YURI JACQUES AGRA BEZERRA DA SILVA

HEAVY METALS IN WATER, SUSPENDED SEDIMENTS, AND BEDLOAD IN IPOJUCA RIVER, BRAZIL

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HEAVY METALS IN WATER, SUSPENDED SEDIMENTS, AND BEDLOAD IN IPOJUCA RIVER, BRAZIL

Thesis presented to the Graduate Program in Soil Science of the Federal Rural University of Pernambuco, as part of the requirements to obtain the Doctor Scientiae degree.

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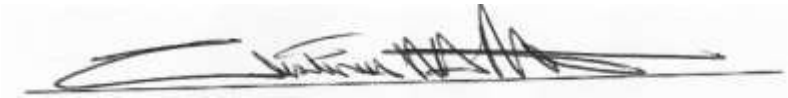

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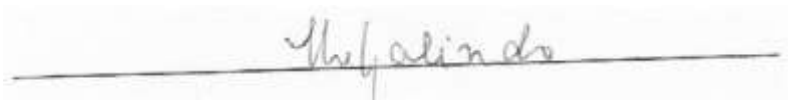

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O Senhor está sempre à nossa espera, para nos acolher no seu amor: é uma coisa maravilhosa que não cessa jamais de nos surpreender.

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CONTENTS

LIST OF FIGURES

CHAPTER I

CHAPTER II

CHAPTER III

LIST OF TABLES

CHAPTER I

CHAPTER II

CHAPTER III

BACKGROUND

Given the persistence, toxicity, and abundance, heavy metals in soils, water, and sediments have been a major concern for environmental management policies. The first step to study heavy metal contamination is taking into account the levels of metals expected to occur naturally (i.e. background concentrations) in soils or sediments. For soils, samples taken from forest areas – where the soils are mineralogically and texturally comparable with river sediments – are used; for sediments, preindustrial samples – samples that are unaffected by industrial activities – usually obtained from pristine areas or deep core samples are used.

Heavy metals in soils or sediments can originate from either natural or anthropogenic sources. Rivers play an important role in heavy metals transport from continent to oceans. Their concentration in water shows mainly a short history of contamination; however; bedload and suspended sediments can provide a long-term fingerprint of contamination in rivers, which is an effective index for changes that pose a risk to human and aquatic life.

Several effective tools have been used to assess heavy metal contamination in aquatic environments. For instance, multivariate statistical techniques; pollution index, such as contamination factor, pollution load index, and enrichment factor; and Sediment Quality Guidelines (SQGs). Applying combined tools is often recommended and both advantages and drawbacks of each tool are discussed further herein.

Regarding heavy metal contamination studies in sediments, Brazil has lagged far behind other countries. Likewise, the data are scarce along brazilian northeast region, being fundamental to study, at least, the most impacted rivers, such as Ipojuca River – a vital water resource of Northeast region and one of the most contaminated rivers in Brazil owing to industrial and economic development. Even though Ipojuca River is considered the fifth most polluted river in Brazil (SRH, 2010), very little information exists regarding the levels of heavy metals in water, suspended sediments, bedload and their respective fluxes. Therefore, our study raised the following questions: are heavy metals in sediments mainly derived from natural or anthropogenic sources? Does it pose a risk to the environment? Is bedload an adequate indicator of heavy metal contamination? What are the heavy metal fluxes in sediments of Ipojuca River?

We hypothesize that the industrial and urban growing along Ipojuca River pose a threat due to increase in heavy metal concentrations and fluxes in sediments. Based on the foregoing, the objectives of this study were (1) to determine the environmentally available metal concentrations of mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), zinc (Zn), arsenic (As), iron (Fe) and manganese (Mn) in water, suspended sediment and bedload; (2) to assess the environmental risk of these metals by comparison with sediment quality guidelines; (3) to define the degree and sources of heavy metal contamination using sediment contamination indices and multivariate techniques; and (4) to determine the heavy metal fluxes in suspended and bedload sediments. In summary, we expect to provide support for the development of future studies in the Ipojuca watershed.

CHAPTER I

HEAVY METAL CONTAMINATION IN WATER AND SUSPENDED SEDIMENTS OF THE IPOJUCA RIVER

Abstract

Environmentally available metal concentrations in water and suspended sediments of the Ipojuca River were determined to assess the level of contamination. Both water and suspended sediment samples were obtained using a depth-integrated and isokinetic sampling. Contamination assessment of ten heavy metals (As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb and Zn) was studied using enrichment factor (EF), statistical multivariate techniques and comparison with background values and sediment quality guidelines (SQGs). For both the upstream and downstream sites, the highest heavy metals concentrations in water were observed during the summer. On the other hand, no seasonal variation was observed in suspended sediment. The mean available metal concentration in suspended sediment followed the order Fe > Mn > Zn > Pb > Cr > Cu > Ni > As > Cd > Hg and Fe > Mn > Pb > Zn > Cr > Cu > Ni > As > Cd > Hg, upstream and downstream, respectively. The concentration of Mn (upstream) and Pb in both sites are likely to result in harmful effects on sediment dwelling organisms based on the comparison with SQGs. However, SQGs underestimate the harmful effect of studied metals on sediment-dwelling organisms. Notably, Pb is the most harmful of the heavy metals for aquatic life in Ipojuca River. The upstream portion of the Ipojuca River is moderately contaminated, with higher contaminant levels for Mn and As; and that the sediments of the downstream portion are highly contaminated with heavy metals, mainly Zn, Pb, and As.

Keywords: Sediment quality, Multivariate statistical techniques, Environmentally available metals, Enrichment factor.

1. Introduction

Heavy metal contamination in both water and suspended sediments is a particular concern given the toxicity, abundance, and persistence of these elements in aquatic environments. This contamination is traceable to a variety of sources, including sugarcane farming (which involves the large—and often inappropriate—use of chemical substances, such as pesticides and insecticides), domestic sewage, and wastewater from industrial and agricultural operations. Because of their sorption by sediments, only small amounts of metals get dissolved in water. As a result, sediments function as a long-term storehouse of heavy metals originating from either natural or anthropogenic sources (Sin et al., 2001; Davutluoglu et al., 2011; Nasehi et al., 2013), and from them, therefore, we can derive a short and long history of pollution in rivers (Taylor et al., 2003) —a useful indicator of changes that pose a health risk to human and aquatic life.

The simplest approach to assessing heavy metal pollution in aquatic environments is the use of sediment quality guidelines (SQGs) and/or calculation of pollution indices, as exemplified by several studies (MacDonald et al., 2000; MacDonald et al., 2003; Varejão et al., 2011; Garcia et al., 2011; Gao et al., 2012; Weber et al., 2013; Xiao et al., 2013; Gawel et al., 2014). Comparison with SQGs is essential to protect aquatic organisms, maintain water quality, and develop remediation actions. At the same time, heavy metals concentrations in sediment should be compared with data from site background samples (Adamo et al., 2005; Raju et al., 2012), to consider the levels of metals expected to occur naturally. Such an approach has been successfully used to develop guidelines and make management decisions, especially in cases lacking adequate data for the use of other approaches (CCME, 1995).

The Ipojuca River is one of the most important natural resources of Brazil, but owing to industrial and economic development, it is also one of the most polluted rivers in the country. Even though the Ipojuca is considered the fifth most polluted river in Brazil according to department of water resources (SRH, 2010), very little information exists regarding the levels of heavy metals in the water and suspended sediments. Most studies of the Ipojuca River system have focused either on modeling nutrient emissions (Barros et al., 2013), on the effects of the construction of the Industrial and Harbor Complex on the river's hydrology, chemistry, and phytoplankton (Koening et al., 2003; Muniz et al., 2005), or on contamination of the water caused by the sugarcane industry (Gunkel et al., 2007). Our study, therefore, has as objectives (1) determining the status of

heavy metal concentrations in water and suspended sediments, (2) distinguishing between natural and anthropogenic sources of metals in suspended sediments, and (3) evaluating the risk, to the environment, posed by the heavy metals in the river system (by comparison with SQGs).

2. Material and Methods

2.1 Study area

The Ipojuca watershed has a total river length of 290 km (08°09'50''– 08°40'20'' S and 34°57'52''– 37°02'48'' W). Its watercourse allows a unique opportunity to evaluate water and sediment pollution in a semiarid and coastal region of Brazil. The river drains a catchment area of about 3,435 km^2 (Figure 1). Average annual rainfall ranges from 600 mm in the semiarid region to 2,400 mm in the coastal zone. The annual average air temperature is approximately 24 °C (SRH, 2010). Streamflow is intermitent for the first 100 km.

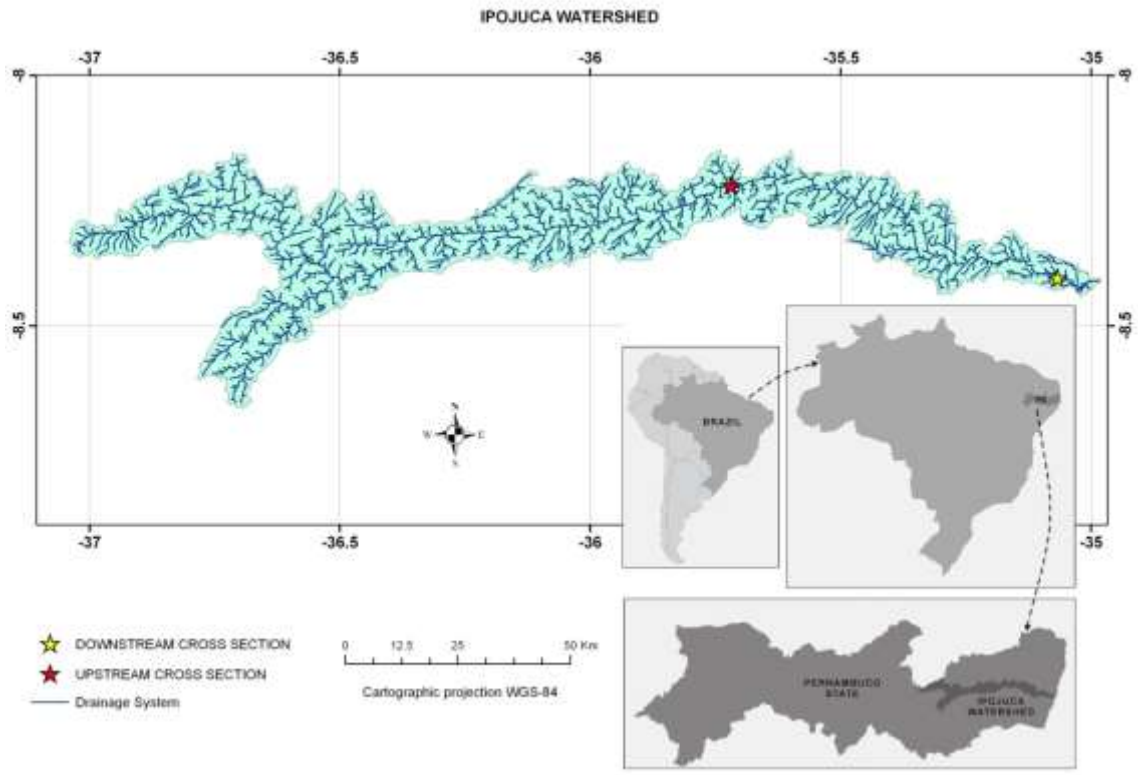

Figure 1. Location of the Ipojuca River watershed.

Soils in the Ipojuca watershed range from Entisols to Oxisols (ZAPE, 2002; EMBRAPA, 2006). The different soil types and the percentage found of each were obtained using the software ArcGIS 9.3 (Figure 2). In general, the amount of sediment

supplied to the studied cross sections is partly a result of the sugar cane agricultural activities, which trigger erosion—mainly in the form of interrill and rill erosion.

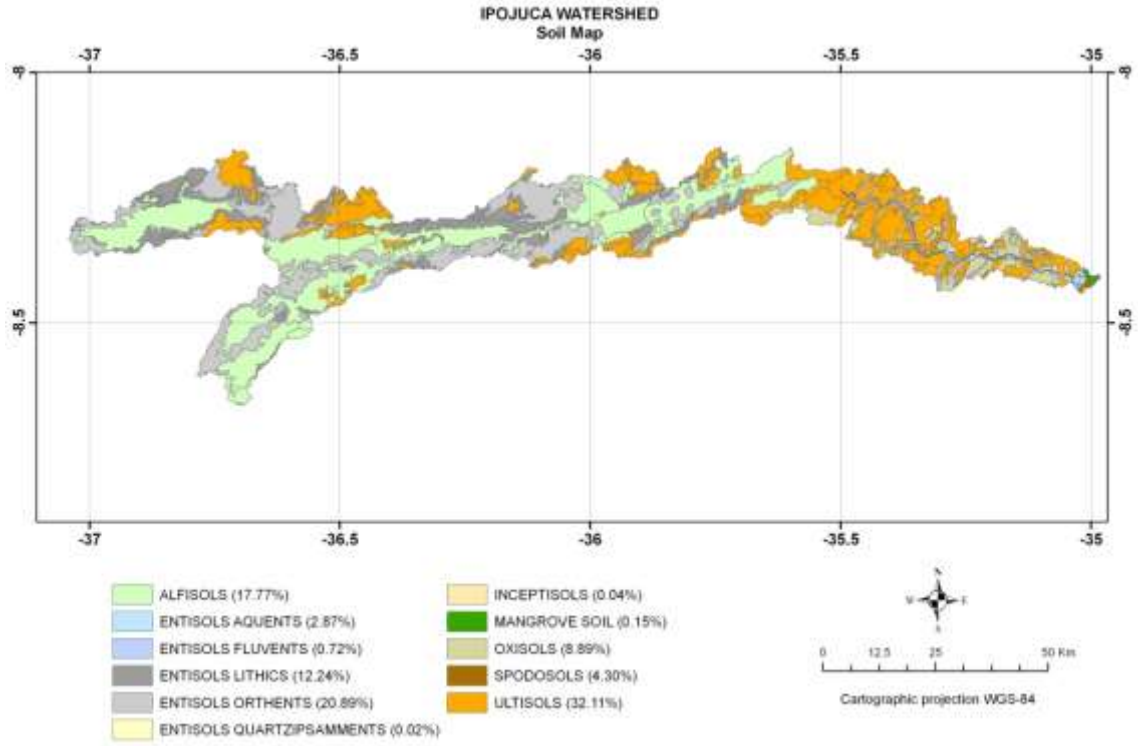

Figure 2. Distribution of soils in the Ipojuca watershed.

