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Dynamics of metals in lacustrine sediments: case study of the Madeira River, Amazon region

Dinâmica de metais em sedimentos lacustres: estudo de caso no Rio Madeira, região Amazônica

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ABSTRACT

The studies on metals in Madeira River's principal flow show high variability of Co, Cr, Cu, Fe, Ni, Pb and Zn concentrations. However, the transfer of these metals from the main river channel, whose physical and chemical characteristics differ from those of lakes, has not been fully characterized. The objective of this study was to discuss how the transfer of Madeira River's metals changes the spatial dynamics of these metals in sediments of the Puruzinho Lake (AM). The principal component analysis pointed to differences in the order of the data, creating two distribution zones of metals. The average concentrations of Co, Cu, Cr, Mn and Fe are higher in the area under the influence of the suspended solids coming from the Madeira River. The zoning of metals in lakes is structured by the forces acting across the river's course at the same time as plains flood and generates ecotones.

Keywords: Trace elements; Biogeochemistry of metals; Puruzinho Lake.

RESUMO

Os estudos sobre metais no canal principal do Rio Madeira demostram alta variabilidade nas concentrações dos elementos Co, Cr, Cu, Fe, Ni, Pb e Zn. No entanto, a dinâmica da transferência destes metais da calha central do rio, que possui características físicas e químicas distintas às dos lagos, permanece não compreendida. O objetivo deste estudo foi discutir como a transferência de metais do Rio Madeira influencia a dinâmica espacial destes metais no sedimento de fundo do Lago Puruzinho (AM). A análise de componentes principais mostrou as diferenças na ordenação dos dados, gerando duas zonas de distribuição de metais. As concentrações médias de Co, Cu, Cr, Mn e Fe são superiores na região do lago sob influência dos sólidos em suspensão provenientes do Rio Madeira. A zonação de metais em lagos é estruturada pelas forças que atuam transversalmente ao curso do rio no momento da inundação das planícies, formando zonas de ecótonos.

Palavras-chave: Elementos-traço; Biogeoquímica de metais; Lago Puruzinho.

INTRODUCTION

Metals are present in aquatic ecosystems due to both natural and anthropic processes (KABATA-PENDIAS, 2011). The considerable contribution of natural processes to the mobilization of metals in the aquatic environments is a consequence of weathering of rocks and leaching of soils (SAHOO et al., 2017). In turn, anthropic contribution results from a number of factors, like mining activities (RIBEIRO et al., 2017), the misuse of soil in agriculture, and the discharge of untreated industrial and domestic effluents (LOPES et al., 2004). Every year tons of metals are mobilized through soil, air, and water, and are inevitably incorporated in food chains, with hazards to human and environmental health (NRIAGU; PACYNA, 1988; BUBB; LESTER, 1991; LOPES et al., 2004).

Sediments deserve special attention in studies on environmental ecotoxicology. As a compartment, sediment is directly influenced by metal accumulation processes. Several aquatic ecosystems have been investigated in this regard, showing that lakes are the most affected of these ecosystems due to their intrinsic depositional characteristics (MOZETO, 2004).

However, lakes stand as the most important compartments in the profiling of geochemical patterns and analysis of the diffuse metal distribution gradients that may influence pollution and contamination of the environment (WASSERMAN; QUEIROZ, 2004; SAHOO et al., 2017).

The metals present in lacustrine environments may interact with other solutes, forming complexes or remaining in solution (GUINOISEAU et al., 2016). These metals may also present themselves as particulate matter, when they bind to inorganic and organic molecules by adsorption or are assimilated by microorganisms (BUBB; LESTER, 1991). Particulate forms of metals may precipitate, depositing on the floor of a water body. But a metal may go back to the dissolved form due to mineralization processes mediated by the biota or, as also observed, the desorption of particles, which in turn depends on physicochemical parameters like the levels of dissolved oxygen, redox potential, pH, and sulfide concentration (MOZETO, 2004; GUILHERME et al., 2005).

In this scenario, it is important to highlight the fundamental role of flood pulses in the ecological interactions between terrestrial and aquatic ecosystems in the Amazon (JUNK; WANTZEN, 2003; VIERS et al., 2005). The changeable physical and chemical patterns in the aquatic environments in the Amazon influence the distribution of metals in these ecosystems (GUINOISEAU et al., 2016). For example, the sediments in blackwater rivers such as Negro River are rich in organic matter. This means that the metals found in these rivers originate mainly from the leaching of the forest soils along their banks, where more mobile elements like zinc (Zn) and copper (Cu) may adsorb onto the organic substrate, entering riverine and lacustrine systems (LACERDA et al., 1990). On the other hand, whitewater rivers like the Madeira and the Solimões have high levels of cations like Ca^{2+} and Mg^{2+}, which account for 48% and 28%, respectively, of the total concentration of cations in these water bodies (LEITE et al., 2011). These rivers also have significant amounts of suspended sediment material, which are predominantly clay sediments (illite and chlorite) (GUYOT et al., 2007). In the water column, elements like iron (Fe), aluminum (Al), and manganese (Mn) bind mainly to the particulate fraction under 0.22 μm in size (AUCOUR et al., 2003; GUINOISEAU et al., 2016). Except for studies that looked into the pollution caused by mercury (Hg) (PFEIFFER; LACERDA, 1988; PFEIFFER et al., 1989; BASTOS et al., 2006, 2007), the region of the Amazonian lakes in the Madeira River has not been comprehensively investigated for the presence of other metals and their dynamic in these environments.

Sioli (1979) proposed a classification of the waters of the Amazon basin based on the differences in physical and chemical characteristics, but Lacerda et al. (1990) showed that this classification should be used to understand the dynamic of metal levels in the sediments of Madeira River. The authors also noted the significant variation in concentrations of chrome (Cr), lead (Pb), cobalt (Co), nickel (Ni), Cu, Zn, and Hg in particular, which are associated with intense gold mining (Au) along the 1,500-km-long river. However, the variation of metal levels in sediments may be the result of grain size, since finer particles tend to have a higher potential to adsorb chemical elements (SINGH et al., 2004).

