extraction activities ceased in the 1990s, tailing residues located on the upper part of the basin still represent sources of metals to the aquatic system (Cunha et al. 2005). Latest investigations have determined that the basin is under a restoration process since the metals inputs have decreased and the trawling of metals associated with particulate matter towards the Atlantic Ocean (Cunha et al. 2005; Abessa et al. 2012, 2014). Nevertheless, few studies have undertaken the process in the lower part of the basin, where the deposition of sediments and particles occur and the mobility of metals could be linked to potential toxic risks.

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The potential risk of elements is link to the chemical form in the environment, which is governed by physicochemical parameters (Hamelink et al. 1994). Therefore, the chemical form can vary with climatic phenomena and other hydrological events in aquatic systems. Due to that, the assessment of the ecological risk is associated with the chemical fractionation. The sequential extraction procedures are widely accepted as appropriate methods for assessing the speciation of metals in sediments (Tessier et al. 1979; Kestern and Förstner 1986). Metals bound to the first fractions are considered more susceptible to remobilization than metals residing in the lattices of sediment minerals (Luoma and Davis 1983; Riba et al. 2002a).

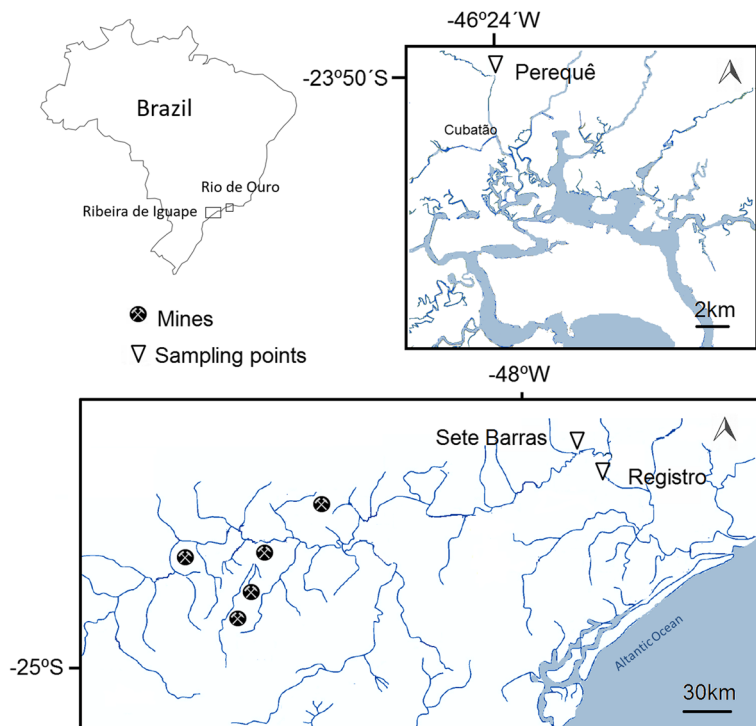
The results presented in this work are part of an integrative approach conducted in the area to assess the sediment quality. The main objective of this research is to determine the possible risks associated with metals and metalloids in the lower RIR, considering the mobility of these elements. To achieve that, the concentration of some elements (Al, As, B, Ba, Be, Ca, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sr, Ti, U, V, and Zn) was assessed plus the geochemical fractionation in sediment determined by means of a chemical fractionation analysis using a sequential extraction procedure. The potential

environmental risk was calculated based on freshwater sediment quality benchmarks, and integrated to understand potential risk associated with mobility of metals in the lower part of the basin.

Materials and methods

The geomorphology of the valley has been demonstrated as a crucial factor (Abessa et al. 2014) for the deposition of contaminants in the lower part of the river (Moraes et al. 2004) as the river leaves the sloppy zone and starts flowing through a plain area. This sink effect is also incremented by the meanders formation in the flooding plain, sequestering contaminants in elbows. Sediment sampling stations were situated in the lower part of the RIR basin (Fig.1): Sete Barras (SB; $24^{\circ} 23' 16''$ S, $47^{\circ} 55' 33''$ W) and Registro (REG; $24^{\circ} 29' 15''$ S, $47^{\circ} 50' 37''$ W). SB is located closer to the mining discharges; it is also characterized with strong flooding episodes. In contrast, REG is affected by flooding episodes of many tributaries. Superficial sediment samples were manually collected from the river banks and transported in dark conditions into plastic recipients with a layer of water from the adjacent river. A third

Fig. 1 Map of the sampling sites in the lower basin of the Iguape River in the Vale do Ribeira and the sampling site in the Rio Douro in the Ecological Park Perequê



sediment sampling site was selected as reference site from the Rio de Ouro (Cubatão, São Paulo) in the Ecological Park of Perequê (EPP; 23° 50' 29" S, 46° 24' 57" W).