2.2 Sampling sites and measurements

We collected samples of suspended sediment and water from both the upstream (08º13’10’’ S–35º 43’09’’ W) and the downstream (08º24’16’’ S–35º04’03’’ W) cross sections. For both, flat stretches of river with well-defined banks were selected, free from any features that could cause disturbances in the flow. The region of the upstream cross section has a mean flow depth of 0.27–0.56 m and a mean width of 6.0–10.8 m; that of the downstream cross section has a mean flow depth of 0.8–2.43 m and a mean width of 21.8–30.3 m. The water discharge was determined by computing the product of the mean flow velocity and the area of influence. To obtain the flow velocity an electromagnetic current meter was used.

To collect both the suspended sediment and water samples, we used a US DH-48 sampler calibrated with a stainless steel intake nozzle having a ¼-inch diameter. Twenty-four direct measurements (twelve in each cross section) were made during 2013, in accordance with the equal-width-increment (EWI) depth-integrated and isokinetic sampling method proposed by Edwards and Glysson (1999). This approach enabled us to

obtain representative samples of both water and suspended sediments for the depth profile of the river. The samples were stored in polyethylene bottles until analysis. Mass values for the suspended sediments were obtained by the evaporation method (USGS, 1973).

2.3 Chemical analysis for heavy metals

Background values for heavy metals were determined from uncontaminated soil samples (taken from forest areas where the soils are mineralogically and texturally comparable with the river sediments), which were passed through a 2-mm-mesh nylon sieve. Aliquots (0.5 g each) of the soil and suspended-sediment samples were macerated in an agate mortar and passed through a 0.3-mm-mesh stainless steel sieve (ABNT nº. 50). They were then digested in Teflon vessels with 9 mL of HNO_3 and 3 mL of HCl according to USEPA 3051A (USEPA, 1998) in a microwave oven (MarsXpress) for 8 min 40 s—until the temperature reached 175 °C. The samples were maintained at this temperature for an additional 4 min 30 s. High purity acids were used in the analysis (Merck PA). The same procedure was used for the water samples (5 mL each).

After digestion, all extracts were transferred to 50-mL certified flasks (NBR ISO/IEC), which were filled with ultrapure water (Millipore Direct-Q System) and filtered in a slow filter paper (Macherey Nagel®). Glassware was cleaned and decontaminated in a 5% nitric acid solution for 24 h and then rinsed with distilled water.

Calibration curves for metal determination were prepared from standard 1,000 mg L^{-1} (Titrisol®, Merck). A sample was analyzed only if the coefficient of determination (r^2) of its calibration curve was higher than 0.999. We also carried out analytical data quality and standard operation procedures, such as curve recalibration, analysis of reagent blanks, spike recovery, and analysis of standard reference materials 2710a Montana I Soil (Cd, Pb, Zn, Cu, Ni, Cr, Fe, and Mn) and 2709a San Joaquin Soil (As and Hg) (NIST, 2002), were carried out. The percentage recovery of metals in the spiked samples ranged from 87.20% to 101.42%. In addition, the NIST recoveries ranged from 83% to 116%. All analyses were carried out in duplicate.

The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn were determined by inductively coupled plasma (ICP-OES/Optima 7000, PerkinElmer); and As and Hg were determined by an atomic absorption spectrophotometer (PerkinElmer AAnalyst™ 800) coupled to a hydride generator (FIAS 100/Flow Injection System/PerkinElmer) with an electrodeless discharge lamp (EDL). The detection limits were 0.0006, 0.00009, 0.004,

0.0002, 0.0006, 0.00075, 0.003, 0.001, 0.003, and 0.004 mg L^{-1} for Fe, Mn, Pb, Cd, Zn, Cr, Cu, Ni, Hg, and As, respectively.

2.4 Assessment of sediment pollution in the Ipojuca River

Pollution in the suspended sediment of the river was assessed by the enrichment factor (EF), comparison with background samples and SQGs. As background values we used four composite uncontaminated soil samples from each site. One drawback is that both the SQGs and the EF consider total concentration, and thus the assumption that all the species of a particular metal possess an equal impact with regard to the ecosystem (Dung et al., 2013). To address and minimize this problem, we limited our analysis to environmentally available metal concentrations in suspended sediment (i.e., exchangeable, bound to carbonates, bound to iron and manganese oxides, or bound to organic matter fractions).

Once the concentration of heavy metals found in suspended sediments does not enable the discrimination between natural and anthropogenic sources, the EF was calculated as:

$$EF = (metal / Fe)sample/(metal / Fe)background \quad (1)$$

The EF values were interpreted according to Sakan et al. (2009), as follows: EF <1 (no enrichment); <3 (minor enrichment); 3–5 (moderate enrichment); 5–10 (moderately severe enrichment); 10–25 (severe enrichment); 25–50 (very severe enrichment); and >50 (extremely severe enrichment). To compensate for differences in the grain size and composition of samples, we used geochemical normalization with Fe as a conservative element (Varol and Şen, 2012; Thuong et al., 2013). Other elements could be used—such as Al or Li (see detailed discussion in Dung et al., 2013)—but Fe offers the advantages of high affinity with solid surfaces and a geochemistry similar to that of many heavy metals (Varol, 2011).

To evaluate the effects on the environment of the heavy metal concentrations found in the suspended sediments, we compared the levels with background values as well as two sets of SQGs for aquatic systems (CCME, 1995; MacDonald et al., 2000). The numerical limits suggested to support and maintain the quality of aquatic environment are summarized in Tables 3 and 4.

2.5 Statistical Analysis

Descriptive and multivariate statistical analysis methods were used. Firstly, we did principal component analysis (PCA) of the data set, to determine whether the heavy metals in the suspended sediments were derived from anthropogenic or natural sources. To extract the significant principal components while diminishing the contribution of those variables with little importance, we used Varimax rotation (Kaiser, 1958). Secondly, we applied cluster analysis (CA), using Ward's method (Euclidean distance as a measure of similarity). We chose this method chiefly because it merges clusters on the basis of the sum of squares and the best-performing hierarchical clustering, which minimizes information loss (see detailed discussion in Templ et al., 2008). For both the PCA and CA analyses, we used standardized data to avoid misclassification due to differences in data dimensionality (Webster, 2001).

3. Results and Discussion

3.1 Heavy metal concentrations in the water of the Ipojuca River

Table 1 shows the concentrations of metals found in the water samples. For both the upstream and downstream sites, the highest concentrations were observed in February, March, and April; the lowest concentrations were seen from May to October, the period of highest water discharge, which increased dilution of the metals. These patterns were confirmed by CA, which distinguished two groups according to the metal concentrations in water (Figure 3).

Table 1. Heavy metal concentrations found in the Ipojuca River water, compared with water quality guidelines

Months	Metal concentration in water - upstream (mg L^{-1})										Q
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As	$m^3 s^{-1}$
FEB	0.80	0.81	0.49	0.02	11.76	0.03	0.14	0.45	0.003	0.01	0.27
MAR	0.75	0.07	0.42	0.02	9.92	0.02	0.29	0.43	<DL	<DL	0.28
APR	0.34	0.29	0.38	0.01	4.52	0.02	0.34	0.51	<DL	<DL	0.94
MAY	<DL	0.47	<DL	<DL	1.06	<DL	0.06	<DL	<DL	0.01	0.36
MAY*	<DL	<DL	<DL	<DL	0.90	<DL	0.05	<DL	<DL	<DL	0.52
JUN	<DL	<DL	<DL	<DL	0.63	0.01	0.06	<DL	<DL	0.01	0.75
JUN*	4.01	0.22	<DL	<DL	0.88	<DL	0.06	<DL	<DL	0.01	0.52
JUL	<DL	<DL	<DL	<DL	0.60	0.11	0.04	<DL	<DL	0.01	0.75
JUL*	<DL	0.07	<DL	<DL	0.69	<DL	<DL	<DL	<DL	0.01	1.02
AUG	<DL	<DL	<DL	<DL	0.65	0.11	<DL	<DL	<DL	0.01	0.46
SEP	<DL	<DL	0.13	<DL	0.60	<DL	0.04	<DL	<DL	0.02	0.31
OCT	<DL	<DL	0.06	<DL	0.14	<DL	<DL	<DL	0.004	0.02	0.29
Months	Metal concentration in water - downstream (mg L^{-1})										Q
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As	$m^3 s^{-1}$
FEB	2.24	0.61	0.45	0.02	14.43	0.03	0.17	0.53	<DL	<DL	1.32
MAR	0.44	0.28	0.50	0.01	8.19	0.03	0.07	0.49	<DL	<DL	1.21
APR	0.72	0.01	0.49	0.01	11.23	0.01	0.10	0.37	<DL	0.02	2.94
MAY	<DL	0.02	<DL	<DL	1.14	<DL	0.05	<DL	<DL	<DL	6.49
MAY*	<DL	<DL	<DL	<DL	0.83	<DL	0.06	<DL	<DL	0.01	8.98
JUN	<DL	<DL	<DL	<DL	0.83	<DL	0.07	<DL	<DL	0.02	19.13
JUN*	<DL	<DL	<DL	<DL	0.64	<DL	0.06	<DL	<DL	<DL	20.38
JUL	<DL	<DL	<DL	<DL	0.59	<DL	0.06	<DL	<DL	0.01	25.26
JUL*	<DL	<DL	<DL	<DL	0.82	<DL	0.05	<DL	<DL	0.01	25.01
AUG	<DL	0.24	<DL	<DL	1.51	<DL	0.05	<DL	<DL	0.01	20.94
SEP	<DL	<DL	0.20	<DL	0.52	<DL	0.02	0.01	<DL	0.02	12.63
OCT	<DL	<DL	0.04	<DL	0.17	<DL	<DL	<DL	0.0029	0.02	8.92
WHO[a]	5.00	0.20	5.00	0.01	2.00	0.10	0.20	0.20	na	0.10	
USEPA[b]	na	na	na	0.002	0.12	na	0.01	0.47	0.001	0.34	

Q = water discharge; na = data not available; * = second measurement in the same month; WHO = Irrigation water standard (WHO, 2006); USEPA = Acute values for protection of freshwater aquatic life (USEPA, 2006); <DL = below detection limit.

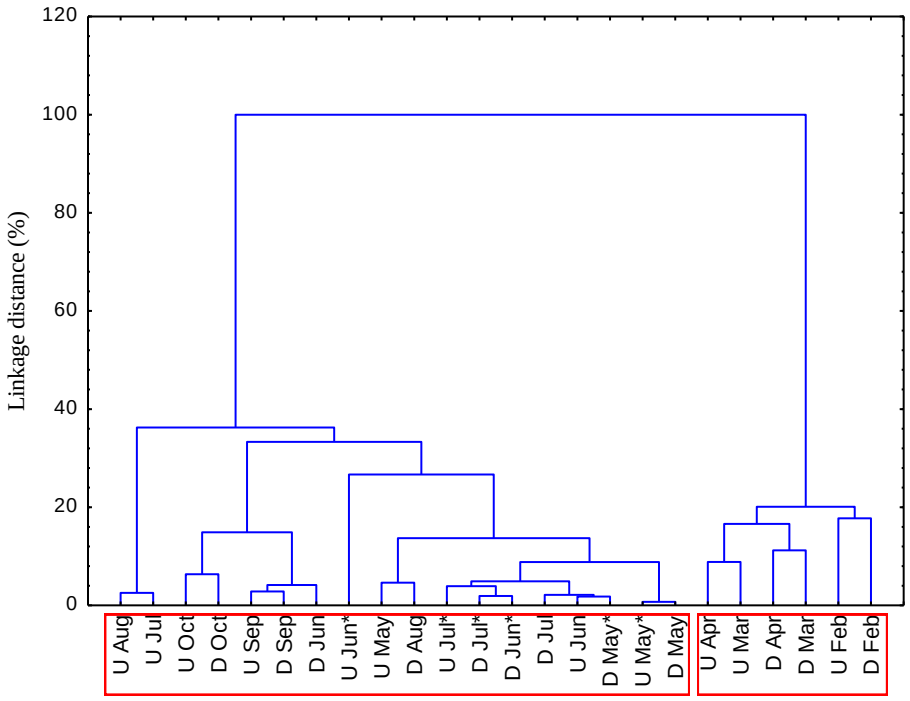

Figure 3. Cluster analysis of metal concentrations in water, according to Ward's method. U = Upstream; D = Downstream; * = second measurement in the same month.

The mean metal concentrations the water samples from the upstream cross section followed the order Zn > Fe > Mn > Pb = Ni > Cu > Cr > As > Cd = Hg; those from the downstream cross section followed the order Zn > Fe > Pb > Ni > Mn > Cu > Cr = As > Cd = Hg. The highest concentration found, for Zn, was 14.43 mg L^{-1} (probably owing to its extreme mobility, which enables it to easily pass from sediments to water under changing environmental conditions [Morillo et al., 2002]). The concentrations of Fe, Pb, and As were lower than the permitted level in the irrigation water standard (WHO, 2006), but others metals exceeded the WHO guidelines as follows, in terms of number of samples: Mn (7) > Zn (6) = Ni (6) > Cd (3) > Cr (2) = Cu (2). In addition, the concentration of As was lower than acute values for protection of freshwater aquatic life (USEPA, 2006), but others metals exceeded the USEPA guidelines as follows, in terms of number of samples: Zn (24) > Hg (21) > Cu (20) > Cd (6) > Ni (3). Despite not being in conformity with these guidelines, the water of the Ipojuca River has been widely used for both irrigation (Pimentel, 2003) and fishing.

3.2 Heavy metal concentrations in the suspended sediments of the Ipojuca River

3.2.1 Comparison with rivers in other parts of the world

The heavy metal concentrations found in the suspended sediments from the upstream cross section was lower (fraction < 63 µm) than the average levels found in sediments for selected rivers (Shing Mun, Tinto, Danube, Tigris, Lich and Langat) and average values for suspended sediment from continent and world rivers (Martin and Meybeck, 1979; Viers et al., 2009), except both Hg (for which several studies lacked data) and Mn that was higher than in all the comparison datasets except those from the European continent (Table 2). Results from the downstream Ipojuca site suggested that metal contamination was more serious than that of the Langat River (Lim et al., 2013) but less serious than that of the Shing Mun, Tinto, Danube, Tigris, and Lich rivers. These differences may reflect different anthropogenic inputs from one catchment area to another. For instance, the high Cu concentration in the Tigris River (Varol, 2011) can be attributed to metallic discharges from a copper mine plant; likewise, the high concentrations of Cd, Cu, and Zn in the sediments of the Shing Mun River were linked to the large surface runoff discharges into the river from various cottage industries in the region (Sin et al., 2001).