Santos et al. (2015) determined the concentrations of metals like Cr, Co, Ni, Cu, Zn, and Pb in sediments in the upper Madeira River and its main tributaries. But the authors did not investigate the transfer of metals from the river mainstem to lacustrine environments, whose physical and chemical characteristics vary compared with the those of the river during the best part of a year. Knowing the dynamic of metals in the sediment of lakes is essential to understand the interactions between riverine and lacustrine systems (JUNK; WANTZEN, 2003; GUILHERME et al., 2005). For example, chemical elements like Al, Mn, Fe, Co, Cu, Mo, Rb, Sr, Ba, and U are cycled in floodplains and vegetation, showing that these areas play a fundamental role in the maturation of sediment and transfer of metals to the mainstem (VIERS et al., 2005; BOUCHEZ et al., 2012).

Factors like the construction of hydropower plants, the establishment of river navigation routes, the growth of the industrial sector, and the expansion of urban environments point to the increase of the anthropic contribution to the natural cycle of metals in the Madeira River Basin (LEITE et al., 2011; SANTOS et al., 2015). The study of heavy metals in lacustrine environments in the Madeira River Basin is an important tool to monitor these environments. In addition, the transfer of metals from whitewater to blackwater rivers has not been investigated in this important aquatic ecosystem. In this context, the present study analyzed the presence of metals in areas characterized by low anthropic activity in the Madeira River Basin, and sheds light on the spatial dynamic of the accumulation of metals in the bottom sediment of Puruzinho Lake, state of Amazonas (AM), Brazil. We studied the compartmentalization of this water body based on the formation of accumulation zones influenced by the interaction between the mainstem flow of Madeira River and the waters of Puruzinho Lake.

MATERIALS AND METHODS

Study area

The study area included Puruzinho Lake, located on the left bank of the lower Madeira River, 20 km away from the town of Humaitá, state of Amazonas (AM), north Brazil (Figure 1).

Table 1. Percent recovery of metals in sediments collected in Puruzinho Lake, Amazon, Brazil against standard soil material (EnviroMatt SS2 – SCP-SCIENCE, 2005).

Reference material (SS2)	[Co] $mg.kg^{-1}$	[Mn] $mg.kg^{-1}$	[Cr] $mg.kg^{-1}$	[Cu] $mg.kg^{-1}$	[Pb] $mg.kg^{-1}$	[Zn] $mg.kg^{-1}$	[Fe] $g.kg^{-1}$
Reference value	12.0	457.0	34.0	191.0	126.0	467.0	21.5
Value found	11.7	385.3	36.5	216.5	130.4	498.3	16.8
Recovery (%)	98	84	107	113	103	107	80

The Madeira River Basin covers three countries (Bolivia, Brazil, and Peru), representing 23% of the Amazon basin in area and draining 35% of the Andean strip in the Amazon basin (GUYOT et al., 1999). Mean annual flow rate of Madeira River discharges 26,820 $m^3 \cdot s^{-1}$ of water, and the basin covers 1,420,000 km^2. The mean flow of suspended solids is $406 \cdot 10^3$ $t \cdot year^{-1}$ (MOLINIER et al., 1994; GUYOT et al., 1999; FILIZOLA; GUYOT, 2011).

The environment investigated is a *ria*, an arm formed by *Igarapé* Puruzinho. Lake Puruzinho is located in a flood and storage area (FSA) formed by river sediments and has the same characteristics as the Western Amazon depression (IBGE, 1978). Similarly to the other rivers on the left bank of Madeira River, the mouth of *Igarapé* Puruzinho is flooded during the rainy season due to the rise in levels of the Madeira River.

During the dry season, the *igarapé* flows along a narrow canal, while the lacustrine formation called *ria* is seen 5 km upstream the mouth.

Mean annual rainfall varies between 1,800 mm and 2,800 mm. The rainy season lasts from December to May, while the dry season starts in June and ends in November (LEOPOLDO, 1983; LEOPOLDO et al., 1987). The soil is formed by recent clay and silt sedimentary deposits established in the Quaternary. The plant cover includes open stand riparian forests or pioneer grasslands (IBGE, 1978). These forest areas are flooded by the water that accumulates in the basin, in a condition that persists during the rainy season and the beginning of the dry season.

Experimental design

The experimental design was based on the methodology proposed by Bernardi et al. (2001). Briefly, 11 transects were established by GPS, nine of which had three collection points (one on each margin and one halfway along the transect). Two transects had collection points halfway along the transect only. In total, 29 points were defined. The mean distance between transects was 1,000 m, totaling a surveyed area measuring 10 km in length.

Additionally, the area was divided in two zones. Zone **A** is characterized by no direct influence of the waters of Madeira River on the physical and chemical characteristics of Puruzinho Lake, and included six transects (1 to 6, n = 14; four transects had two collection points on either margin and one point halfway along the transect, and two had collection points only halfway along the transect). Zone **B** is exposed to the influence of the clear waters of Madeira River, and included transects 7 to 11, (n = 15) (Figure 1).

Collection and analyses

The values of limnologic parameters like pH, electric conductivity, temperature, and dissolved oxygen were obtained from the study published by Almeida et al. (2014) about the behavior of Hg. That study was carried out concomitantly with the present work. Bottom sediments were collected using an Ekman dredge during the floods. Samples were stored in self-sealing plastic bags and immediately chilled. Next, samples were shipped to the Environmental Biogeochemistry Laboratory Wolfgang Christian Pfeiffer, Federal University of Rondônia, Brazil. Subsequently, they were wet-sifted through a 200 mesh size sieve shaker (Bertel 9601) to obtain the 0.075 mm fraction of the sediment. After, samples were dried in an oven at 40 °C, macerated, and stored in polyethylene vials upon quantification of metals.

Levels of Co, Cu, Cr, Pb, Mn, Zn, and Fe were determined using a 2.0 g sample of dry sediment. Briefly, the sample was weighed in an 80 mL beaker. Next, 10.0 mL HNO_3 65%, 20.0 mL H_2O_2 30%, and 10.0 mL HCl 37% (Tédia Brasil) were added. The mixture was heated to 80 °C on a heating plate and kept at this temperature for 16 h. After extraction and drying, samples were resuspended in 20.0 mL HCl 0.1 N and strained through a paper filter (Whatman 44) (USEPA, 1996). Levels of metals were determined by flame atomic absorption spectrophotometry (AAS - GBC Avanta, Modelo-3000).

Two samples collected in each point were analyzed, and two spectrophotometry readings were carried out for each replicate. Therefore, the values used presented relative standard deviation (RSD) below 15%. Research has established that RSD values of up to 20% are acceptable in the analysis of trace elements (RIBANI et al., 2004).