Sediment samples were dried at 60 °C, homogenized in mills and then analyzed for the total organic carbon (TOC), nitrogen (N), and sulfur (S) by using an elemental analyzer model Vario MACRO Cube. The pseudo-total digestion of sediments was performed following the International Organization for Standardization (ISO) standard procedure 11466 (1995). The chemical partitioning of metals in sediment was studied by the modified Bureau Community of Reference (BCR) sequential extraction procedure. An initial step, performed with Milli-Q water as reagent, yielded the most soluble fraction (F0); acetic acid was employed as exchangeable fraction and bound to carbonates (F1); the reducible fraction (F2) bound to the Mn-Fe oxides was extracted with hydroxylammonium chloride; the oxidizable (F3) considered as the fraction bound to organic matter and sulfides was determined with peroxide and ammonium acetate; and the last step with aqua regia digestion, yielded the residual fraction (F4). The sediment digestion procedure and analytical procedures are detailed in Bonnail et al. (2016). The trace metal analysis of major and trace elements of solutions took place by means of an Agilent Technologies 7700 Series inductively coupled plasma mass spectrometer (ICP-MS) and an Iris Intrepid Model atomic emission spectroscopy (ICP-AES) by the certified SC-ICYT. To demonstrate the reproducibility of the results, the analysis sequences consisted of calibration standards, standard solutions analyzed as an unknown (quality control solutions), method blanks, and the certified reference material BCR-701 for sediment-extractable trace elements. Furthermore, an internal check was performed on the sequential extraction by comparing the total amount of elements extracted by different reagents during the sequential extraction procedure with the results of the pseudo-total digestion: $[(C_{F0} + C_{F1} + C_{F2} + C_{F3} + C_{F4}) / C_{\text{Pseudototal digestion}}] \times 100$.

The ecological risk factor (ERF) was calculated as outline in Riba et al. (2002b) based on the metal concentration of each metal (C_i). The C_{SQV} concentrations used in this study were the freshwater sediment quality thresholds of the USEPA. These values are widely used all over the world as sediment guidelines, as due to there is a consensus that they are effective to predict sediment toxicity to biota, based on chronic direct exposure, and/

or non-lethal endpoint studies designed to be protective of sensitive species (Pluta 2006; Hübner et al. 2009).

$$ERF = \frac{C_i - C_{SQV}}{C_{SQV}}$$

A cluster analysis (Ward's method) was applied to the set original set of variables of sediment characterization (textural distribution, N, S, H, organic matter-OM, total organic content-TOC), the total metal concentrations, the environmental risk factors (ERF) calculated for toxic elements (standardized as the percentage of deviation) and the concentrations of metal(loid)s in mobile (M) and residual form (R). According to Mooi and Sarstedt (2011), cluster analyses have no requirements of minimum size samples and, thus, it could be used in our study. Statistical analyses were performed with the aid of the statistical software PAST 1.34 for Windows (Hammer et al. 2001).

Results and discussion

Table 1 shows the sediment characterization of the sediment samples and the total metal concentrations in the collected sediments from the lower basin of the RIR and the Ecological Park Perequê (EPP). Sandy sediments were predominant in SB (98%) and EPP (99%) with lower concentration of organic matter (1.40 and 0.60%, respectively). In contrast, the station REG displayed greater percentage of fines (14%) and greater organic matter (1.60%). The TOC was slightly higher in the RIR than in EPP.