Table 2. Heavy metal concentrations in suspended sediment from the Ipojuca River compared with those from selected rivers (fraction <63 µm pseudo total digestion) in other parts of the world (mg kg^{-1})

Locations	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	References
Ipojuca River, Upstream	0.41—2.30	0.00—0.25	2.25—34.15	0.00—11.38	1,091—6,380	0.01—0.05	518.43—3,216	1.00—6.75	1.40—142.90	18.23—154.13	This study
Ipojuca River, Downstream	6.25—15.07	0.05—0.09	15.15—332.17	10.83—90.28	10,350—39,845	0.03—0.14	200.52—1,049	5.15—35.25	4.13—682.05	38.58—534.27	This study
Shing Mun River, Hong Kong	—	22—47	13—66	207—1,660	—	—	—	—	126—345	32—2,200	Sin et al. 2001
Tinto River, Spain	—	0.13—12	11—151	22—2,700	—	—	—	1.6—36	17—13,400	68—5,280	Morillo et al. 2002
Danube River, Europe	8.1—388	1.1—32.9	26.5—556.5	31.1—8,088	17,600—64,400	0.10—2.56	442—1,655	17.5—173.3	14.7—541.8	78—2,010	Woitke et al. 2003
Tigris River, Turkey	2—18	0.7—4.9	28.4—163.4	11.2—5,075	—	—	282.2—1,657	74—288	62.3—566.6	60.1—2,396	Varol (2011)
Tigris River, Turkey	2.08—12.44	0.77—7.90	72.12—158.35	98.65—2,860	—	—	786.23—1,681	122.14—534.58	146.24—660.11	149.67—1,061	Varol and Şen (2012)
Lich River, Vietnam	19.3—501.8	0.8—11.8	77.1—174.0	35.1—155.9	15,323—148,912	—	311.1—912.7	23.9—111.4	33.2—90.5	305.2—718.1	Thuong et al. 2013
Langat River, Malaysia	4.47—30.04	—	4.31—29.04	2.24—14.84	—	—	—	2.33—8.25	5.57—55.71	12.26—74.70	Lim et al. 2013

Average concentration of heavy metals in suspended sediment from Ipojuca River, World Rivers and Continents (mg kg^{-1})

	As	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Pb	Zn	References
Ipojuca River, Upstream	1.10	0.07	9.10	4.42	3,002	0.02	1,482	3.01	36.27	63.27	This study
Ipojuca River, Downstream	9.71	0.27	91.83	37.83	28,251	0.08	723.59	16.62	302.22	225.20	This study
World Rivers	5	-	100	100	48,000	—	1,050	90	100	250	Martin and Meybeck (1979)
World Rivers	36.3	1.55	130	75.9	58,100	—	1,679	74.5	61.1	208	Viers et al. 2009
South America	—	—	79	59	52,900	—	700	46	76	184	
North America	—	—	115	34	45,000	—	1,430	50	22	137	
Asia (China)	—	—	117	53	46,000	—	970	68	64	145	Viers et al. 2009
Africa	—	—	130	53	75,000	—	1,478	78	46	130	
Europe	—	—	164	172	43,000	—	1,884	66	71	346	

In the sediments from the downstream cross section, Pb and Zn were the most harmful metals. The mean Pb concentration was higher than those found in average values in suspended sediments in World Rivers and continents (Martin and Meybeck, 1979; Viers et al., 2009); whereas in the case of Zn, the mean value was higher those of world rivers and continents except the rivers of Europe (Viers et al., 2009) and the values of World Rivers reports by Martin and Meybeck (1979). Although these analyses and comparisons with other rivers yield some useful insights, the source of heavy metals in the Ipojuca River system is still uncertain, as is whether these metals pose a risk to aquatic life. For example, Mn in the upstream cross section seems to have a different behavior in comparison with the downstream site, making it difficult to assess the extent of possible contamination without comparison with background values and applying of others tools. To explain such issues we used the additional techniques of enrichment factor, multivariate statistical analysis, and comparison with background values and SQGs.

3.2.2 Enrichment factor

The EF mean values for the upstream cross section followed the order Mn (28.73) > As (22.17) > Pb (6.69) > Cu (4.49) > Cd (3.4) > Zn (3.22) > Hg (2.51) > Cr (1.70) > Ni (1.36); those for the downstream cross section followed the order Zn (22.92) > Pb (15.51) > As (9.67) > Mn (5.48) > Ni (5.38) > Cu (4.49) > Cr (2.68) > Hg (1.32) > Cd (0.95). According to Sakan et al. (2009), the EF mean values were as follows: no enrichment (Cd – downstream); minor enrichment (Ni – upstream, Cr and Hg – both sites); moderate enrichment (Cu – both sites; Cd and Zn – upstream); moderately severe enrichment (Pb – upstream; As, Mn, and Ni – downstream); severe enrichment (As – upstream; Pb and Zn – downstream); and very severe enrichment (Mn – upstream).

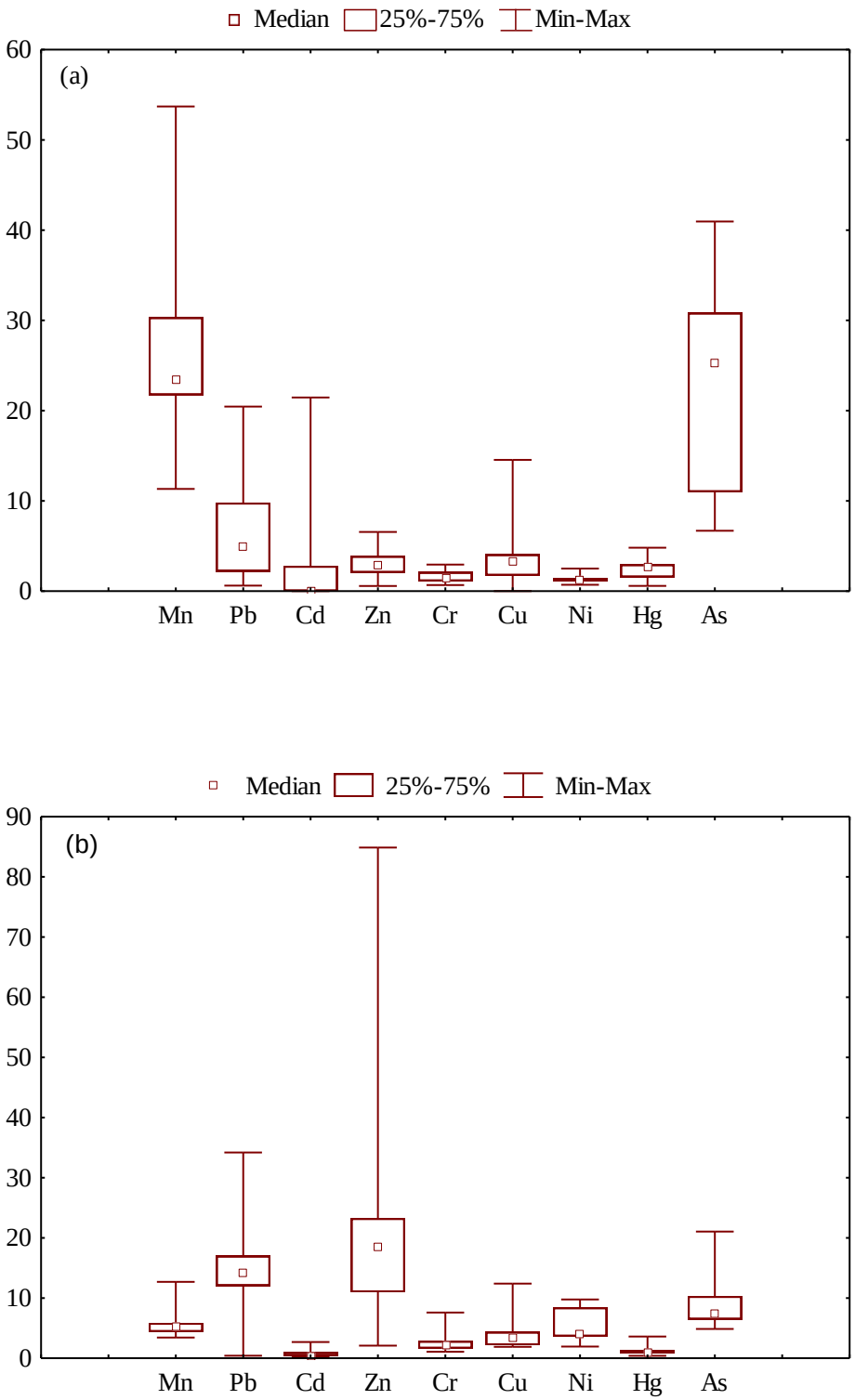

Figure 4. Enrichment factors for heavy metals found in suspended sediments from the upstream (a) and downstream (b) cross sections of the Ipojuca River.

The highest EF observed in all the suspended sediments were for Mn (54) and Zn (85) at the upstream and downstream sites (Figure 4a and b); Mn has also been reported

as one of the elements showing the highest EF relative to the upper crust (Viers, 2009). The lowest EF mean value observed was for Cd at the downstream cross section (0.95), which may be linked with low energy bound to soil and sediment. In addition to Mn (upstream), EF was particularly high for As (upstream) and for Zn, Pb, and As (downstream). The high readings for As seem to reflect a common source at both sites; those for Zn and Pb, which fall in about the same range, suggest similar inputs; and those for Mn may be associated with some upstream input or natural process, as discussed by Ponter et al. (1992).

3.2.3 Comparison with sediment quality guidelines

For the upstream site, As, Cd, Zn, Cr, Cu, Hg, and Ni showed values lower than the SQG probable effect concentration (PEC) and the probable effect level (PEL) in 100% of the samples. On the other hand, Mn exceeded the threshold effect concentration (TEC) and the PEC in 100% and 67% of the samples, respectively. In 25% of the samples, Pb exceeded TEC and Threshold Effect Level (TEL) and in 8% and 17% of the samples, Pb exceeded PEC and PEL. Samples showing values between the guidelines were not reported, chiefly because SQGs are not intended to provide guidance for these concentrations (MacDonald et al., 2000). The mean available metal concentration for the upstream site followed the order Fe > Mn > Zn > Pb > Cr > Cu > Ni > As > Cd > Hg (Table 3). According to the SQGs, only Mn and Pb show concentrations potentially having harmful effects on sediment-dwelling organisms.

Table 3. Comparison of heavy metal concentrations in suspended sediments from the upstream cross section with SQGs and background values

Month	Metal concentration in suspended sediment – upstream (mg kg^{-1})									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	1,171	1,345	1.40	0.25	20.95	3.30	7.40	1.75	0.02	0.97
MAR	1,801	2,164	17.43	0.05	99.73	3.85	1.93	1.20	0.03	1.21
APR	1,843	968.97	5.08	<DL	47.08	2.25	0.01	1.00	0.02	1.15
MAY	5,181	1,483	27.48	0.05	95.51	11.14	11.38	6.75	0.05	1.23
MAY*	5,325	1,172	17.13	0.20	18.23	10.05	3.40	4.55	0.02	1.11
JUN	2,686	867.43	10.21	<DL	45.80	3.75	1.03	2.18	0.02	1.08
JUN*	3,700	1,996	19.79	<DL	92.87	6.76	3.86	3.19	0.02	2.30
JUL	1,164	518.43	19.84	<DL	42.25	5.45	2.08	2.55	0.01	0.65
JUL*	1,091	575.43	10.29	<DL	34.30	2.95	1.90	1.80	0.01	0.57
AUG	6,380	3,216	142.90	0.25	31.45	34.15	4.80	5.60	0.02	1.96
SEP	2,693	1,827	106.90	<DL	154.13	14.11	10.76	2.55	0.03	0.55
OCT	2,991	1,656	56.84	<DL	77.01	11.42	4.53	3.03	0.03	0.41
Mean	3,002	1,482	36.27	0.16	63.27	9.10	4.42	3.01	0.02	1.10
Comparison with sediment quality guidelines and background values										
TEC	20,000	460.00	35.80	0.99	121.00	43.40	31.60	22.70	0.18	9.79
PEC	40,000	1,100	130.00	5.00	460.00	110.00	150.00	49.00	1.10	33.00
TEL	na	na	35.00	0.60	123.00	37.30	35.70	18.00	0.17	5.90
PEL	na	na	91.30	3.50	315.00	90.00	197.00	35.90	0.49	17.00
Background (B)	10,682	238.92	20.73	0.11	93.11	19.46	4.64	8.19	0.05	0.22
Samples > TEC	0	12	3	0	1	0	0	0	0	0
Samples > PEC	0	8	1	0	0	0	0	0	0	0
Samples > TEL	na	na	3	0	1	0	0	0	0	0
Samples > PEL	na	na	2	0	0	0	0	0	0	0
Samples > B	0	12	4	3	3	1	4	0	0	12

na = data not available; B = Background value * = second measurement in the same month; <DL = below detection limit. Note: TEL and PEL (Canadian Sediment Quality Guidelines) are the values used by Brazilian legislation CONAMA (2012).

For the downstream cross section, the concentrations of heavy metals in suspended sediments were higher than those in the upstream samples, except for Mn (Table 4). The mean available metal concentration followed the order Fe > Mn > Pb > Zn > Cr > Cu > Ni > As > Cd > Hg. The SQG comparison showed that Fe and Mn exceeded TEC in 75% and 83% of the samples, respectively, and that Pb exceeded TEC and TEL in 92% of the samples. Notably, Pb is the most harmful of the heavy metals for aquatic life at the downstream site, and it was higher than PEC and PEL in 67% and 75% of the samples,

respectively (Table 4). In contrast, for the upstream site no metal exceeded PEC and PEL in more than 17% of the samples (two samples) except for Mn. Other metals exceeded guidelines as follows, in terms of percentages of samples: (1) TEC: Zn 58%, Cr 75%, Cu 42%, Ni 8%, As 42%; (2) PEC: Zn 8%, Cr 25%; (3) TEL: Cd 8%, Zn 58%, Cr 75%, Cu 33%, Ni 25%, As 100%; and (4) PEL: Zn 33%, Cr 25%. In 42% and 100% of the samples, respectively, As exceeded both TEC and TEL.