A control blank was analyzed for each duplicate, and all chemicals were of analytical grade. Also, EnviroMAT SS-2 (SCP Science 140-025-002, QC, Canada) was used as soil reference material for analysis (SCP-SCIENCE, 2005). Percent recovery of metals remained within accuracy and precision standards of 80% to 120% (Table 1). Recovery values between 80% and 120% with precision of 20% are considered acceptable; however, precision of 15% may be adopted depending on the kind of sample and the intrinsic complexity of analysis (RIBANI et al., 2004).

All analytical solutions were prepared with ultrapure water (Milli-Q Plus, Millipore, Bedford, MA USA). All glassware was previously decontaminated with HNO_3 5% for 24 h and then rinsed with ultrapure water.

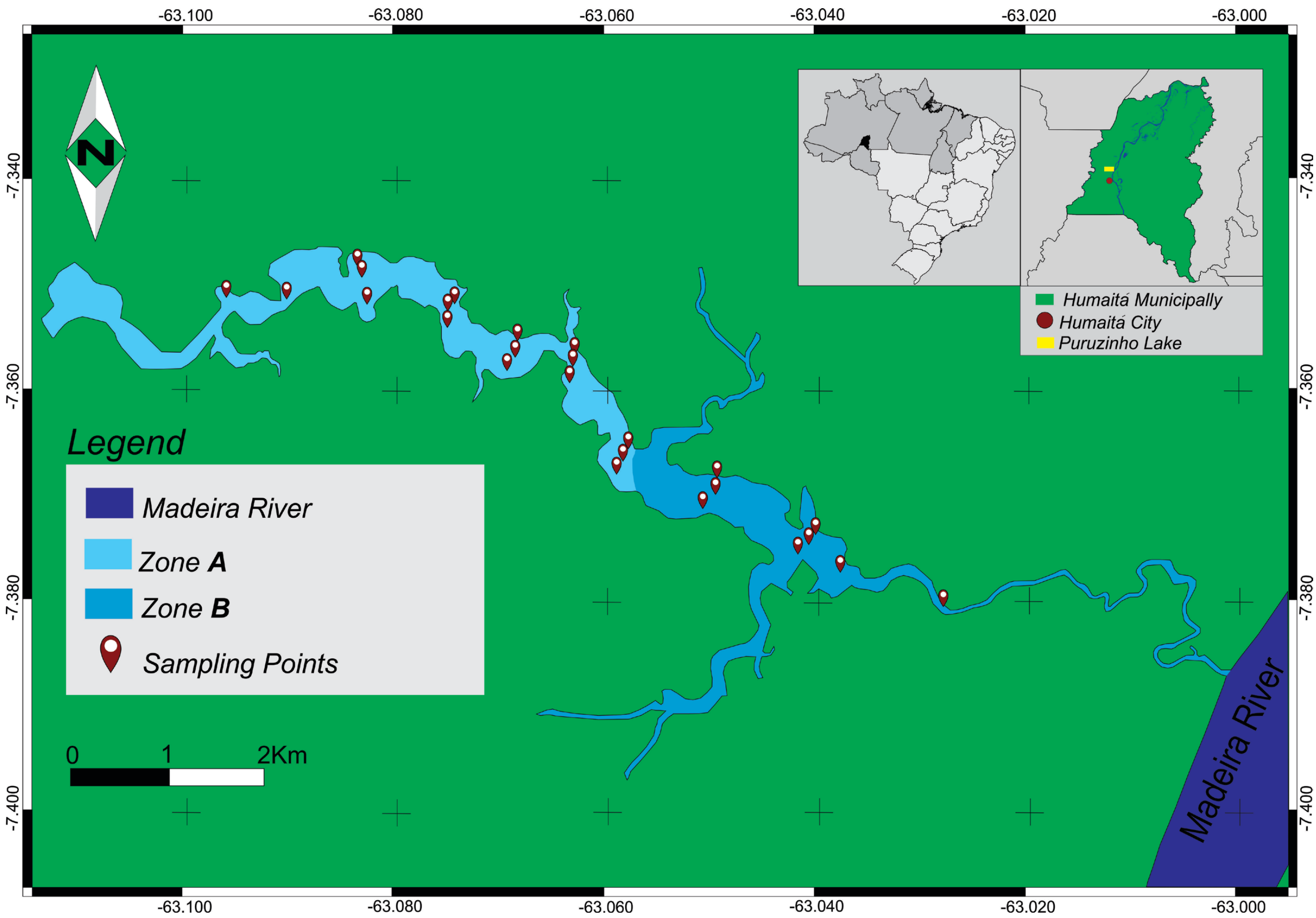

Figure 1. Area of study in Puruzinho Lake (AM) revealing the sample design.

Statistical analysis

Normality of data was assessed using the Shapiro-Wilk test ($\alpha = 0.05$). Data were normalized using the logarithmic function $y = \log(x) + 1$, according to Zar (2010). The one-way ANOVA was used to test the significant difference between mean metal levels in the two zones (**A** and **B**, not exposed and exposed to the influence of the whitewaters of Madeira River, respectively).

The principal component analysis (PCA) was used to arrange the distribution of metals along the deposition gradient at the interface of Puruzinho Lake and Madeira River. The results obtained for the first two axes of the PCA were used as predictor variables to assess the spatial effect of the influence of Madeira River waters on the distribution profile of the metals and on the hydrological patterns of the aquatic system studied (the distance between the collection points and Madeira River).

RESULTS AND DISCUSSION

While pH of sediment samples varied between 4.90 and 5.85 during the study, etectric conductivity oscillated between 7.50 $\mu S \cdot cm^{-1}$ and 11.00 $\mu S \cdot cm^{-1}$. Water levels increase in the floodplains of Puruzinho Lake between November and March, when the dry season starts, which lasts until June. The maximum volumes of water transported from the lake to Madeira River are observed in August and September. This pattern of residence and transport has been observed by Viers et al. (2005) in other lakes of the Amazon, this demonstrates the long residence times of water in these floodplains.

According to Junk and Wantzen (2003), the physical and chemical characteristics of floodplains are influenced by the flooding of vast areas covered with vegetation that produces large amounts of organic matter, which is gradually deposited in the environment during the dry season. As water levels rise, the organic matter in flooded plains is oxidized, in a process that consumes oxygen and promotes hypoxia of the aquatic environment. The data obtained in the present study highlight the depletion of dissolved oxygen in Puruzinho Lake during the floods. Almeida et al. (2014) observed that the concentration of dissolved oxygen in the same period varied between 2.69 $mg \cdot L^{-1}$ and 3.82 $mg \cdot L^{-1}$. Also, the authors noted that the highest value of electric conductivity (11.0 $\mu S \cdot cm^{-1}$) was recorded near the mainstem of the lake, where the water is influenced by the river.