Table 1 also shows the results of the calculated ERF for the studied area and all the elements. Positive values of ERF indicate about adverse effects associated with the metal (Riba et al. 2002b). However, no positive value was obtained in the current study which is pointing any risk associated with the metal concentrations in the sediment SB, REG, and EPP. Nevertheless, it is possible to rank the elements according to the ERF values obtained and associated with the element enrichment in each station:

SB : Mn > Pb > Zn > Ni > Cu > Co > Fe > Cr > As

REG : Mn > Pb > Zn > Ni > Cu > Co > Fe > Cr > As

EPP : Fe > Ni > Zn > Mn > Cr > Cu > Pb > Co > As

The sequences of the stations from the RIR are homologous, but the lower values attributed to Mn displayed greater ERF values associated with a stronger

Table 1 Sediment characterization as textural and organic matter (OM), total organic content (TOC), nitrogen (N), hydrogen (H), and sulfurs (S) expressed in percentage, and metal and metalloid concentrations in the sediment samples (in mg/kg dried weight) from the study stations. Environmental risk factors (ERF) calculated for the concentrations of the study (expressed in percentage)

	SB	REG	EPP	ERF (%)		
				SB	REG	EPP
Sand	98.2	85.8	99.5			
Fines	1.83	14.3	0.47			
OM	1.40	1.60	0.60			
TOC	0.68	0.44	0.30			
N	0.06	0.09	0.05			
H	0.25	0.25	0.28			
S	2061	0.90	1163			
Al	2903	3732	10,576			
As	0.56	0.63	1.31	As	-0.94	-0.87
B	4.84	0.37	0.10			
Ba	41.6	63.1	42.1			
Be	0.38	0.38	0.33			
Ca	643	941	130			
Co	6.67	6.75	4.62	Co	-0.87	-0.91
Cr	3.26	3.55	11.1	Cr	-0.92	-0.75
Cu	4.67	6.21	7.32	Cu	-0.85	-0.77
Fe	2045	2480	10,071	Fe	-0.90	-0.50
Li	1.32	2.35	6.01			
Mg	1089	2155	3993			
Mn	394	362	129	Mn	-0.14	-0.72
Ni	5.37	6.78	7.46	Ni	-0.76	-0.67
Pb	10.1	18.9	3.87	Pb	-0.72	-0.89
Sr	4.49	7.48	1.18			
Ti	26.0	42.0	215			
U	0.28	0.48	0.26			
V	1.82	1.77	8.00			
Zn	29.7	47.4	34.4	Zn	-0.75	-0.72

enrichment of this metal against the rest of the metals. Lead displayed the greatest ERF in the lower part of the RIR. In contrast, the greatest ERF in sediments from station EPP was associated with Fe. The enrichment in Fe is usually associated with industrial contamination, in this case likely to atmospheric dispersion and deposition from a major steel plant located in Cubatão.

To establish the potential bioavailability of the elements in the studied sediments, a chemical fractionation of the total concentration was conducted. Figure 2

shows the results of the metal(loid) fractionation according to the sequential extraction procedure for the stations SB, REG, and EPP. The total sum of elements contents in the mobile fraction ($M = \Sigma F(0-3)$) seems to be more bioavailable (Pérez-López et al. 2008) and with potential toxicity and hazardous for the environment (Vives et al. 2007). Meanwhile, elements collected in the residual fraction ($R = F4$) are associated with the lithological form considered less reactive and less bioavailable. The most bioavailable form of the elements bonds to the most labile fractions (F0, F1, and F2).

The concentration of elements in sediment from the station EPP (Al, Ba, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Ti, and Zn) was mainly associated with the residual fraction ($F4 > 50\%$), indicating that they were as non-bioavailable form. In contrast, the elements extracted from sediment of the RIR (As, B, Ba, Be, Ca, Co, Fe, Mn, Pb, and V) presented a higher concentration associated with the most labile forms ($\Sigma F0-2$). What is more, the metal mobility was greater in SB than in REG. The main elements extracted were Al (~37% in SB and EPP; and 33% in REG) and Fe (~25% in sediments from RIR; and 35% in EPP) in relative abundance, followed by Mg, Ca in the RIR. In spite of the high concentration of Fe and Al, they were below the guidelines of the USEPA (Table 1). On the other hand, the averaged As concentrations of RIR registered 0.60 and 1.31 mg/kg As in EPP, it was mainly presented as reducible fraction for both cases. Cd contamination was not detected for any of the sediment samples in the studied sites. Cr concentration in EPP was slightly greater than in RIR (11 and 3 mg/kg Cr, respectively), however in this last, it was presented under a greater mobile form (>50%). There was a slight increment of Cu concentration close to the mouth of the RIR (6.21 mg/kg Cu in REG) in comparison with waters-upstream in SB (4.67 mg/kg Cu); both sites almost exceeded half of the concentration as bioavailable form. In contrast, most of the Cu concentration found in EPP sediments (7.32 mg/kg Cu) was extracted from the residual fraction (Fig.2).