Table 4. Comparison of heavy metal concentrations in suspended sediments from the downstream cross section with SQGs and background values

Month	Metal concentration in suspended sediment – downstream (mg kg^{-1})									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	16,450	972.50	4.13	0.69	70.06	19.81	72.50	17.63	0.05	6.25
MAR	10,350	245.47	90.13	0.35	435.63	18.60	13.43	12.85	0.03	6.69
APR	12,565	200.52	45.58	0.20	158.83	15.15	10.83	5.15	0.12	11.37
MAY	31,122	959.03	320.20	0.17	534.27	60.63	77.22	19.58	0.11	15.07
MAY*	31,814	759.90	682.05	0.23	68.53	141.88	19.90	13.34	0.07	12.81
JUN	25,966	718.76	379.38	0.15	299.98	72.00	18.51	16.73	0.08	11.86
JUN*	39,845	939.48	223.26	0.32	56.16	81.94	33.13	19.69	0.08	7.40
JUL	34,504	656.95	123.30	0.28	50.19	58.52	25.69	15.14	0.06	9.01
JUL*	28,635	612.90	496.11	0.05	269.58	89.30	20.84	16.95	0.06	9.11
AUG	39,006	796.90	325.23	0.12	357.15	332.17	46.61	17.90	0.06	8.16
SEP	31,516	770.90	662.00	0.22	363.43	123.62	90.28	35.25	0.14	8.75
OCT	37,236	1,049	275.23	0.51	38.58	88.31	24.97	9.17	0.04	10.08
Mean	28,251	723.59	302.22	0.27	225.20	91.83	37.83	16.62	0.08	9.71
Comparison with sediment quality guidelines and background values										
TEC	20,000	460.00	35.80	0.99	121.00	43.40	31.60	22.70	0.18	9.79
PEC	40,000	1,100	130.00	5.00	460.00	110.00	150.00	49.00	1.10	33.00
TEL	na	na	35.00	0.60	123.00	37.30	35.70	18.00	0.17	5.90
PEL	na	na	91.30	3.50	315.00	90.00	197.00	35.90	0.49	17.00
Background (B)	24,454	113.94	15.02	0.38	12.13	27.41	8.70	3.11	0.06	1.05
Samples > TEC	9	10	11	0	7	9	5	1	0	5
Samples > PEC	0	0	8	0	1	3	0	0	0	0
Samples > TEL	na	na	11	1	7	9	4	3	0	12
Samples > PEL	na	na	9	0	4	3	0	0	0	0
Samples > B	9	12	11	2	12	9	12	12	6	12

na = data not available; B = Background value * = second measurement in the same month; Note: TEL and PEL (Canadian Sediment Quality Guidelines) are the values used by Brazilian legislation CONAMA (2012).

In 100% of the samples, from both the upstream and downstream sites, As exceeded the background values—indicating that the source of this metal was anthropogenic. In addition, concentrations of several metals at the upstream site exceeded background values, as follows: Mn 100%, Pb 33%, Cd 25%, Zn 25%, Cr 8%, Cu 33%, and As 100% of the samples (Table 3). These values are much higher for the downstream site, where Mn, Zn, Cu, Ni, and As exceeded the background values in 100% of the samples, followed by Pb (92%), Cr (75%), Hg (50%), and Cd (17%). This suggests that both SQGs underestimate the harmful effect of those metals on sediment-dwelling organisms. For this reason, the previous comparison with heavy metal concentration expected to occur naturally should be the first step in sediment quality studies.

We used cluster analysis to confirm the higher levels of heavy metal contamination in suspended sediments at the downstream cross section (Figure 5). Based on similarity, twenty-four measurements were grouped into two statistically significant clusters (linkage distance < 40%). Regardless of the time of year (temporal variability), the concentrations of metals in suspended sediment at the downstream site were similar. The same was observed at upstream site. However, the concentrations measured at the downstream site are completely different from those measured upstream (spatial variability).

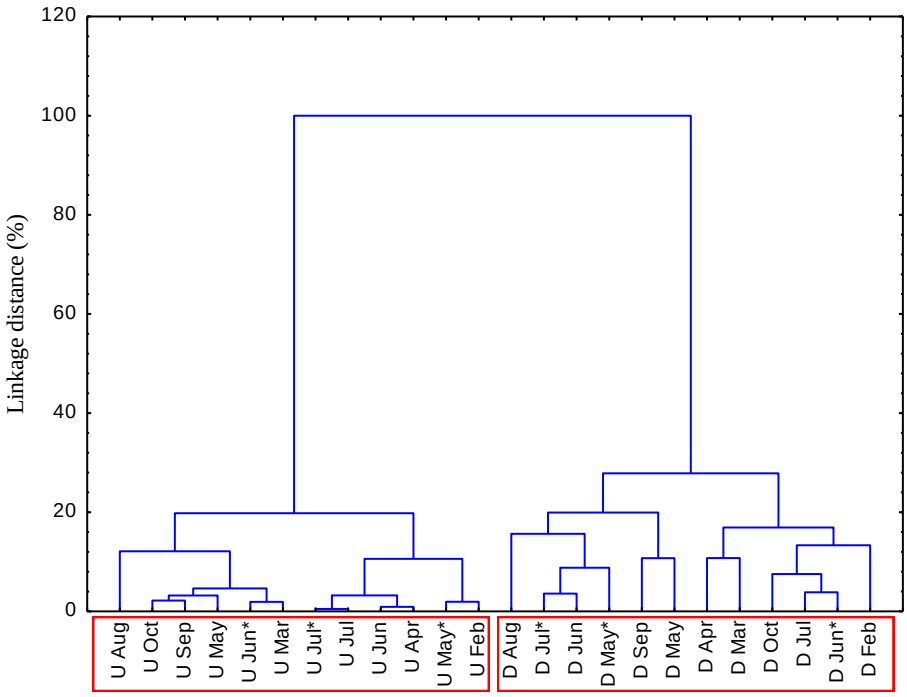

Figure 5. Cluster analysis of metal concentrations in suspended sediment, according to Ward's method. U = Upstream; D = Downstream; * = second measurement in the same month

The cluster for the downstream cross section, on the right in the figure, shows higher levels of heavy metal contamination, whereas the cluster for the upstream cross section, on the left, shows moderate levels. Despite the lack of seasonal variation (wet/dry periods) in suspended sediments of the Ipojuca River, some authors have shown this variation in others contaminated rivers (Varol, 2011; Thuong et al., 2013). It is likely that the greater amounts of sediment carried downstream by runoff along the length of the Ipojuca watershed offsets the effects of dilution of contaminants by the higher discharge of water downstream.

3.2.4 Principal component analysis

Principal component analysis (PCA) of standardized data were used to discern patterns among sediment samples and to identify the contribution of each heavy metal to each PC (Table 5). The entire data set showed PCs with eigenvalues > 1, which explains roughly 80% and 74% of the total variance in suspended sediment quality in the upstream and downstream cross sections, respectively.

In the upstream cross section, PC1 (accounting for 45.70% of the total variance) was correlated with Fe, Mn, Pb, Cr, and As; PC2 (accounting for 22.94% of the total variance) was correlated with Cu, Ni, and Hg; and PC3 (accounting for 11.90% of the total variance) was correlated with Cd and Zn. Both PC2 and PC3 at the upstream site represent metals derived from natural sources, as supported by the data in Table 3. In contrast, PC1 appears to represent heavy metals from a mixture of sources: Fe, Pb, and Cr come mainly from natural sources, whereas Mn and As seem to have mainly an anthropogenic source (Table 3 and Figure 4a). Such PCA-indicated mixtures of sources for heavy metals in soils and sediments has been reported by several authors (Facchinelli et al., 2001; Micó et al., 2006; Thuong et al., 2013).

Table 5. Contributions of heavy metals to significant principal components in sediment samples from the Ipojuca River

	Upstream			Downstream		
Variables	PC1	PC2	PC3	PC1	PC2	PC3
Fe	**0.73**	0.35	-0.42	**0.93**	0.11	0.08
Mn	**0.92**	0.09	0.07	**0.75**	-0.36	0.36
Pb	**0.85**	0.18	0.17	0.53	**0.60**	0.26
Cd	0.37	0.07	**-0.76**	-0.09	**-0.94**	0.05
Zn	0.21	0.46	**0.83**	-0.29	**0.57**	0.45
Cr	**0.91**	0.17	-0.19	**0.70**	0.32	0.05
Cu	0.24	**0.88**	0.07	0.15	-0.13	**0.94**
Ni	0.53	**0.58**	-0.45	0.25	0.11	**0.88**
Hg	0.00	**0.91**	0.20	-0.15	0.49	**0.63**
As	**0.62**	-0.24	-0.25	0.08	**0.64**	-0.05
Eigenvalues	4.57	2.29	1.19	3.429	2.189	1.744
EV (%)	45.70	22.94	11.90	34.30	21.90	17.44

Values in bold indicate significant contributions; EV = explained variance. Note: rotation done by Varimax method.

In the downstream cross section, PC1 accounted for 34.30% of the total variance and was correlated with Fe, Mn, and Cr; PC2 accounted for 21.90% and was correlated with Pb, Cd, Zn, and As; and PC3 accounted for 17.44% and was correlated with Cu, Ni, and Hg (Table 5). These results suggest that heavy metals represented by PC1 were predominantly derived from natural sources—except for Mn, which showed a similar pattern in the samples from the upstream site, reinforcing the hypothesis that this element

may be associated with both natural and anthropogenic sources. The strongest contributions to PC2 were from Pb, Cd, Zn, and As; those to PC3 were from Cu, Ni, and Hg—results that suggest these two are derived from different anthropogenic sources (as supported by the data in Table 4 and Figure 4b).

Of all the heavy metals, the highest concentrations found were of Mn and As in suspended sediments at the upstream cross section. The suspended sediment samples were significantly higher in Mn than the water samples. Previous research has suggested a mainly anthropogenic source for Mn, but high Mn concentrations have been found in pristine rivers as well as polluted ones. According to Andersson et al. (1998), high Mn concentrations might be associated with the formation of authigenic particles in the aquatic environment. The enrichment might be provided by natural processes, as observed by Ponter et al. (1992) in the Kalix River (Sweden). Between possible explanations in Kalix River, the increase in Mn seems to be associated with the increase in temperature (optimum range from 15° C to 30° C) under pH from 7 to 8, and the large quantity of biogenic particles in suspended sediment. The optimum range for temperature was also observed in upstream cross section in Ipojuca River (24 ºC – 28.5 ºC), as well as the presence of large quantity of biogenic particles during the measurements. However, the pH was not evaluated in the study period. Likely, it might have increased the oxidation rate of dissolved Mn and consequently the concentration of Mn in suspended sediment of Ipojuca River.

The PCA for the samples from both sites suggest that the predominant source of As is anthropogenic. Concentrations of As in samples from both the upstream and downstream sites exceeded background values by 100%. These high concentrations might be associated with several small industries close to the upstream site that produce leather products. At least 75.9 t day^{-1} of textile wastes are generated in the Ipojuca watershed (CPRH, 2003), and arsenate and arsenite are used in the production of dye stuffs and as a preservative for leather products (Thuong et al., 2013).

At the downstream site, both Pb and Zn represent a major concern and may be related to the high vehicular traffic in the region—associated not only with sugarcane farms on both sides of the river, but also with the nearby highway (roughly 50 m away). Both Pb and Zn found in urban soils have been linked to tire residues (Krčmová et al., 2009). In addition, although leaded gasoline was banned in 1989 in Brazil, Pb has a long half-life in soils and sediments, which may be another possible explanation for the high

Pb levels in suspended sediment. According to Horowitz (2009), Pb is usually linked with petroleum and coal combustion products, such as tires and oil. Martínez and Polleto (2010), studying the distribution of Pb in urban sediments, pointed out that commercial areas showed higher concentrations than industrial areas because of the higher vehicle traffic. Further, the negative correlation between Cd (-0.94) and Pb (0.60) shown by PC2 reflects Pb's relative insolubility and high affinity for soil and sediment, in contrast to the relative solubility and low binding energy of Cd (Banerjee, 2003; Wong et al., 2006).

The major sources of Cd are untreated sewage sludge and wastewater from industrial and agricultural activities. The major source of both Cu and Zn, found in high concentrations in the suspended sediments, is most likely the sugarcane industry, with its large-scale use of agrochemicals and fertilizers. Another factor that could be contributing to the increased concentrations of all the heavy metals in the downstream cross section is the extraction of sand from the bed layers (SRH, 2010), a typical activity in that area which can lead to re-suspension of heavy metals.

4. Conclusions

In addition to analyzing water and suspended sediments from the Ipojuca River, we made use of other methods—enrichment factor, multivariate statistical techniques, and comparison with both background values and SQGs—to assess the pollution status of the river. Analysis of the water samples, although essential for the concurrent analysis of the sediments, would have been inconclusive by itself, especially considering that during the winter the increased levels of water discharge meant decreased concentrations of metals. At the same time, analysis of the suspended sediments showed no temporal (seasonal) variation, but only spatial variation.

The results of the combined methods indicated that the suspended sediments of the upstream portion of the Ipojuca River are moderately contaminated, with higher contaminant levels for Mn and As; and that the sediments of the downstream portion are highly contaminated with heavy metals, mainly Zn, Pb, and As. The comparison of our data with SQGs indicated that for the upstream portion, it is the concentrations of Mn and Pb that are likely to pose a risk for sediment-dwelling organisms; for downstream portion are Pb and Zn. However, this comparison does not take into account the potentially harmful effect of some heavy metals—a remarkable example being As, which does not exceed either of the SQG guidelines (TEL/PEL or TEC/PEC), but does exceed the

background values in 100% of measurements. For this reason, we conclude that strategies for future remediation to protect aquatic life and human health, must be based primarily on analysis of sediments and comparison with background values.

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CHAPTER II

BEDLOAD AS INDICATOR OF HEAVY METAL CONTAMINATION

Abstract

Heavy metal contamination has been considered a worldwide concern for water quality. Most studies have focused on heavy metal concentration in water, suspended and bottom sediments; however, the concentration transported by river-bottom sediment, known as bedload, has been ruled out. In order to fill this gap, this study aimed to determine the concentration of Hg, Pb, Cd, Ni, Cu, Cr, Zn, As, Fe and Mn in bedload of an environmentally impacted river in Brazil. The use of bedload in heavy metal contamination studies raises the following question: Is the bedload an adequate indicator of heavy metal contamination? Sediment contamination assessment was done using sediment contamination indices, principal component analysis and comparison with background values and sediment quality guidelines (SQGs). Comparison with sediment quality guidelines, probable effect level (PEL) and Threshold Effect Level (TEL) seems to underestimate the harmful effect on sediment-dwelling organisms, being essential either to calibrate the SQGs for site specific conditions or develop site specific guidelines in Ipojuca River. The pollution load index (PLI) indicated that the upstream and downstream sites are not polluted and polluted, respectively. Principal component analysis explained roughly 91% and 81% of the total variance in heavy metal contamination upstream and downstream, respectively, and distinguished natural and anthropogenic contributions in Ipojuca River. Multiple lines of evidence suggested that the heavy metal concentrations in bedload were clearly an adequate and feasible indicator of anthropogenic impacts.

Keywords: Environmentally available metals, Sediment quality guidelines, Principal component analysis, Enrichment factor.

1. Introduction

Environmentally contaminated rivers have been studied in the last decades due to the worldwide concern for water quality (Woitke et al., 2003; Shafie et al., 2013). Heavy metal contamination has been pointed out as one of the major concerns in aquatic ecosystems, given the toxicity, persistence, and ability to be transferred into food chain. Moreover, sediments are widely accepted as the most important sink or source of heavy metals (Lee et al., 2003; Singh et al., 2005; Chon et al., 2012) that enter into the environment through different pathways (Bednarova et al., 2013).