The concentrations of metals obtained point to the compartmentalization of Puruzinho Lake. The lowest levels of metals were detected in zone **A** (points 1 to 6), where the lake waters are less exposed to the river. Zone **B** includes points 7 to 11 and is under the direct influence of the waters of Madeira River during floods (Figure 1). The descriptive statistics and the one-way ANOVA results for zones **A** and **B** are shown in Table 2. The lowest levels of all chemical elements analyzed were observed in zone **A**, which is not exposed to the direct influence of Madeira River. Almeida et al. (2014) concluded that the concentration of organic matter in the sediment is lower in zone **B**, which is under the direct influence of Madeira River waters, showing that organic sediment comes from zone **A**, which is not exposed to the direct action of these waters.

Aquatic blackwater environments such as Puruzinho Lake are rich in organic matter (ALMEIDA et al., 2014). The metals present in these environments originate mainly from the leaching of the soil of adjacent forests, where more mobile elements like Zn and Cu may adsorb onto organic substrates and subsequently enter the river system (LACERDA et al., 1990). Dissolved organic matter plays an essential role in natural aquatic ecosystems, especially because metals like Cu(II), Cd(II), and Pb(II) interact with it by adsorption, ionic exchange, or complexation (BEZERRA et al., 2009). In the natural environment, Zn is normally found as sulfide, and may associate with metals like Pb, Cd and Cu (SIQUEIRA et al., 2006). The level of Zn obtained in the present study is similar to the values recorded by Siqueira et al. (2006) (52.8 and 159.5 $mg.kg^{-1}$). For the authors, these values are due to the presence of sediments rich in organic matter; also, they note that the concentrations of Zn in coastal sediments are around 4.39 $mg \cdot kg^{-1}$. Pb is a cationic metal of low mobility in soils, since it forms a complex by adsorption onto minerals. In the ecotone water-sediment, Fe(III) and Mn(IV) oxides may be reduced under anoxic conditions, releasing cationic metals like (Cu(II), Cd(II), Zn(II) and Pb(II), which were adsorbed onto it (GUILHERME et al., 2005).

The one-way ANOVA revealed significant differences between concentrations of metals in zones **A** and **B** ($p < 0.05$). Higher values were observed in zone **B**, which is more exposed to the waters of Madeira River (Table 2). However, the levels of Zn and Pb did not vary significantly between the two zones of Puruzinho Lake.

The PCA demonstrated the differences in metal distribution for the two zones. Two data clusters were formed: one corresponds to the transects 1 to 6 (zone **A**), one corresponds to transects 7 to 11 (zone **B**), indicating the zoning of the lake due to the influence of the whitewaters of Madeira River (Figure 2).

Table 2. Descriptive statistics of the metal concentrations ($mg.kg^{-1}$) in the bottom sediment of Puruzinho Lake, Amazon, Brazil.

Metal	Zone (A) (n = 14) No direct influence of Madeira River				Zone (B) (n = 15) Under direct influence of Madeira River				*F*	*p-value*
	Min	Max	Mean	SD	Min	Max	Mean	SD		
Pb	8.2	15.5	11.9	2.5	5.4	16.5	10.8	2.6	1.359	0.2540
Co	1.9	7.7	5.4	1.6	4.4	11.1	8.6	1.9	13.540	0.0010*
Cu	4.1	16.4	11.1	3.0	10.4	22.4	17.3	3.1	17.650	0.0020*
Cr	6.8	19.3	11.8	3.4	12.6	24.2	16.8	3.3	16.010	0.0004*
Mn	33.8	86.9	63.6	17.8	59.1	568.3	222.0	166.1	31.610	0.0001*
Zn	17.9	113.9	66.6	24.6	26.9	112.9	74.9	27.6	0.525	0.4752
Fe	8465.7	28929.7	17115	6416.8	15949.9	42626.4	27492.5	8567.6	14.150	0.0008*

* One-way ANOVA indicates the significant difference between Zone **A** and Zone **B** ($p < 0.05$).

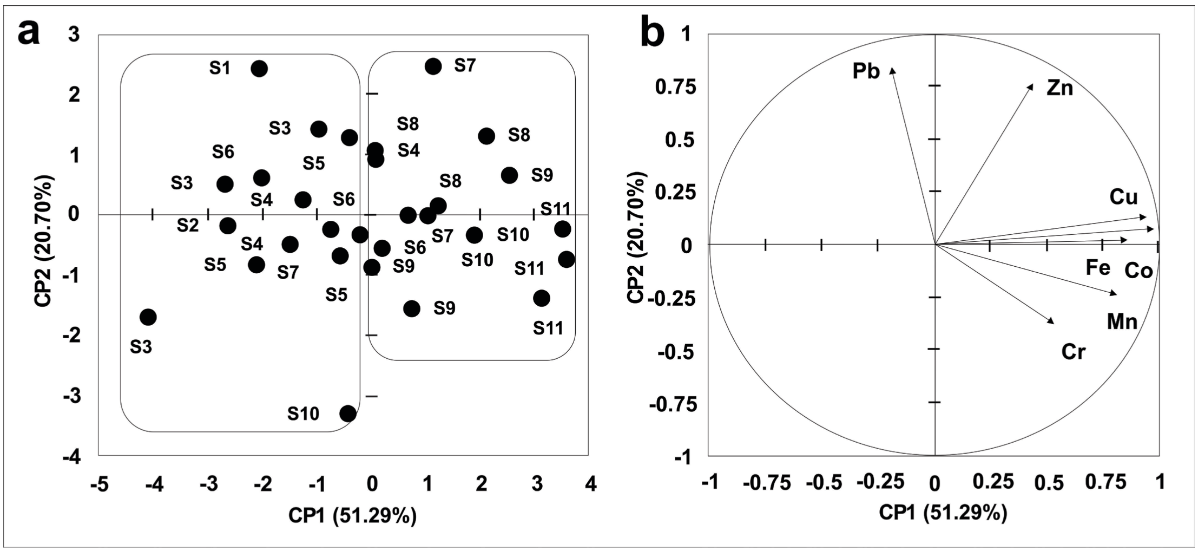

Figure 2. Principal components analysis for metals in the bottom sediment of Puruzinho Lake. (a) projection of the points surveyed; (b) projection of metals.