Lead, the characteristic element mining discharges in RIR, has been recognized as tracer of the environmental status of the basin by many authors (Charalampides and Manoliadis 2002; Moraes et al. 2004; Abessa et al. 2014; Nakata et al. 2017). The mobility of Pb close to the abandoned mines corresponds to the release kinetics data fitting to parabolic equations of diffusion, greater associated with the first phase (Buschle et al. 2010). The

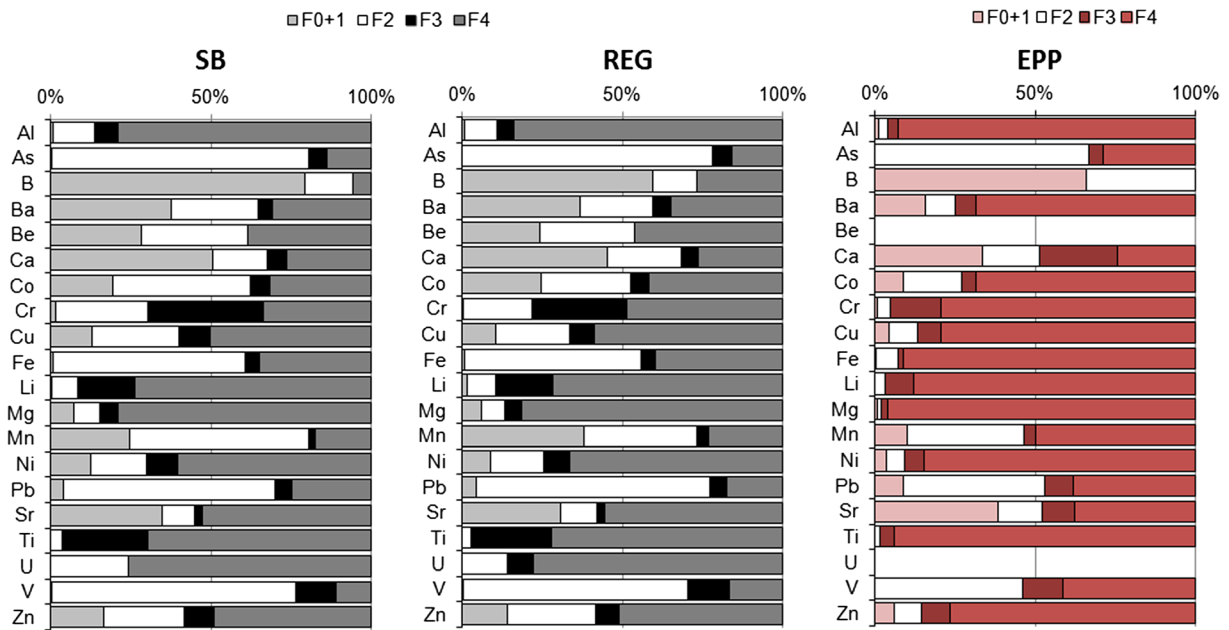


Fig. 2 Metal fractionation in four geochemical fractions (F0 + 1: water soluble; F2: exchangeable; F3: iron and manganese hydroxides; F4: residual fraction) for the sediment samples in the RIR (SB and REG) and the Ecological Park of Perequê (EPP)

concentration of Pb found in sediments from SB was the triple (10.12 mg/kg Pb) and in REG supposed six-times (18.88 mg/kg Pb) the concentration found in sediments from station EPP (3.89 mg/kg Pb); this might be indicative of an anthropogenic contamination. Nevertheless, the background Pb level reported by Lopes (2007) is 25 mg/kg Pb. Despite of Pb has been historically the main contaminant of interest of RIR, concentrations in SB and REG did not exceed the TEL values of the USEPA, but they are characterized by a high mobility ($\Sigma F(0-3) > 70\%$). In contrast, previous studies found greater concentrations: 90 mg/Kg Pb in REG (Moraes et al. 2004),

As a result, the concentrations of toxic elements in the mobile phases (up to 50% of bioavailable fraction) can be ranked for each site as the following in the RIR.