Most studies on heavy metal contamination have focused on suspended and bottom sediments (Horowitz, 2008; Viers et al., 2009; Varol, 2011). Nevertheless, the concentration and subsequent transport by river-bottom sediment (hereafter referred to as bedload) has been ruled out. Therefore, the use of bedload in heavy metal contamination studies raises the following question: Is the bedload an adequate indicator of heavy metal contamination? We hypothesize that the heavy metal concentration in bedload can distinguish whether the heavy metals come from natural or anthropogenic sources and also provide insights regarding harmful effects on sediment-dwelling organisms. Several authors have used principal component analysis and/or enrichment factor to distinguish heavy metal sources (Varol, 2011; Raju et al., 2012; Tang et al., 2013; Castillo et al., 2014), whereas sediment quality guidelines have been applied to assess the harmful effects on sediment-dwelling organisms (Choueri et al., 2009; Deckere et al., 2011; Yang et al., 2012; Kalender and Uçar, 2013). Due to the lack of national numerical thresholds and also evidence about which Sediment Quality Guideline (SQG) is adequate to assess the potential for biological effects related to heavy metals (Bay et al., 2012), Canadian Sediment Quality Guidelines (CCME, 1995) have been used by the Brazilian legislation (CONAMA, 2012).

The Ipojuca River has been identified as the fifth most polluted river in Brazil; however, studies about heavy metal contamination in sediments are still lacking. Most studies have focused on modeling nutrient emissions; effect of the construction of the Industrial and Harbor Complex on river's hydrology, chemistry, and phytoplankton, and the contamination of water caused by the sugarcane industry (Koening et al., 2003; Muniz et al., 2005; Gunkel et al., 2007; Barros et al., 2013).

Thus, the objectives of this study were (1) to determine the environmentally available metal concentrations of mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni),

copper (Cu), chromium (Cr), zinc (Zn), arsenic (As), iron (Fe) and manganese (Mn) in bedload; (2) to assess the environmental risk of these metals by comparison with sediment quality guidelines; and (3) to define the degree and sources of heavy metal contamination using sediment contamination indices and principal component analysis.

2. Material and Methods

2.1 Study area

The Ipojuca watershed extends from the semiarid region of northeastern Brazil to the coast, with a total river length of 290 km (08°09'50'' – 08°40'20'' S and 34°57'52'' – 37°02'48'' W). Toward the downstream site, the river is affected by agricultural, urban, and industrial wastes. The river drains a catchment area of about 3,435 km^2 (Figure 1), along which are located 25 municipalities having approximately 1,110,841 inhabitants, most of them being in the urban zones (SRH, 2010).

Soils are predominantly Entisols (36.74%), Ultisols (32.11%), Alfisols (17.77%), and Oxisols (8.89%). The remaining soils comprise 4.49% of the Ipojuca watershed. The average annual rainfall ranges from 600 mm in the semiarid region to 2,400 mm in the coastal zone. The annual average air temperature is approximately 24 °C (SRH, 2010). The flow rate, intermittent roughly in the first 100 km, ranges from 2 $m^3 s^{-1}$ to 35 $m^3 s^{-1}$ in dry and rainy seasons, respectively.

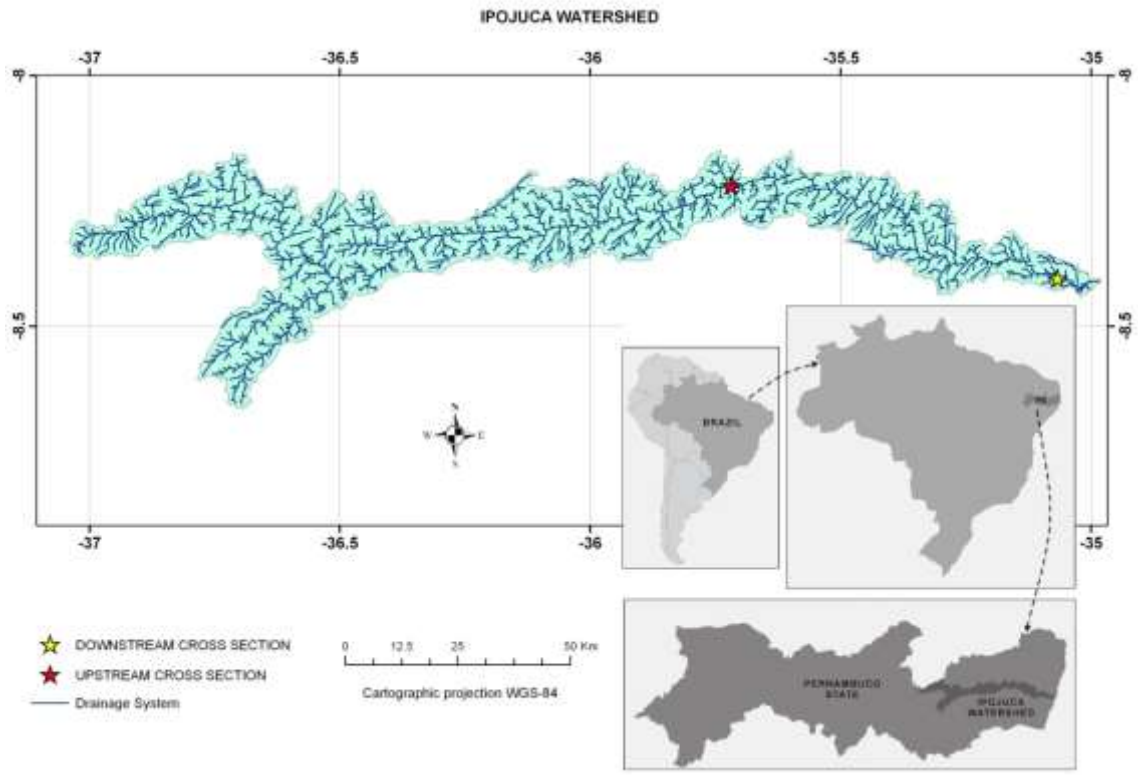

Figure 1. Location of the Ipojuca River watershed.

2.2 Sampling sites and measurements

Bedload from both the upstream (08º13'10'' S – 35º 43'09'' W) and the downstream (08º24'16'' S – 35º04'03'' W) cross sections were collected. The cross sections were divided in five verticals equally spaced following the Equal-Width-Increment Method (EWI) proposed by Edwards and Glysson (1999). The mean flow depth ranged from 0.27 m to 0.56 m and 0.8 m to 2.43 m, while the mean width ranged from 6.0 m to 10.80 m and 21.80 m to 30.3 m, in the upstream and downstream cross sections, respectively.

The bedload was sampled using the US BLH 84 sampler. After sampling, the sediment was stored in polyethylene bottles for further analysis. In addition, the sediment mass values were obtained by the evaporation method. Afterward, the bedload was calculated according to Gray (2005):

$$QB = \sum \left(\frac{m}{wt} \right) L 0.0864 \quad (1)$$

where QB is the bedload discharge, m is the mass of sediment from bedload transport, w is the width of nozzle - US BLH – 84, t is the sampling time, L is the equivalent width, and 0.0864 is for the transformation of data in t day^{-1}.

2.3 Chemical analysis

Heavy metals were measured in bedload and uncontaminated soil samples (background values). The background values for heavy metals were determined from uncontaminated soil samples (i.e. six composite soil samples taken from surrounding forest areas at each site, where soils are mineralogically and texturally comparable with river sediments). The uncontaminated soil samples were sieved on a 2-mm mesh nylon sieve, then soil and sediment samples were macerated in an agate mortar and sieved with a stainless steel 0.3-mm mesh sieve (ABNT no. 50). For heavy metal determination, 0.5 g soil or sediment was digested in Teflon vessels with 9 mL of HNO_3 and 3 mL of HCl USEPA 3051A (USEPA, 1998) in a microwave oven (MarsXpress) for 8 min 40 s on the temperature ramp, the necessary time to reach 175 °C. Then, this temperature was maintained for an additional 4 min 30 s.

After digestion, all extracts were transferred to 50-mL certified flasks (NBR ISO/IEC), filled with ultrapure water (Millipore Direct-Q System) and filtered in a slow filter paper (Macherey Nagel®). High purity acids were used in the analysis (Merck PA). Glassware was cleaned and decontaminated in a 5 % nitric acid solution for 24 h and then rinsed with distilled water.

Calibration curves for metal determination were prepared from standard 1,000 mg L^{-1} (Titrisol®, Merck). Sample analysis was done only when the coefficient of determination (r^2) of the calibration curve was higher than 0.999. Analytical data quality and standard operation procedures, such as curve recalibration, analysis of reagent blanks, recovery of spike, and analysis of standard reference material 2710a Montana I Soil (Cd, Pb, Zn, Cu, Ni, Cr, Fe, and Mn) and 2709a San Joaquin Soil (As and Hg) (NIST, 2002), were carried out. The percentage recovery of metals in the spiked samples ranged from 87.20% to 101.42%. In addition, the NIST recoveries ranged from 83% to 116%. All analyses were carried out in duplicate.

The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined by inductively coupled plasma (ICP-OES/Optima 7000, Perkin Elmer). As and Hg were determined by an atomic absorption spectrophotometer (PerkinElmer AAnalyst™ 800)

coupled to a hydride generator (FIAS 100/Flow Injection System/PerkinElmer) using an electrodeless discharge lamp (EDL). The detection limits were 0.0006, 0.00009, 0.004, 0.0002, 0.0006, 0.00075, 0.003, 0.001, 0.003, and 0.004 mg L^{-1} for Fe, Mn, Pb, Cd, Zn, Cr, Cu, Ni, Hg, and As, respectively.

2.4 Assessment of contamination

In the interpretation of geochemical data, we used sediment contamination indices, such as contamination factor (CF), pollution load index (PLI), enrichment factor (EF), as well as comparison with sediment quality guidelines (SQGs). Choosing adequate background values plays an essential role, because it reflects the heavy metal concentrations expected to occur naturally. Many authors have used the earth crust values as background (Yap and Pang, 2011); however, owing to the fact that earth crust values are not representative of site geochemical differences and may yield misinterpretation in the interpretation of geochemical data, many authors have used regional uncontaminated soils, sediments or rocks as background values (Varol, 2011; Kaidao et al., 2012; Tang et al., 2013; Kalender and Uçar, 2013). Aiming to solve this drawback, we used average soil background concentration from both upstream and downstream surrounding uncontaminated areas.

Other hindrance is that both the SQGs and sediment contamination indices consider total concentration, and thus the assumption is that all species of a particular metal possess an equal impact with regard to the ecosystem (Dung, 2013). To address and minimize this problem, we limited our analysis to environmentally available metal concentrations in bedload (i.e., exchangeable, bound to carbonates, bound to iron and manganese oxides, or bound to organic matter fractions) inasmuch as the metals associated in these fractions are chiefly derived from anthropogenic sources and might be taken up by organisms (Yang et al., 2012).

2.4.1 Contamination factor

The contamination factor (CF) was obtained by dividing the concentration of each heavy metal in bedload by the background values:

$$CF = \frac{C_{heavymetal}}{C_{background}} \quad (2)$$

The CF values were interpreted, according to Hakanson (1980), as follows: CF <1 (low contamination); 1 < CF < 3 (moderate contamination); 3 < CF < 6 (considerable contamination); CF > 6 (very high contamination).

2.4.2 Pollution load index

The heavy metal pollution was assessed as the nth root of the product of the n CF:

$$PLI = (CF_1 x CF_2 x CF_3 x CF_4 x ..... x CF_n)^{1/n} \quad (3)$$

This simple index assesses the heavy metal pollution for the entire cross section. The PLI values were interpreted, according to Tomlinson et al. (1980), as follows: PLI > 1 (pollution exists) and PLI < 1 (no metal pollution).

2.4.3 Enrichment Factor

Once the concentration of heavy metals found in bedload does not enable the discrimination between natural and anthropogenic sources, the EF was calculated as:

$$EF = \frac{(Metal / Fe)_{sample}}{(Metal / Fe)_{background}} \quad (4)$$

The EF values were interpreted, according to Sakan et al. (2009), as follows: EF <1 (no enrichment); <3 (minor enrichment); 3–5 (moderate enrichment); 5–10 (moderately severe enrichment); 10–25 (severe enrichment); 25–50 (very severe enrichment); and >50 (extremely severe enrichment). To compensate for the difference in the grain size and composition of samples, we used geochemical normalization with Fe as a conservative element (Varol and Şen, 2012; Thuong et al., 2013). Other elements could be used, such as Al or Li (see detailed discussion in Dung, 2013).

2.5 Sediment Quality Guidelines

To evaluate the effect of the heavy metal concentrations found in bedload on the environment, we compared the levels with the background values and SQGs for aquatic systems (CCME, 1995). The numerical limits established to support and maintain the quality of aquatic environment, Probable Effect Level (PEL) and Threshold Effect Level (TEL), are summarized in Tables 1 and 2.

2.6 Statistical analysis

We used descriptive statistics and principal component analysis (PCA). PCA was applied to the correlation matrix of dataset in order to identify whether the heavy metals in bedload were derived from natural or anthropogenic sources. Principal component analysis consists of converting the original group of variables X_1, X_2,….., X_n, into a new group of variables Z_1, Z_2,…., Z_n, with equal dimension, but uncorrelated. These new groups of variables are known as principal components, linear combination of the original variables, which aim to explain the maximum total variability associated with these independent variables (Manly, 2008).

3. Results and Discussion

3.1 Sediment quality guidelines

The mean bedload discharge was equal to 0.23 t day^{-1} upstream and 0.12 t day^{-1} downstream. The mean available metal concentration for the upstream site followed the order of Fe > Mn > Zn > Pb > Cr > Cu > Ni > As > Cd > Hg. Based on SQGs, Cd, Hg, and As showed values lower than TEL. On the other hand, Pb, Cr, Cu, and Ni exceeded TEL in 8% of samples, as well as Zn in 25%. The metals exceeded the background values, as follows: Cd and Ni 17%; Pb, Cr, and Hg 25%; Zn 33%; Cu 42%; Mn 58%; and As 67% (Table 1).