The seasonal change in residence and resuspension of sediment has been observed in rivers of all sizes across the globe (MEADE et al., 1985). Eventually, these seasonal patterns may influence compartmentalization of metals in sediments of lacustrine environments, such as Puruzinho Lake (Figure 2). Zone **B** is exposed to strong influence of Madeira River in the transport of metals by suspended particulate matter (SPM), since the SPM in Madeira River is composed mainly by clays like kaolinite, smectite, chlorite, and illite (chlorite group + illite = approximately 30%) of Andean origin (GUYOT et al., 2007). These clay minerals have high cationic exchange potential (KABATA-PENDIAS, 2011), which explains why they play such an important role in the transport of metals like Cu, Zn, Pb, Ni and Co in the natural environment, because these elements normally occur as cations in aquatic systems. The presence of smectite indicates lateral erosion of mature sediments, which are not necessarily Andean in the present case, suggesting that the Madeira sediments are a mixture of Andean sediments and those that are remobilized from margins and tertiary terraces (GUYOT et al., 2007). The PCA also demonstrates the correlating between the set of variables analyzed (Figure 2). The first two axes explained 71.9% of the global variance of data. The highest concentrations of elements like Cu, Co, Cr, Mn and Fe were observed between points 7 and 11, located in the region that is more exposed to the SPM in Madeira River during the floods. In the natural environment, elements like Cu, Cr, Pb, Fe and Al are found associated with SPM. However, a different situation is observed for Zn and Cd: between 30% and 40% of these metals remain in suspension (FORSTNER, 1977; BUBB; LESTER, 1991).

The *ria* formed by Puruzinho Lake and the lateral flood caused by Madeira River control the horizontal deposition of sediments along the mainstem of the lake. Immediately after the lake is formed, the river banks shrink, becoming an *igarapé furo* as it reaches Madeira River, like flooded *igarapé,* which is characteristic of the rivers on the left bank of Madeira River (Figure 1).

The formation of these two environments next to each other that yet have different chemical and physical characteristics generates an ecotone, with direct implications in metal accumulation.

The data obtained in this study also show that metals occurring as particulate matter may deposit on the bottom of Puruzinho Lake, which means that the levels of these metals may increase during the floods in the zones more exposed to the influence of Madeira River. But the waters of the lake are not affected by those of the river in the dry season, when part of the sediment deposited during the floods is remobilized. The deposition of sediments rich in metals and the cycle of resuspension of these elements influence the mass balance of metals. Besides, these processes are considered an important source of metals in the water column (CHON et al., 2012).

The concentrations of metals in Puruzinho Lake are considerably different from the values recorded for other aquatic systems in the Madeira River Basin (Table 2). In some cases, the maximum values were 10 times as high as the minimums, indicating the high degree of diversity across the ecosystems forming Madeira River Basin (Table 3).

The concentrations of metals varied between zone **A** and zone **B** in Puruzinho Lake. This zoning is governed by forces that work transversally to the river flow as of flooding of plains, forming ecotones, as observed by Neiff (2003).

During the rainy season, the waters of Madeira River invade the floodplains, influencing the physical and chemical characteristics of tributaries and marginal lakes. In turn, this affects the biogeochemical cycle and the patterns of mobilization and accumulation of metals in these areas.

Viers et al. (2005) observed that large amounts of metals that mobilize from water and sediment may accumulate in plants, returning to the dissolved phase when these die, eventually accumulating again in the sediment. The high variation in the concentration of metals is partly due to the oscillations in the conditions that favor redox reactions, which control mainly the levels of Fe and Mn in lakes in floodplains (GUILHERME et al., 2005).

The high levels of SPM transported by Madeira River (GUYOT et al., 1999) are deposited on the floodplains. But the metals mobilized by SPM in Madeira River are more likely to reach the lake as the level of the river rises, depending on the duration of the process. The rise in the level of the river reverts the direction of the flow, forming a physicochemical gradient due to the mixture of the waters of the lake and of the river (ALMEIDA et al., 2014). This gradient affects the deposition of sediments and, as a result, the transfer of metals from SPM to the bottom sediment (Figure 3). Aucour et al. (2003) observed that the levels of Fe, Al and Mn in SPM are 10 times as high in Solimões River that in Negro River. The authors noted that these metals mobilize from SPM to the dissolved phase in the zone where the whitewaters of Solimões River mix with the blackwaters of Negro River.

Table 3. Comparison of the concentration of metals (minimum, maximum, and standard deviation) in the bottom sediment in different fluvial systems of the Madeira River Basin.

Fluvial system	Pb ($mg.kg^{-1}$)	Co ($mg.kg^{-1}$)	Cu ($mg.kg^{-1}$)	Cr ($mg.kg^{-1}$)	Mn ($mg.kg^{-1}$)	Zn ($mg.kg^{-1}$)
Madeira River[a*]	6.7-22.9	7.1-17.9	9.9-25.6	2.6-14.1	-	18.4-117.7
Jaci Paraná River[a***]	3.0-21.3	1.6-9.9	0.9-17.1	2.2-11.1	-	13.5-124.8
Branco River[a*]	2.3-19.7	2.6-11.7	4.7-17.1	3.2-11.7		18.6-88.7
Madeira River[b*]	24.0±7.1	29.0±5.5	27.0±24.0	52.0±9.8	409.0±76.0	101.0±30.0
Tributaries of Madeira River[b**]	39.0±20.0	22.0±5.0	276.0±250.0	46.0±15.0	293.0±97.0	223.0±168.0
Tributaries of Madeira River[b***]	43.0±23.0	28.0±6.0	12.40±10.1	33.0±6.0	1092.0±938.0	194.0±110.0
Mamoré River[c***]	5.9	7.1	8.5	6.0	260.7	55.0

Whitewaters *; Blackwaters **; Clearwaters ***; [a] Santos et al. (2015); [b] Lacerda et al. (1990); [c] Bernardi et al. (2009).