SB : B > V > As > Mn > Pb > Ca > Ba > Co > Cr >

Fe > Zn > Cu

REG : As > V > Pb > Mn > Ca > B > Ba > Fe > Co >

Cr > Be

Multivariate analysis results are shown in Figs. 3 and 4 as the clusters of sets of variables. Basically, this analysis showed that sediments from RIR presented similar composition, which also differed from that of

EPP (Fig.3). Chemical elements in sediments from EPP also tended to be greater associated with the residual fractions. Among the variables (Fig.4), two main clusters were formed: the first one joined the total and residual concentrations for most of elements, together with the ERFs, N, and H levels, and mobile phases of As and Pb. The second cluster joined the mobile phases of the resting elements, fine particles, TOC, OM, and total concentrations of Mn, Pb, and Co. The association of

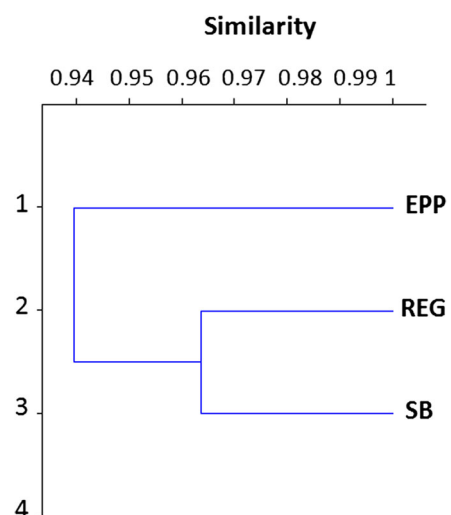


Fig. 3 Cluster analysis formed with sampling stations from the RIR (SB and REG) and the Ecological Park Perequê (EPP)

ERFs and residual fractions is due to the low concentrations of metals detected in the sediments, and that for the majority of elements the residual fractions were predominant. Abnormalities were observed for As and Pb, and despite their low concentrations (and low associated risks), these two elements are present in potentially bioavailable form. In fact, previous studies reported for bioaccumulation of Pb in invertebrates from RIR (Guimarães and Sígolo 2008b; Rodrigues et al. 2012), while contamination by As occurs along the basin, as this element is associated with mining residues from gold mines.

Slag from the smelting processes was characterized as sand grained (94%) with metal concentration of 118 g/kg of Zn and 34 g/kg Pb by Guimarães and Sígolo (2008a) and 100 g/kg Zn and 28 g/kg Pb (Abessa et al. 2014) in the upper part of the basin. However, the strong rainy events disaggregate metal enriched materials that increase the chemical load of the fluvial course (Costa et al. 2009). Moraes et al. (2004) reported 90 mg/kg of Pb reaching the lower basin; while Guimarães and Sígolo (2008a, 2008b) also reported a decline in the concentration of Pb from SB to REG (74 and 32 mg/kg Pb, respectively), in contrast to findings in this study for the same stations (10 and 18 mg/kg Pb). Therefore, these temporal variations evidence about the chemical wash up of the sediments. Floods are considered the primary mechanism whereby particulate wastes are transported, and then deposited (Luoma and Rainbow 2008). Particle size might be modified due to the motion (dragging, erosion, and resuspension), and some authors observed associations between what might be explaining the association of greater textural with the lithological fraction (Guimarães and Sígolo 2008a); while most labile form are associated with finest fractions, TOC and OM (Fig.4). The results from the sequential extraction for Pb (Fig.2) point that transport in sediments occurs mainly bound to iron and manganese oxyhydroxides (F2 > 50%), in agreement with Corsi and Landim (2003) findings for the upper part of the basin, whose research indicated transport of lead mainly associated with the same fraction, followed by organic matter, carbonates, and residual fraction. On the other hand, due the high mobility of Pb ($\Sigma F(0-3)$), this element could be released into the water column in either dissolved (F0) or particulate form (F1) or adsorbed onto iron oxides (F2). In other words, scavenging metals by colloid formation or adsorption over fines and TOC add extra surface for dissolved