Table 1. Comparison of heavy metal concentrations in bedload from the upstream cross section with SQGs and background values

Month	Metal concentration in bedload - upstream (mg kg^{-1})									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	6665.00	147.05	31.35	0.40	15.00	21.85	19.15	10.10	0.032	0.39
MAR	5795.91	238.17	26.78	0.10	350.10	53.00	42.03	34.65	0.040	0.89
APR	4637.91	210.32	8.03	<DL	59.88	8.25	3.78	2.95	0.030	0.40
MAY	10199.76	790.52	40.14	<DL	276.90	27.10	10.54	14.61	0.045	1.18
MAY*	3167.41	322.12	5.96	<DL	38.35	5.75	1.63	1.98	0.062	0.17
JUN	3204.91	712.72	6.13	<DL	39.05	5.42	1.33	1.80	0.042	0.32
JUN*	4348.50	692.56	18.50	<DL	150.77	14.63	5.37	7.31	0.086	0.48
JUL	2479.16	203.34	5.91	<DL	35.68	4.47	1.61	1.15	0.030	0.04
JUL*	6822.69	725.36	12.80	0.03	85.55	10.78	5.83	4.67	0.032	0.35
AUG	3184.78	192.80	6.09	<DL	36.40	6.77	2.28	2.10	0.027	0.18
SEP	4604.41	622.97	8.93	<DL	58.53	6.42	3.66	2.95	0.029	0.30
OCT	6592.50	326.34	6.05	0.13	8.48	9.20	2.98	3.00	0.035	0.26
Mean	5141.91	432.02	14.72	0.16	96.22	14.47	8.35	7.27	0.04	0.41
Comparison with sediment quality guidelines and background values										
TEL	na	na	35.00	0.60	123.00	37.30	35.70	18.00	0.17	5.90
PEL	na	na	91.30	3.50	315.00	90.00	197.00	35.90	0.49	17.00
Background (B)	13407.59	254.55	21.54	0.12	82.20	20.06	5.27	10.71	0.043	0.26
Samples > TEL	na	na	1	0	3	1	1	1	0	0
Samples > PEL	na	na	0	0	1	0	0	0	0	0
Samples > B	0	7	3	2	4	3	5	2	3	8

na = data not available; B = Background value * = second measurement in the same month; <DL = below detection limit. Note: TEL and PEL (Canadian Sediment Quality Guidelines) are the values used by Brazilian legislation CONAMA (2012).

At the downstream site, the mean available metal concentration followed the order of Fe > Mn > Zn > Cr > Pb > Cu > Ni > As > Hg > Cd. As observed in the upstream cross section, Cd, Hg, and As showed values lower than TEL; nevertheless, the metals exceed TEL as follows: Pb and Ni 8%, Cr and Cu 17%, Zn 25%. Both Zn and Ni exceeded PEL in 8% of the samples. Furthermore, the metal concentration at the downstream site exceed background values in terms of percentages of samples as follows: Fe and Cd 8%, Cr 25%, Hg 50%, Pb 58%, Mn and Cu 67%, Ni and As 83%, Zn 100% (Table 2). According to the SQGs, Zn at both sites and Ni at the downstream site showed concentrations potentially having harmful effects on sediment-dwelling organisms. As the heavy metal concentrations in bedload considerably exceeded the background values, such as Mn 58% and 67% of the samples, upstream and downstream, respectively, as well as Zn 100% and

Ni and As 83% of the samples at the downstream site, the TEL and PEL seem to underestimate the harmful effect of those metals on sediment-dwelling organisms.

Table 2. Comparison of heavy metal concentrations in bedload from the downstream cross section with SQGs and background values

Month	Metal concentration in bedload - downstream (mg kg^{-1})									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	9360.00	98.30	11.55	0.35	29.35	44.35	41.65	14.00	0.05	2.96
MAR	6495.91	51.22	41.53	<DL	475.45	57.45	16.48	40.35	0.08	2.74
APR	9965.91	76.32	15.63	<DL	271.58	14.00	39.93	9.40	0.07	4.27
MAY	3712.95	160.64	8.23	<DL	80.60	8.83	5.53	6.67	0.06	1.63
MAY*	7460.91	115.59	8.91	<DL	70.25	9.55	8.01	6.00	0.09	2.61
JUN	3230.91	66.92	4.68	<DL	33.20	15.60	3.38	1.00	0.04	0.33
JUN*	14763.41	527.39	18.48	0.03	81.93	19.07	13.86	5.13	0.08	3.52
JUL	5833.41	147.07	7.78	<DL	65.53	7.87	5.73	3.63	0.04	1.74
JUL*	12945.91	941.97	19.66	<DL	103.30	15.25	16.06	5.53	0.04	2.96
AUG	15487.78	308.58	25.56	0.05	111.75	21.17	18.08	8.48	0.05	2.58
SEP	27683.41	426.92	34.51	0.18	143.88	34.50	19.93	12.25	0.06	2.95
OCT	3984.16	27.32	4.81	<DL	44.95	5.12	4.16	1.70	0.03	0.36
Mean	10077.06	245.68	16.78	0.05	125.98	21.06	16.07	9.51	0.06	2.39
Comparison with sediment quality guidelines and background values										
TEL	na	na	35.00	0.60	123.00	37.30	35.70	18.00	0.17	5.90
PEL	na	na	91.30	3.50	315.00	90.00	197.00	35.90	0.49	17.00
Background (B)	21079.71	92.00	8.97	0.29	7.11	23.10	6.82	2.34	0.05	1.01
Samples > TEL	na	na	1	0	3	2	2	1	0	0
Samples > PEL	na	na	0	0	1	0	0	1	0	0
Samples > B	1	8	7	1	12	3	8	10	6	10

The TEL and PEL do not discriminate between natural and anthropogenic heavy metal sources and also seem inappropriate to assess the heavy metal contamination in bedload from Ipojuca River, being essential either to calibrate the SQGs for site specific conditions (Long et al., 2006) or develop site specific guidelines (Choueri et al., 2009; Deckere et al., 2011). To support the insights provided by the background values, we used additional tools, such as sediment contamination indices and principal component analysis.

3.2 Sediment contamination indices

The CF mean values for the upstream cross section followed the order Cu (1.83) > As (1.6) > Mn (1.51) > Zn (1.14) > Hg (0.87) > Cr (0.77) > Ni (0.74) > Pb (0.68) > Cd (0.58) > Fe (0.39). According to Hakanson (1980), the CF values for Cu, As, Mn, and Zn

denotes moderate contamination, whilst the other metals showed low contamination. Studying heavy metal contamination in bottom sediments from Tigris River, Varol (2011) also observed the highest CF values for Cu, which was related to municipal and industrial wastewater discharges. Except for March and May (PLI > 1), more than 75% of monthly PLI values were lower than 1 (Figure 2a). According to the mean PLI value (0.82), the upstream site was considered not polluted (Tomlinson et al., 1980).

In the downstream cross section, except for Cd at the upstream site, the CF mean values were higher, as follows: Zn (20.23) > Ni (4.75) > Cu (2.71) > Mn (2.38) > Pb (2.07) > As (1.83) > Hg (1.07) > Cr (1.03) > Fe (0.51) > Cd (0.23). According to Hakanson (1980), the CF values for Fe and Cd in bedload denotes low contamination; Cu, Mn, Pb, As, Hg, and Cr indicates moderate contamination; Ni shows considerable contamination; Zn denotes very high contamination (Figure 2b). Based on the mean PLI value (1.79), the downstream cross section was classified as polluted (Tomlinson et al., 1980).

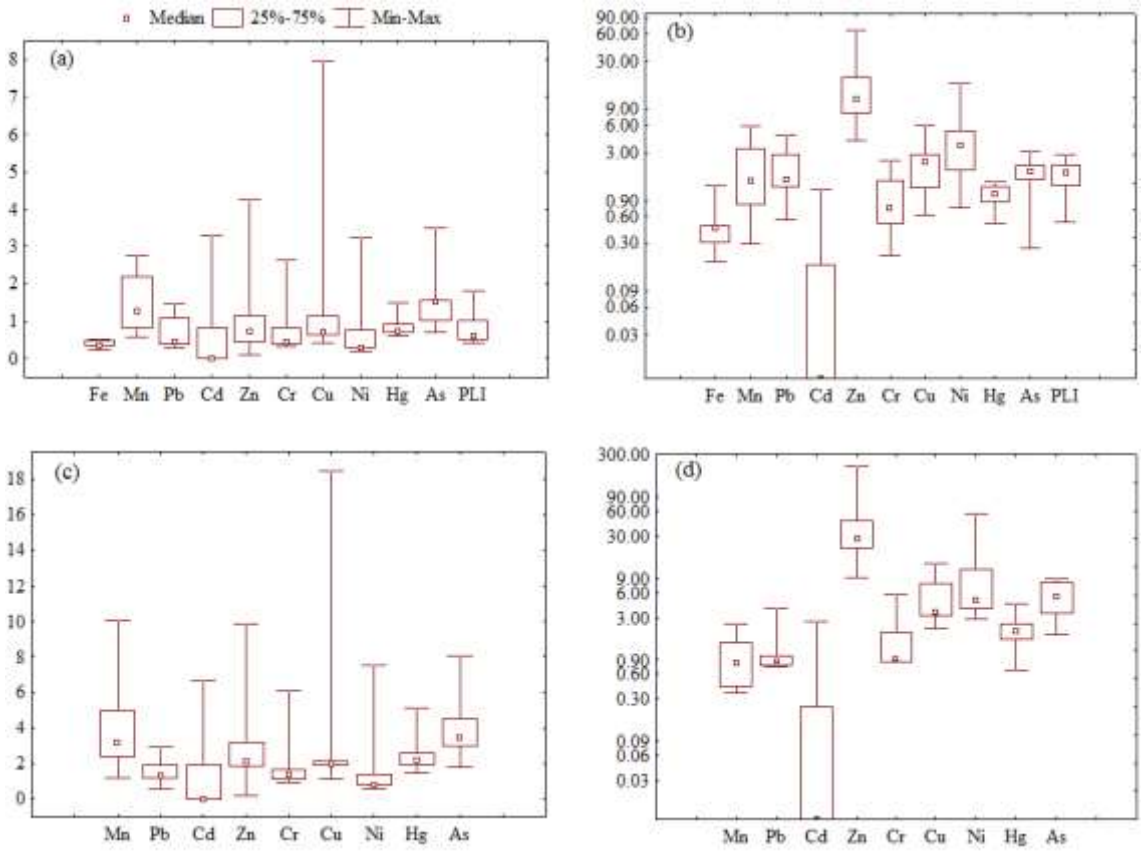

Figure 2. Metal contamination factors (CFs) and pollution load indices for bedload upstream (a) and downstream (b); also enrichment factors (EFs), upstream (c) and downstream (d).

The EF mean values for the upstream and downstream sites followed the order Cu (4.31) > Mn (4.26) > As (3.97) > Zn (2.85) > Hg (2.58) > Cr (1.90) > Ni (1.75) > Pb (1.66) > Cd (1.2) and Zn (52.83) > Ni (12.23) > Cu (5.95) > As (5.46) > Hg (2.21) > Cr (1.86) > Pb (1.23) > Mn (1.02) > Cd (0.39), respectively. Except for Zn at the downstream site, the EF mean values of Ipojuca River are lower than the EF values observed in bottom sediments from Euphrates River (Salah et al., 2012). In the upstream cross section, except for Mn, Cu, and As (moderate enrichment), all metals showed minor enrichment (Sakan et al., 2009). Despite the highest maximum EF for Cu (18.43), 75% of monthly values ranged from 1 to 3 (Figure 2c). The same was observed for Pb, Cd, Cr, Ni, and Hg, whereas Mn, Zn, and As showed 25% of EF values higher than 3.

The highest EF values for Zn, Ni, Cu, and As were observed at the downstream site inasmuch as Mn, Pb, Cd, Cr, and Hg showed at least 75% of EF values between 0–3 (no and minor enrichment, Figure 2d). A slight positive deviation from unity, as observed for

Cd EF 1.2 at the upstream site, as well as Pb EF 1.23 and Mn EF 1.02 at the downstream site does not necessarily mean anthropogenic sources; it might be yielded by natural composition variation between studied sediments and reference soils used (Gao and Chen, 2012). Based on the foregoing, EF between 0.05 and 1.5 suggest that both Pb and Mn are entirely derived from natural processes or crust material; however, an EF value greater than 1.5 suggested that the studied heavy metal is predominantly derived from anthropogenic processes (Zhang and Liu, 2002).

3.3 Principal component analysis

We used principal component analysis (PCA) of standardized data to discern patterns among heavy metal sources and to identify the contribution of each heavy metal to each PC (Figure 3). The entire data set showed PCs with eigenvalues > 1 (e.g. PC1 5.60, PC2 2.23, and PC3 1.29, as well as PC1 4.34, PC2 2.15, and PC3 1.62), which explains roughly 91% and 81% of the total variance in the upstream and downstream cross sections, respectively.

In the upstream cross section, PC1 accounted for 55.99% of the total variance and was correlated with Pb (-0.84), Zn (-0.83), Cr (-0.98), Cu (-0.96), Ni (-0.96), and As (-0.90) (Figure 3a); PC2 accounted for 22.32% and was correlated with Mn (0.79), Cd (-0.76) and Hg (0.74) (Figure 3a); PC3 accounted for 12.92% and was correlated with Fe (0.60) (Figure 3b). PC1 seems to represent heavy metals derived from a mixture of sources: As and Cu were mainly derived from anthropogenic sources as reinforced by the background and EF values (Table 1 and Figure 2c), whereas Pb, Zn, Cr, and Ni were predominantly derived from natural sources. Both PC2 and PC3 suggest metals derived from natural sources.

At the downstream site, PC1 accounted for 43.39% of the total variance and was correlated with Pb (-0.82), Zn (-0.80), Cr (-0.87), Ni (-0.88), Hg (-0.70), and As (-0.71) (Figure 3c); PC2 accounted for 21.47% and was correlated with Fe (0.74), and Cd (0.71) (Figure 3c); PC3 accounted for 16.24% and was correlated with Mn (-0.70), and Cu (0.61) (Figures 3d). These results suggest that heavy metals represented by PC1 were predominately derived from anthropogenic sources. Zn and Ni also showed the highest CF and EF values and exceeded the background values in 100% and 83% of samples, respectively; Pb, Hg and As exceeded the background values at least in 60% of background samples. PC2 represents metals derived from natural sources. The proximity

of lines for Fe and Cd highlight their reciprocal association (Qu and Kelderman, 2001). This result is strongly supported by CF, EF and the background values obtained for Fe and Cd. This PC analysis, the CF and also the background values in comparison with heavy metal concentration in bedload reinforced the adequate choice of Fe for geochemical normalization. PC3 appears to represent heavy metals from a mixture of sources: Cu mainly came from anthropogenic sources, whereas Mn seems to be related to natural sources. Despite exceeding the background values in 67% of the samples, the enrichment factor equal to 1.02 suggested that Mn was derived from natural sources. Such PCA-indicated mixtures of sources for heavy metals in soils and sediments have been reported by several authors (Micó et al., 2006; Thuong et al., 2013).