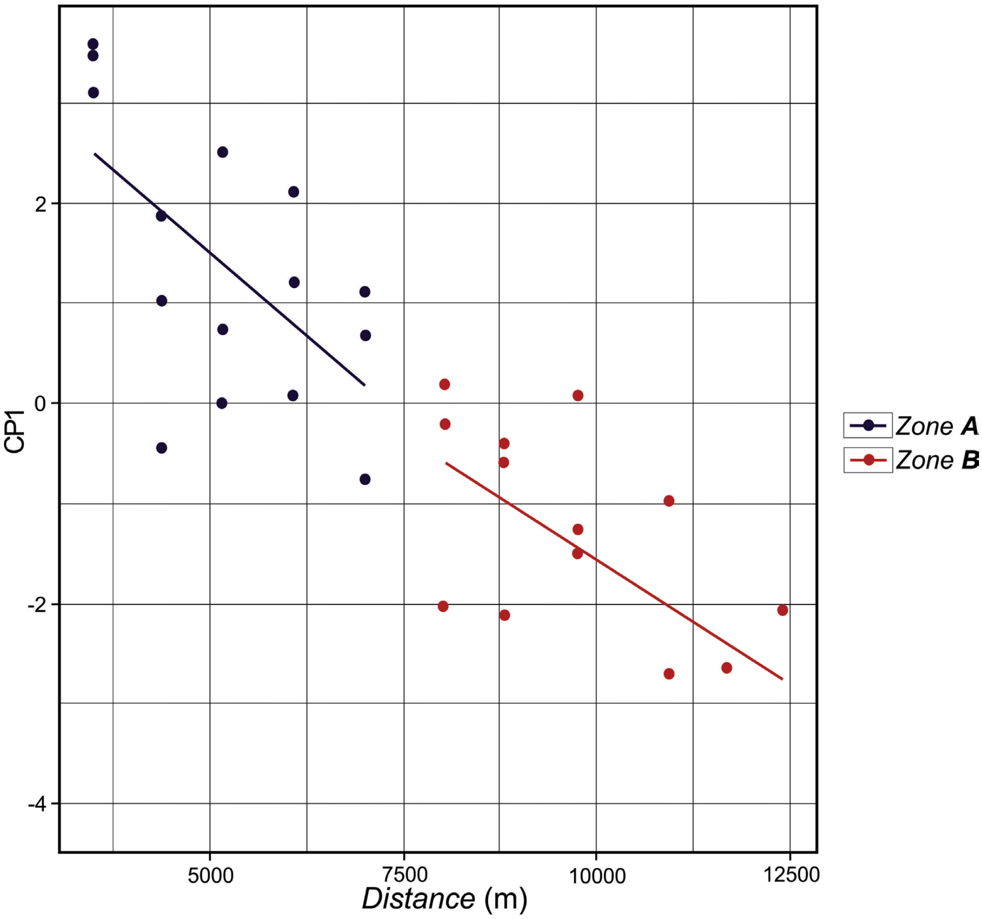

Figure 3. Linear regression of the scores of component 1 *versus* the distance of the points sampled and the channel of the Madeira River.

Previous research showed that the electric conductivity of the waters of Madeira River varied between 71.8 $\mu S.cm^{-1}$ and 95.7 $\mu S.cm^{-1}$, while pH oscillated between 6.50 and 7.20 (BERNARDI et al., 2009). In turn, the values observed for Puruzinho Lake varied from 7.5 $\mu S.cm^{-1}$ to 11.0 $\mu S.cm^{-1}$, and pH was low, between 4.90 and 5.85 (ALMEIDA et al., 2014). This indicates that Madeira River, with its whitewaters rich in metals bound to SPM, plays a significant role in the mobilization and accumulation of metals in sediments of lakes associated with this aquatic system.

The concentrations of metals obtained in the present study are lower than the maximum permissible values established by CETESB (2006), suggesting that these metals are not contaminating Puruzinho Lake. Nevertheless, several anthropic factors may alter the distribution pattern of metals in the environments around the Madeira River Basin, like the expansion of the agricultural boundaries towards the west Amazon facilitated by restoration of an important highway in the region (which connects the capital cities of the states of Amazonas and Rondônia), the increase in hydropower generation due to the construction of plants along Madeira River, the extension of the Urucu-Amazonas-Porto Velho gas pipe, and gold and cassiterite mining activities in Madeira River Basin (in the Madre Dios River, in Peru, and Jamari River, in Rondônia state, Brazil, respectively).

CONCLUSIONS

The distribution of metals in zones in lakes is governed by transversal forces along the course of Madeira River during flooding of the plains, forming ecotones. The levels of metals obtained in the present study may be considered background values in zones not affected by pollution in the region.

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REFERENCES

ALMEIDA, R.; BERNARDI, J. V. E.; OLIVEIRA, R. C.; CARVALHO, D. P.; MANZATTO, A. G.; LACERDA, L. D.; BASTOS, W. R. Flood pulse and spatial dynamics of mercury in sediments in Puruzinho lake, Brazilian Amazon. *Acta Amazonica*, v. 44, n. 1, p. 99-105, 2014. http://dx.doi.org/10.1590/S0044-59672014000100010.

AUCOUR, A.-M.; TAO, F.-X.; MOREIRA-TURCQ, P.; SEYLER, P.; SHEPPARD, S.; BENEDETTI, M. F. The Amazon River: behaviour of metals (Fe, Al, Mn) and dissolved organic matter in the initial mixing at the Rio Negro/Solimões confluence. *Chemical Geology*, v. 197, n. 1-4, p. 271-285, 2003. http://dx.doi.org/10.1016/S0009-2541(02)00398-4.

BASTOS, W. R.; ALMEIDA, R.; DÓREA, J. G.; BARBOSA, A. C. Annual flooding and fish-mercury bioaccumulation in the environmentally impacted Rio Madeira (Amazon). *Ecotoxicology*, v. 16, n. 3, p. 341-346, 2007. http://dx.doi.org/10.1007/s10646-007-0138-0. PMid:17356898.

BASTOS, W. R.; GOMES, J. P. O.; OLIVEIRA, R. C.; ALMEIDA, R.; NASCIMENTO, E. L.; BERNARDI, J. V. E.; LACERDA, L. D.; SILVEIRA, E. G.; PFEIFFER, W. C. Mercury in the environment and riverside population in the Madeira River Basin, Amazon, Brazil. *The Science of the Total Environment*, v. 368, n. 1, p. 344-351, 2006. http://dx.doi.org/10.1016/j.scitotenv.2005.09.048.

BERNARDI, J. V. E.; FOWLER, H. G.; LANDIM, P. M. B. Um estudo de impacto ambiental utilizando análises estatísticas espacial e multivariada. *Holos Environment*, v. 1, n. 2, p. 162-172, 2001. http://dx.doi.org/10.14295/holos.v1i2.1625.