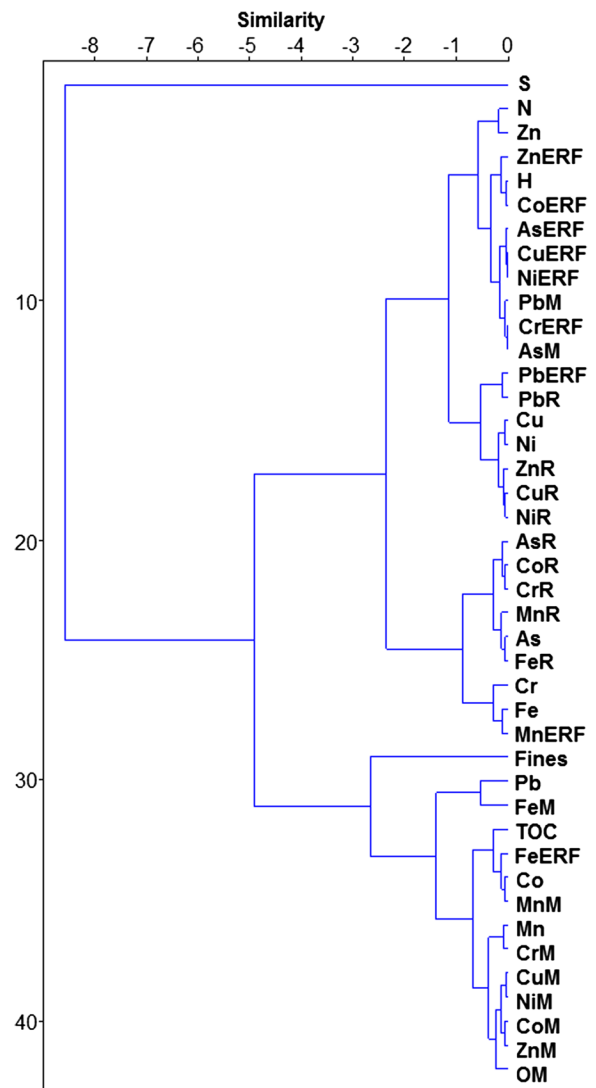


Fig. 4 Cluster analysis with the 43 variables analyzed in the sediments from RIR

metal (F3) as transporter towards the Cananéia-Iguape Estuarine Complex. Biological data gives support to our findings, as bioaccumulation of metals were observed in bivalves, and significant correlations were observed between Pb concentrations in sediments and in soft tissues of the bivalves *Anodontites tenebricosus* and *Corbicula fluminea* (Guimarães and Sígolo 2008b; Rodrigues et al. 2012), with higher levels being reported for the lower RIR.

There is an increase of metal concentrations and nutrients in the sediments of the RIR during the rainy season as reported by Cunha et al. (2007a, b). This is fomented by the erosion and the extra caudal supplied

by floods; so that, the restoration of the basin in this segment it might be occurring by metal sequestration onto particulate matter that flows towards the ocean. This idea is also supported by other research studies (Moraes et al. 2004; Cunha et al. 2007a, b; Morais et al. 2013; Abessa et al. 2014). Therefore, metal content in areas close to the estuary would reflect the influences of weathering, local geology, hydrological events (floods), and inputs of upstream anthropogenic discharges (mining activities in this case).

Conclusions

Despite the former metallurgical spillages in the Vale do Ribeira, the metal concentration in the sediments from the lower basin displayed a slight risk strongly associated with the mobile phases of the geochemical matrix. The mobilization of Pb and its associated risk was linked with the finest fraction of the sediment in the station closest to the ocean, displacing the associated risk of the metal water downstream.

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