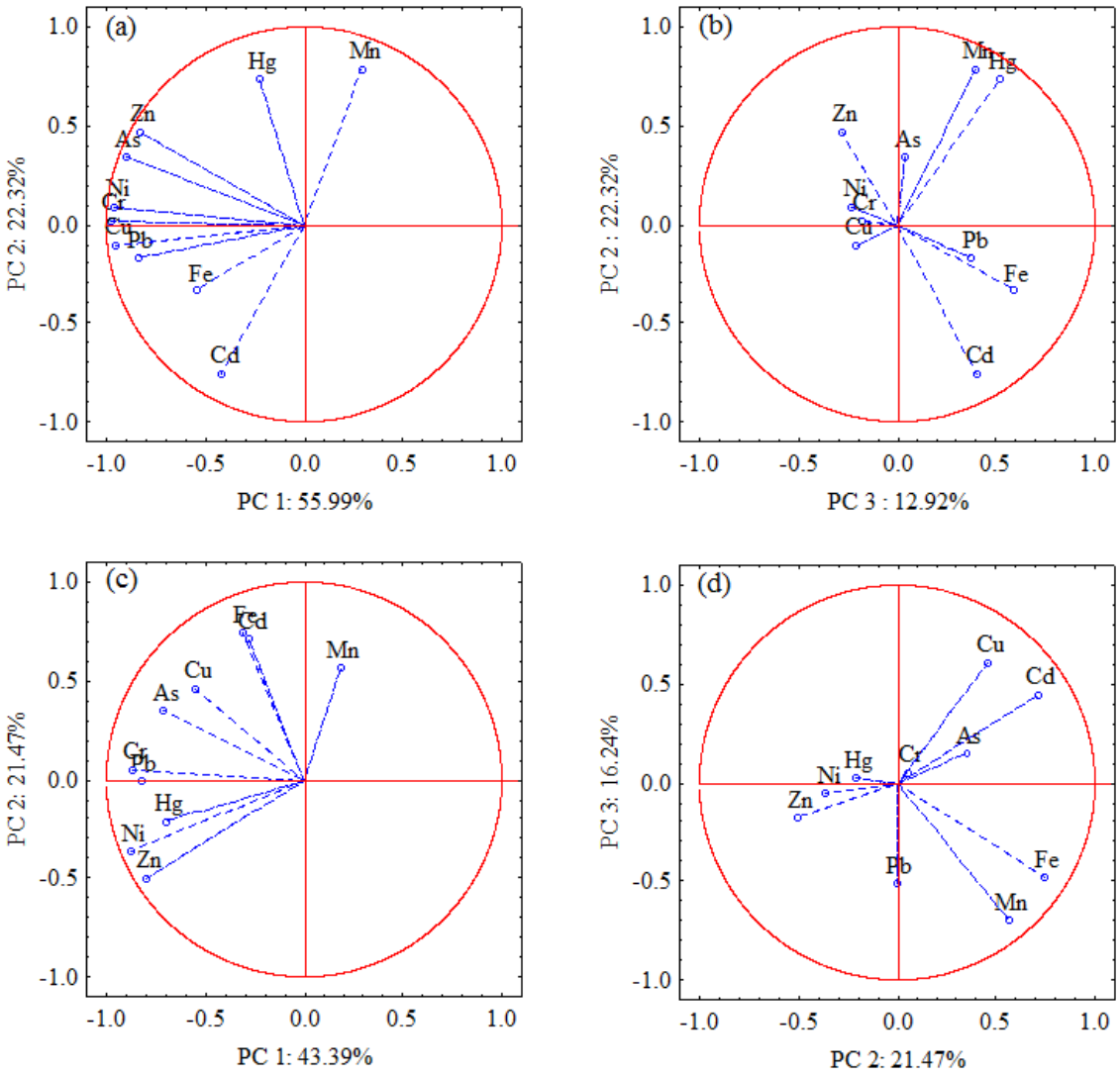

Figure 3. Loadings of heavy metals on significant principal components for the upstream (a and b) and downstream (c and d) sites in Ipojuca River.

In comparison with some important contaminated rivers around the world, such as Euphrates, Tigris, and Danube, the sediments from Ipojuca River are contaminated to a lesser extent (Woitke et al., 2003; Varol, 2011; Salah, 2012). On the other hand, the heavy metal concentrations in the downstream cross section clearly reflect the inputs of anthropogenic sources. Our results do not address atmospheric deposition within Ipojuca watershed. It may have some influence due to the number of sites under the industrial influence (Hejabi et al., 2011).

By far Zn and to a less extent Ni, Cu, and As in the downstream cross section represent a major concern. The major source of Cu and Zn, found in bedload, is most likely the urban/municipal wastes (537 tons daily considering the 25 municipalities along Ipojuca River) and agriculture with its large-scale use of agrochemicals and fertilizers (Raju et al., 2012; Bednarova et al., 2013), whereas As may be related to leather industry in Ipojuca River, which generates about 76 tons of textile wastes daily (CPRH, 2003). Furthermore, the Zn supply may be related to runoff from vehicle related sources and tire residues (Krčmová et al., 2009). Other possible sources for heavy metal contamination in the catchment area include oil wastes (20 tons daily), battery wastes (2 tons daily) and also municipal wastewaters.

4. Conclusions

We combined different tools, such as enrichment factor, principal component analysis, and comparison with sediment quality guidelines and background values to assess the heavy metal contamination in the bedload of Ipojuca River. The environmental heavy metal concentrations in bedload were clearly an adequate and feasible indicator of anthropogenic impact along Ipojuca River. Taking into account the mean heavy metal concentrations in bedload, harmful effects on sediment-dwelling organisms are not supposed to occur; however, comparison with regional background seems to be more reliable than the comparison with Canadian SQGs. According to the PLI values, the upstream and downstream sites were considered not polluted and polluted, respectively. This finding was reinforced by the highest EF values observed mainly for Zn, Ni, Cu, and As in the downstream cross section. Principal component analysis explained roughly 91% and 81% of the total variance in heavy metal contamination upstream and downstream, respectively, and distinguished natural and anthropogenic contributions in Ipojuca River. Multiple lines of evidences observed by means of EF, comparison with background

values, and PCA suggested that Zn, Ni, Cu and As at downstream site were mainly derived from anthropogenic sources and can be easily remobilized under natural conditions encountered in Ipojuca River.

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CHAPTER III

HEAVY METAL FLUXES IN SEDIMENTS OF AN ENVIRONMENTALLY IMPACTED RIVER IN BRAZIL

Abstract

The Ipojuca River is one of the most polluted rivers in Brazil. Its watercourse allows a unique opportunity to evaluate water pollution in the semiarid and coastal region of Brazil. However, there is no information regarding heavy metal concentrations and fluxes in suspended sediment and bedload. In order to fill this gap and meet the international need to include polluted rivers in future world estimation of heavy metal fluxes, this study aimed to determine the fluxes of Hg, Pb, Cd, Ni, Cu, Cr, Zn, As, Fe and Mn transported in suspended sediment and bedload. To collect both the suspended sediment and water samples, we used the US DH-48. Bedload measurements were carried out using the US BLH 84 sampler. The total heavy metal flux in solid phase (suspended sediment + bedload) followed the order Fe > Zn > Mn > Pb > Ni > Cu > Cr > As > Cd > Hg and Fe > Zn > Mn > Pb > Cu > Ni > As > Cr > Hg > Cd, upstream and downstream, respectively. Both upstream and downstream the suspended sediment contributed more than 99% of the heavy metal flux. By far Pb and to a less extent Zn at the downstream site represent a major concern. The flux of Pb and Zn in suspended sediment was 4.20 kg km^2 $year^{-1}$ and 2.93 kg km^2 $year^{-1}$, respectively. These fluxes were higher than the values reported for Pb and Zn for Tuul River (highly impacted by mining activities), 1.60 kg km^2 $year^{-1}$ and 1.30 kg km^2 $year^{-1}$ (suspended + dissolved phase), respectively, as well as the Pb flux (suspended + dissolved) to the sea of some Mediterranean rivers equal to 3.4 kg km^2 $year^{-1}$. Therefore, the highest flux of Pb and Zn in Ipojuca River highlighted the importance to include also medium or small rivers in the future estimation of world heavy metal fluxes in order to protect ecosystems, estuaries and coastal zones.

Keywords: Heavy metal contamination, Sediment transport, Sediment quality, Water discharge.

1. Introduction

The growing industrial and urban development, along Ipojuca River that is a vital water resource of Northeast Brazil, poses a threat due to the increase in heavy metal fluxes. Its watercourse comprises the Industrial and Harbor Complex of Suape, responsible for a large development of the region. Despite being considered as one of the most polluted rivers in Brazil, there is lack of water pollution studies and hence data regarding this is a concern worldwide. Among the reasons for this scarcity is the considerable investment linked to field measurements and chemical analyses (Viers et al., 2009). Accurate calculation of heavy metal fluxes requires simultaneous data on both discharge and sediment concentration (Horowitz, 2003) as well as metal concentration over time.

The rivers play an important role in heavy metals transport from continents to oceans both in dissolved and solid phases. The last is the focus of this study, because heavy metals are mainly transported by sediments (Horowitz, 1995; Žák, et al. 2009; Ollivier et al. 2011). Moreover, suspended sediments are widely recognized to be of the highest importance in heavy metal fluxes. Nonetheless, the contribution of bedload has been ruled out in several studies. The fact that the bedload usually ranges from 5-25% of suspended sediment discharge (Yang, 1996; Cantalice et al., 2013) does not address the point at which the bedload contribution becomes insignificant. For instance, data from Arkansas and Cowlitz Rivers showed that the > 63μm fraction provided a substantial contribution to suspended sediment-associated chemical concentration (Horowitz, 2008a). Therefore, it seems appropriate to measure also the heavy metal flux in bedload before establishing a general assumption.

Although heavy metal concentrations have been widely adopted in sediment quality studies (CCME, 1995; MacDonald et al., 2000), heavy metal contamination in rivers can be better addressed by comparing heavy metal fluxes (Horowitz, 2008a), chiefly because its concentration at upstream sites may not reach the downstream watercourse and hence may lead to implausible conclusions (Thorslund et al., 2012). Recently, the pioneering work of heavy metal fluxes by Martin and Meybeck (1979) was updated by Viers et al. (2009). However, the new database was calculated, mainly considering the major world rivers responsible for the transport of suspended sediment to ocean. Therefore, there is a need to include small and medium polluted rivers in the future world estimations. In this context, the objective of this study was to determine the heavy metal fluxes of mercury

(Hg), lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), zinc (Zn), arsenic (As), iron (Fe) and manganese (Mn) in suspended and bedload sediments. Besides discussing the heavy metal fluxes in sediments, this paper also aims to provide a snap-shot of heavy metal concentrations in the waters of Ipojuca River.

2. Material and Methods

2.1 Study area

The Ipojuca River watershed extends from the semiarid region to the coast, with a total river length of 290 km (08°09'50'' – 08°40'20'' S and 34°57'52''– 37°02'48'' W). It drains a catchment area of about 3,435 km^2 (Figure 1), along which are located 25 municipalities with a total population of 1,110,841 inhabitants, most of them in urban zones (SRH, 2010). Streamflow is intermittent for the first 100 km. At the outlet the flow rate ranges from 2 $m^3 s^{-1}$ in the dry season to 35 $m^3 s^{-1}$ in the rainy season.

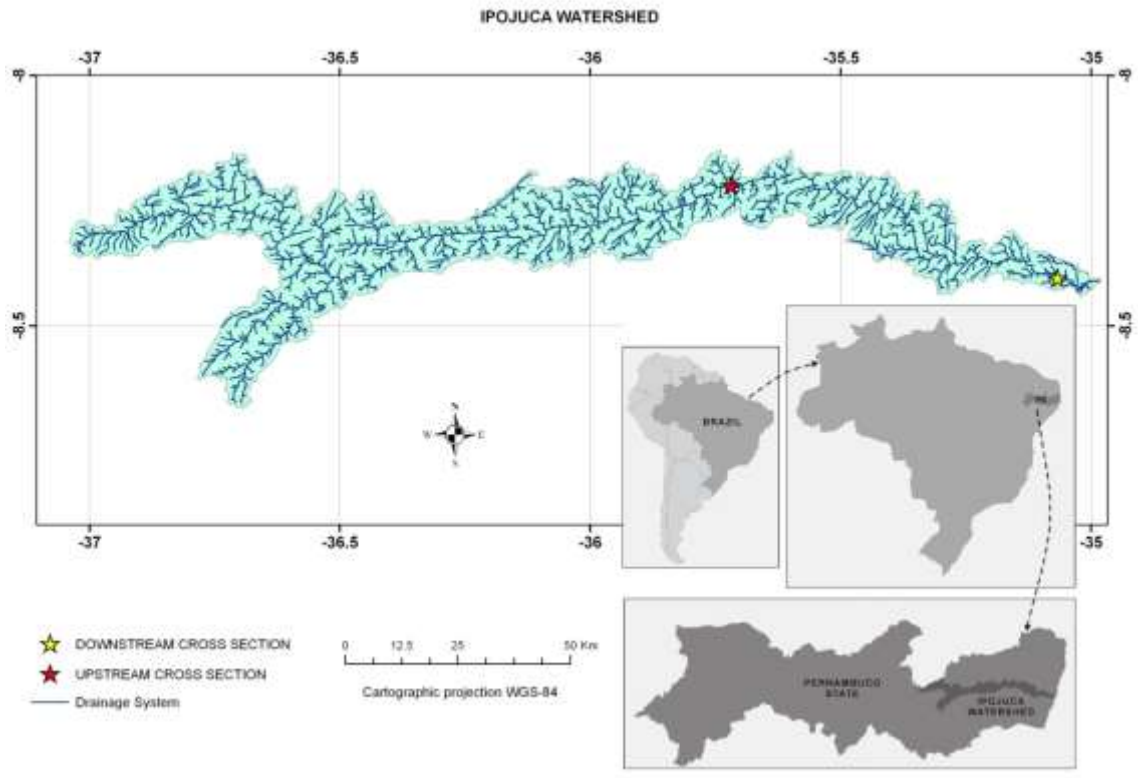

Figure 1. Location of the Ipojuca River watershed.

Soils are predominantely Entisols (36.74%), Ultisols (32.11%), Alfisols (17.77%), and Oxisols (8.89%). The remaining soils comprise 4.49% of the Ipojuca watershed (ZAPE, 2002; EMBRAPA, 2006). In general, the amount of sediment supplied to the

studied cross sections is partly a result of sugarcane agricultural activities, which trigger erosion mainly in the form of interrill and rill erosion. This erosion may also be aggravated by agricultural activities along the river banks in the studied reaches, as well as the predominance of strong relief near the downstream cross section (Figure 2). Annual rainfall ranges from 600 mm in the semiarid region to 2,200 mm in the coastal zone. During the study period monthly rainfall ranged from 0 mm (February) to 147.5 mm (July) and 23 mm (February) to 444 mm (June), upstream and downstream, respectively (Figure 3). The annual average air temperature is approximately 24°C (SRH, 2010).