BERNARDI, J. V. E.; LACERDA, L. D.; DÓREA, J. G.; LANDIM, P. M. B.; GOMES, J. P. O.; ALMEIDA, R.; MANZATTO, A. G.; BASTOS, W. R. Aplicação da análise das componentes principais na ordenação dos parâmetros físico-químicos no Alto Rio Madeira e afluentes, Amazônia Ocidental. *Geochemica Brasiliensis*, v. 23, n. 1, p. 79-90, 2009.

BEZERRA, P. S. S.; TAKIYAMA, L. R.; BEZERRA, C. W. B. Complexação de íons de metais por matéria orgânica dissolvida: modelagem e aplicação em sistemas reais. *Acta Amazonica*, v. 39, n. 3, p. 639-648, 2009. http://dx.doi.org/10.1590/S0044-59672009000300019.

BOUCHEZ, J.; GAILLARDET, J.; LUPKER, M.; LOUVAT, P.; FRANCE-LANORD, C.; MAURICE, L.; ARMIJOS, E.; MOQUET, J. Floodplains of large rivers: weathering reactors or simple silos? *Chemical Geology*, v. 332-33, p. 166-184, 2012. http://dx.doi.org/10.1016/j.chemgeo.2012.09.032.

BUBB, J. M.; LESTER, J. N. The impact of heavy metals on lowland rivers and the implications for man and the environment. *The Science of the Total Environment*, v. 100, p. 207-233, 1991. http://dx.doi.org/10.1016/0048-9697(91)90379-S. PMid:2063183.

CETESB – COMPANHIA DE TECNOLOGIA DE SANEAMENTO AMBIENTAL. *Critério para avaliação da qualidade de sedimento*. São Paulo, 2006. Available from: <www.cetesb.sp.gov.br>. Access on: 14 feb. 2017.

CHON, H.; OHANDJA, D.; VOULVOULIS, N. The role of sediments as a source of metals in river catchments. *Chemosphere*, v. 88, n. 10, p. 1250-1256, 2012. http://dx.doi.org/10.1016/j.chemosphere.2012.03.104. PMid:22546630.

FILIZOLA, N.; GUYOT, J. L. Fluxo de sedimentos em suspensão nos rios da Amazônia. *Revista Brasileira de Geociencias*, v. 41, n. 4, p. 566-576, 2011. http://dx.doi.org/10.25249/0375-7536.2011414566576.

FORSTNER, U. Forms and sediment associations of nutrients (C N & P) pesticides and metals trace. In: SHEAR, H.; WATSON, A. E. P. (Ed.). *The fluvial transport of nutrients and contaminants*. Kitchener: International Joint Commission, 1977. p. 255-266.

GUILHERME, L. R. G.; MARQUES, J. J.; PIERANGELI, M. A. P.; ZULIANI, D. Q.; CAMPOS, M. L.; MARCHI, G. Elementos-traço em solos e sistemas aquáticos. *Tópicos em Ciência do Solo*, v. 4, p. 345-390, 2005.

GUINOISEAU, D.; BOUCHEZ, J.; GÉLABERT, A.; LOUVAT, P.; FILIZOLA, N.; BENEDETTI, M. F. The geochemical filter of large river confluences. *Chemical Geology*, v. 441, p. 191-203, 2016. http://dx.doi.org/10.1016/j.chemgeo.2016.08.009.

GUYOT, J. L.; JOUANNEAU, J. M.; SOARES, L.; BOAVENTURA, G. R.; MAILLET, N.; LAGANE, C. Clay mineral composition of river sediments in the Amazon Basin. *Catena*, v. 712, n. 2, p. 340-356, 2007. http://dx.doi.org/10.1016/j.catena.2007.02.002.

GUYOT, J. L.; JOUANNEAU, J. M.; WASSON, J. G. Characterization of river bed and suspended sediments in the Madeira River drainage basin (Bolivian Amazonian). *Journal of South American Earth Sciences*, v. 12, n. 4, p. 401-410, 1999. http://dx.doi.org/10.1016/S0895-9811(99)00030-9.

IBGE – INSTITUTO BRASILEIRO DE GEOGRAFIA E ESTATÍSTICA. *Folha SB. 20 Purus*: geologia, geomorfologia, pedologia, vegetação, uso potencial da terra/Projeto RADAMBRASIL. 1. ed. Rio de Janeiro: Projeto Radam Brasil, 1978.

JUNK, W. J.; WANTZEN, K. M. The flood pulse concept: new aspects, approaches, and applications: an update. In: INTERNATIONAL SYMPOSIUM ON THE MANAGEMENT OF LARGE RIVERS FOR FISHERIES, 2., Bangkok. *Proceedings*… Rome: FAO, 2003. p. 117-140. Available from: <http://www.fao.org/docrep/007/ad526e/ad526e0c.htm>. Access on: 14 feb. 2017.

KABATA-PENDIAS, A. *Trace elements in soils and plants*. 4th ed. Boca Raton: Taylor & Francis, 2011. 534 p.

LACERDA, L. D.; DE PAULA, F. C. F.; OVALLE, A. R. C.; PFEIFFER, W. C.; MALM, O. Trace metals in fluvial sediments of the Madeira River watershed, Amazon, Brazil. *The Science of the Total Environment*, v. 97-98, p. 525-530, 1990. http://dx.doi.org/10.1016/0048-9697(90)90261-R.

LEITE, N. K.; KRUSCHE, A. V.; BALLESTER, M. V. R.; VICTORIA, R. L.; RICHEY, J. E.; GOMES, B. M. Intra and interannual variability in the Madeira River water chemistry and sediment load. *Biogeochemistry*, v. 105, n. 1, p. 37-51, 2011. http://dx.doi.org/10.1007/s10533-010-9568-5.

LEOPOLDO, P. R. The hydrology of the Amazon region. *The Environmentalist*, v. 3, n. 5, p. 7-12, 1983. http://dx.doi.org/10.1007/BF01910241.

LEOPOLDO, P. R.; FRANKEN, W.; SALATI, E.; RIBEIRO, M. N. Towards a water balance in the Central Amazonian region. *Experientia*, v. 43, n. 3, p. 222-233, 1987. http://dx.doi.org/10.1007/BF01945545.

LOPES, L. F.; COSTA, A. C. S.; D'OLIVEIRA, P. S.; GIL, L. G. Utilização agrícola de lodo industrial como fonte de zinco na cultura do crisântemo. *Horticultura Brasileira*, v. 22, n. 3, p. 620-623, 2004. http://dx.doi.org/10.1590/S0102-05362004000300024.

MEADE, R. H.; DUNNET, T.; RICHEY, J. E.; SANTOS, U. M.; SALATI, E. Storage and remobilization of suspended sediment in the lower Amazon river of Brazil. *Science*, v. 228, n. 4698, p. 488-490, 1985. http://dx.doi.org/10.1126/science.228.4698.488. PMid:17746891.

MOLINIER, M.; GUYOT, J. L.; OLIVEIRA, E.; GUIMARÃES, V.; CHAVES, A. Hidrologia da Bacia do Rio Amazonas. *A Água em Revista*, v. 2, n. 3, p. 31-36, 1994.

MOZETO, A. A. Sedimentos e particulados lacustres: amostragens e análises biogeoquímicas. In: BICUDO, C. E. M.; BICUDO, D. C. (Ed.). *Amostragem em limnologia*. São Carlos: RiMa, 2004. 371 p.

NEIFF, J. J. Planícies de inundação são ecótonos? In: HENRY, R. (Ed.). *Ecótonos nas interfaces dos ecossistemas aquáticos*. São Carlos: RIMa, 2003. p. 31-57.

NRIAGU, J. O.; PACYNA, J. M. Quantitative assessment of worldwide contamination of air, water and solis by trace metals. *Nature*, v. 333, n. 6169, p. 134-139, 1988. http://dx.doi.org/10.1038/333134a0. PMid:3285219.

PFEIFFER, W. C.; LACERDA, L. D. Mercury inputs into the Amazon Region, Brazil. *Environmental Technology*, v. 9, n. 4, p. 325-330, 1988. http://dx.doi.org/10.1080/09593338809384573.

PFEIFFER, W. C.; LACERDA, L. D.; MALM, O.; SOUZA, C. M. M.; SILVEIRA, E. G.; BASTOS, W. R. Mercury concentrations in inland waters of gold-mining areas in Rondônia, Brazil. *The Science of the Total Environment*, v. 87-88, p. 233-240, 1989. http://dx.doi.org/10.1016/0048-9697(89)90238-6. PMid:2609151.

RIBANI, M.; BOTTOLI, C. B. G.; COLLINS, C. H.; JARDIM, I. C. S. F.; MELO, L. F. C. Validação em métodos cromatográficos e eletroforéticos. *Quimica Nova*, v. 27, n. 5, p. 771-780, 2004. http://dx.doi.org/10.1590/S0100-40422004000500017.

RIBEIRO, D. R. G.; FACCIN, H.; MOLIN, T. R. D.; CARVALHO, L. M.; AMADO, L. L. Metal and metalloid distribution in different environmental compartments of the middle Xingu River in the Amazon, Brazil. *The Science of the Total Environment*, v. 605-606, p. 66-74, 2017. http://dx.doi.org/10.1016/j.scitotenv.2017.06.143. PMid:28654810.

SAHOO, P. K.; GUIMARÃES, J. T. F.; SOUZA-FILHO, P. W. M.; SILVA, M. S.; NASCIMENTO, W.; POWELL, M. A.; REIS, L. S.; PESSENDA, L. C. R.; RODRIGUES, T. M.; SILVA, D. F.; COSTA, V. E. Geochemical characterization of the largest upland lake of the Brazilian Amazonia: Impact of provenance and processes. *Journal of South American Earth Sciences*, v. 80, p. 541-558, 2017. http://dx.doi.org/10.1016/j.jsames.2017.10.016.

SANTOS, R. I.; BRAGA, N. A.; RECKTENVALD, M. C. N. N.; DE CARVALHO, D. P.; MIRANDA, M. R.; MANZATTO, A. G.; BASTOS, W. R. Metais em sedimentos de fundo na bacia do alto rio Madeira, Bacia Amazônica. *Scientia Amazonia*, v. 4, n. 1, p. 91-100, 2015. http://dx.doi.org/10.19178/Sci.Amazon.v4i1.91-100.

SCP-SCIENCE. *Certified Reference Materials EnviroMAT™*. Canada: Manufacturing Division, 2005. Available from: <2017www.scpscience.com>. Access on: 14 feb. 2017.

SINGH, K. P.; MOHAN, D.; SINHA, S.; DALWANI, R. Impact assessment of treated/ untreated wastewaters toxicants discharged by sewage treatment plants on health, agricultural and environmental quality in the wastewater disposal area. *Chemosphere*, v. 55, n. 2, p. 227-255, 2004. http://dx.doi.org/10.1016/j.chemosphere.2003.10.050. PMid:14761695.

SIOLI, H. My life in the Amazon. *Biotropica*, v. 11, n. 4, p. 241-250, 1979. http://dx.doi.org/10.2307/2387916.

SIQUEIRA, G. W.; PEREIRA, S. F. P.; APRILE, F. M. Determinação dos elementos-traço (Zn, Co e Ni) em sedimentos da Plataforma Continental Amazônica sob influência da descarga do rio Amazonas. *Acta Amazonica*, v. 36, n. 3, p. 321-326, 2006. http://dx.doi.org/10.1590/S0044-59672006000300005.

USEPA – U.S. ENVIRONMENTAL PROTECTION AGENCY. *Method 3050B*: acid digestion of sediments, sludges, and soils, revision 2. Washington, 1996. 12 p.

VIERS, J.; BARROUX, G.; PINELLI, M.; SEYLER, P.; OLIVA, P.; DUPRÉ, B.; BOAVENTURA, G. R. The influence of the Amazonian floodplain ecosystems on the trace element dynamics of the Amazon River mainstem (Brazil). *The Science of the Total Environment*, v. 339, n. 1-3, p. 219-232, 2005. http://dx.doi.org/10.1016/j.scitotenv.2004.07.034. PMid:15740771.

WASSERMAN, J. C.; QUEIROZ, E. L. The attenuation of concentrations model: a new method for assessing mercury mobility in sediments. *Quimica Nova*, v. 27, n. 1, p. 17-21, 2004. http://dx.doi.org/10.1590/S0100-40422004000100004.

ZAR, J. H. *Biostatistical analysis*. 5th ed. Upper Saddle River: Prentice-Hall/Pearson, 2010. 944 p.

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