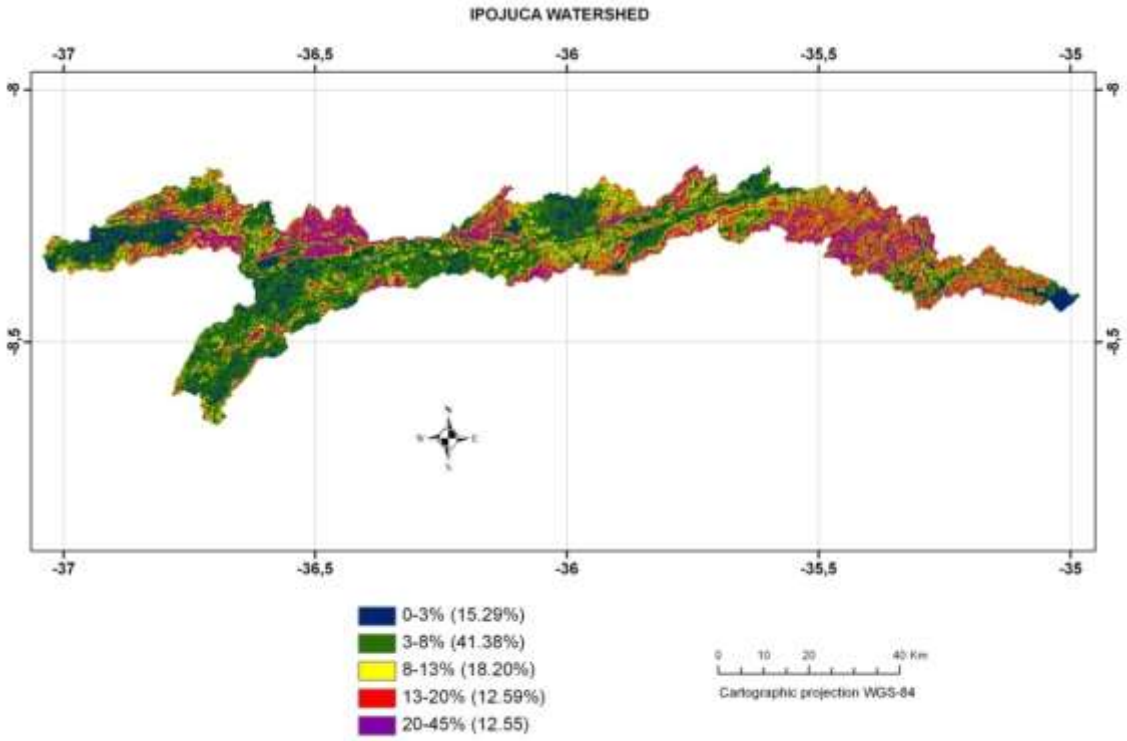

Figure 2. Relief map of Ipojuca watershed. In parentheses the percentage of each slope class.

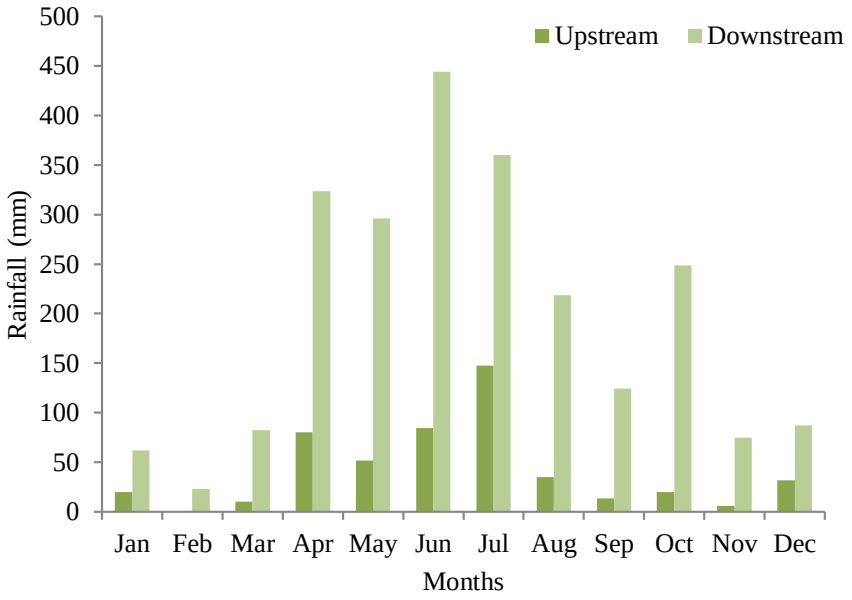

Figure 3. Monthly rainfall of studied cross sections of Ipojuca River during 2013.

2.2 Sampling sites and measurements

Water, suspended sediment and bedload from both the upstream (08º13'10'' S – 35º 43'09'' W) and the downstream (08º24'16'' S – 35º04'03'' W) cross sections were collected. For both sites, flat stretches of river with well-defined banks were selected, free from any features that could cause disturbances in the flow regime. The mean flow depth ranged from 0.27 m to 0.56 m and 0.8 m to 2.43 m while the mean width ranged from 6.0 m to 10.80 m and 21.80 m to 30.3 m, in the upstream and downstream cross sections, respectively. The upstream cross section is chiefly affected by domestic sewage and also wastewater from industrial and agricultural production, whereas the downstream cross section is mainly affected by sugar cane farming and processing.

To collect both the suspended sediment and water samples, we used a US DH-48 sampler calibrated with a stainless steel intake nozzle having a ¼-inch diameter. Twenty-four direct measurements (twelve in each cross section) were made during 2013, in accordance with the equal-width-increment (EWI) depth integrated and isokinetic sampling method proposed by Edwards and Glysson (1999). This approach allowed for obtaining representative samples not only for water but also suspended sediment concentration in the verticals of the studied reaches. The depth-averaged velocity was obtained by an electromagnetic current meter adjusted in each vertical as a function of depth. Furthermore, the transit rate was calculated following USGS (2005). The

information used during the suspended sediment sampling was not the transit rate (K equal to 0.4), but the sampling time calculated by the expression proposed by Carvalho et al. (2000) (Table 1).

Table 1. Description of sediment transport variables of Ipojuca River

Type of variable	Code	Calculation	Unit
Water discharge	Q	$\sum Q_i = A_i V_i$	$m^3 s^{-1}$
Transit rate	V_t	$V_i K$	$m s^{-1}$
Suspended sediment sampling time	t_1	2h/Vt	s
Suspended sediment concentration	SSC	M/V_{sample}	$mg L^{-1}$
Box coefficient	BC	SSC'/SSC_i	Dimens.
Suspended sediment discharge	SSQ	$\sum(SSC_i Q)0.0864$	$t day^{-1}$
Bedload discharge	QB	$\sum(m/wt_2)L_x 0.0864$	$t day^{-1}$

Q_i = water discharge in each vertical segment; A_i = influence area of the vertical; V_i = mean flow velocity in the sampled vertical; K = constant of variable proportionality (dimensionless); h = flow depth; Vt = transit rate; M = suspended sediment mass; V_{sample} = sample volume; SSC' = average of suspended sediments concentration; SSC_i = suspended sediment concentration at each vertical; 0.0864 is for the transformation of data in $t day^{-1}$; m = mass of sediment from bedload transport; w = width of nozzle - US BLH – 84; t_2 = sampling time of bedload transport; L_x = equivalent width.

In the same verticals the bedload was sampled using the US BLH 84 sampler. After sampling, the water, suspended sediment and bedload samples were stored in polyethylene bottles for further analysis. In addition, the sediment mass values were obtained by the evaporation method (USGS, 1973). The methods for calculation of suspended sediment concentration, suspended sediment discharges (Horowitz, 2003) and bedload discharge (Gray, 2005) are summarized in Table 1.

2.3 Chemical analysis

Heavy metals were measured in water, suspended sediment, bedload and uncontaminated soil samples (background values). The background values for heavy metals were determined from uncontaminated soil samples (i.e. four composite soil samples taken from surrounding forest areas at each site, where soils are mineralogically and texturally comparable with river sediments). The uncontaminated soil samples were sieved on a 2-mm mesh nylon sieve then soil and sediment samples were macerated in an agate mortar and sieved with a stainless steel 0.3-mm mesh sieve (ABNT no. 50). For heavy metal determination, 0.5 g soil or sediment (suspended sediment and bedload) was digested in Teflon vessels with 9 mL of HNO_3 and 3 mL of HCl USEPA 3051A (USEPA,

1998) in a microwave oven (MarsXpress) for 8 min 40 s on the temperature ramp, the necessary time to reach 175 °C. Then, this temperature was maintained for an additional 4 min 30 s. The same procedure was applied for 5 mL water samples digestion.

After digestion, all extracts were transferred to 50-mL certified flasks (NBR ISO/IEC), filled with ultrapure water (Millipore Direct-Q System) and filtered in a slow filter paper (Macherey Nagel®). High purity acids were used in the analysis (Merck PA). Glassware was cleaned and decontaminated in a 5 % nitric acid solution for 24 h and then rinsed with distilled water.

Calibration curves for metal determination were prepared from standard 1,000 mg L^{-1} (Titrisol®, Merck). Sample analysis was done only when the coefficient of determination (r^2) of the calibration curve was higher than 0.999. Analytical data quality and standard operation procedures, such as curve recalibration, analysis of reagent blanks, recovery of spike, and analysis of standard reference material 2710a Montana I Soil (Cd, Pb, Zn, Cu, Ni, Cr, Fe, and Mn) and 2709a San Joaquin Soil (As and Hg) (NIST, 2002), were carried out. The percentage recovery of metals in the spiked samples ranged from 87.20% to 101.42%. In addition, the NIST recoveries ranged from 83% to 116%. All analyses were carried out in duplicate.

The concentrations of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn were determined by inductively coupled plasma (ICP-OES/Optima 7000, Perkin Elmer). As and Hg were determined by an atomic absorption spectrophotometer (PerkinElmer AAnalyst™ 800) coupled to a hydride generator (FIAS 100/Flow Injection System/PerkinElmer) using an electrodeless discharge lamp (EDL). The detection limits were 0.0006, 0.00009, 0.004, 0.0002, 0.0006, 0.00075, 0.003, 0.001, 0.003, and 0.004 mg L^{-1} for Fe, Mn, Pb, Cd, Zn, Cr, Cu, Ni, Hg, and As, respectively.

2.4 Heavy metal flux

The heavy metal fluxes in suspended sediments were calculated using the following equation (Horowitz et al., 2001):

$$flux = \left(\frac{\text{MEC.SSC}}{1000}\right) \text{Q}.\, 0.0864 \quad (1)$$

where flux is the heavy metal fluxes in suspended sediment (t day^{-1}), MEC is the metal element concentration (µg g^{-1}), SSC is the suspended sediment concentration (g L^{-1}), Q is the water discharge ($m^3 s^{-1}$), 0.0864 is for the transformation of data in t day^{-1}. Note that the heavy metal flux in suspended sediment was calculated after recalculation of the

concentration from mass mass^{-1} units to mass volume^{-1}. The heavy metal flux in bedload was calculated by the relation between the amount of bed sediment crossing the site (Gray, 2005) and its respective metal concentration.

2.5 Statistical Analysis

Pearson's correlation, descriptive statistics, regression and cluster analysis were applied in this study. To carry out the cluster analysis we used standardized data to avoid misclassification due to differences in data dimensionality (Webster, 2001). In addition, Ward's method was chosen (Euclidean distance as a measure of similarity), mainly because it merges clusters on the basis of the sum of squares and the best performing hierarchical clustering, which minimizes information loss (see detailed discussion in Templ et al., 2008).

3. Results and Discussion

3.1 Hydrology of Ipojuca River

The rating curve relating water discharge and flow depth provided a determination coefficient equal to 0.92 (Figure 4). This depicted the natural variability of hydrological events. This rating curve was fitted to water discharge and flow depth ranging from 0.27 m^3 s^{-1} to 25.26 m^3 s^{-1} and 0.27 m to 2.43 m. The number of measurements and the difference between minimum and maximum values were essential for improving the effectiveness of rating curve (Carvalho, 2008).

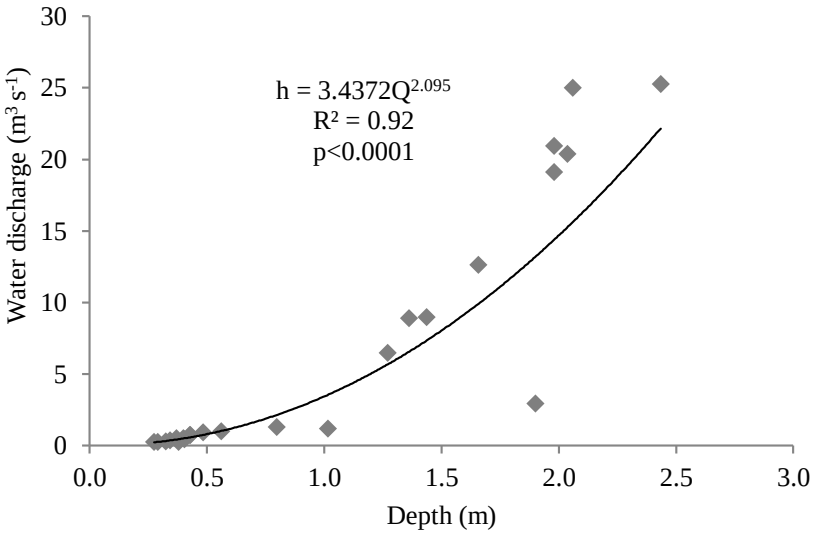

Figure 4. Depth-discharge rating curve of Ipojuca River obtained from twenty four direct measurements during 2013.

In the upstream cross section a multi-modal dominant discharge was observed, with peaks of suspended sediment concentration lagging behind, taking place at the same time as well as after extreme flow events (Figure 5a). The first two trends of sediment concentration to hydrograph are typical of semiarid environment and may be related to low flow or short distance of transport from erosion site in the upstream cross section. The fast hydrological response observed in the upstream cross section has been often reported in semiarid studies (Yuanxu Ma et al. 2010; Cantalice et al. 2013).

Despite being most common in the semiarid environment, the lag far behind the peak of suspended sediment concentration related to the flow (Figure 5b) might be linked to the first flow events provoked by high intensity rainfall, which resulted in more losses of soil particles in the downstream cross-section (Colby, 1963). This hypothesis may be supported by the difference of erosivity between rainfall from coastal zone and semiarid region, ranging from 5,500 to 10,000 Mj mm ha^{-1} h^{-1} $year^{-1}$ and 1,500 a 3,500 Mj mm ha^{-1} h^{-1} $year^{-1}$, respectively (Cantalice et al., 2009). The highest erosivity, predominance of 13-20% and 20-45% slope classes (Figure 2) as well as Ultisols that comprise 32% of the Ipojuca Watershed (i.e. soils highly susceptible to erosion due to the presence of Bt horizon) likely increased the fine sediment supply in the first precipitation events and runoff at the downstream site.

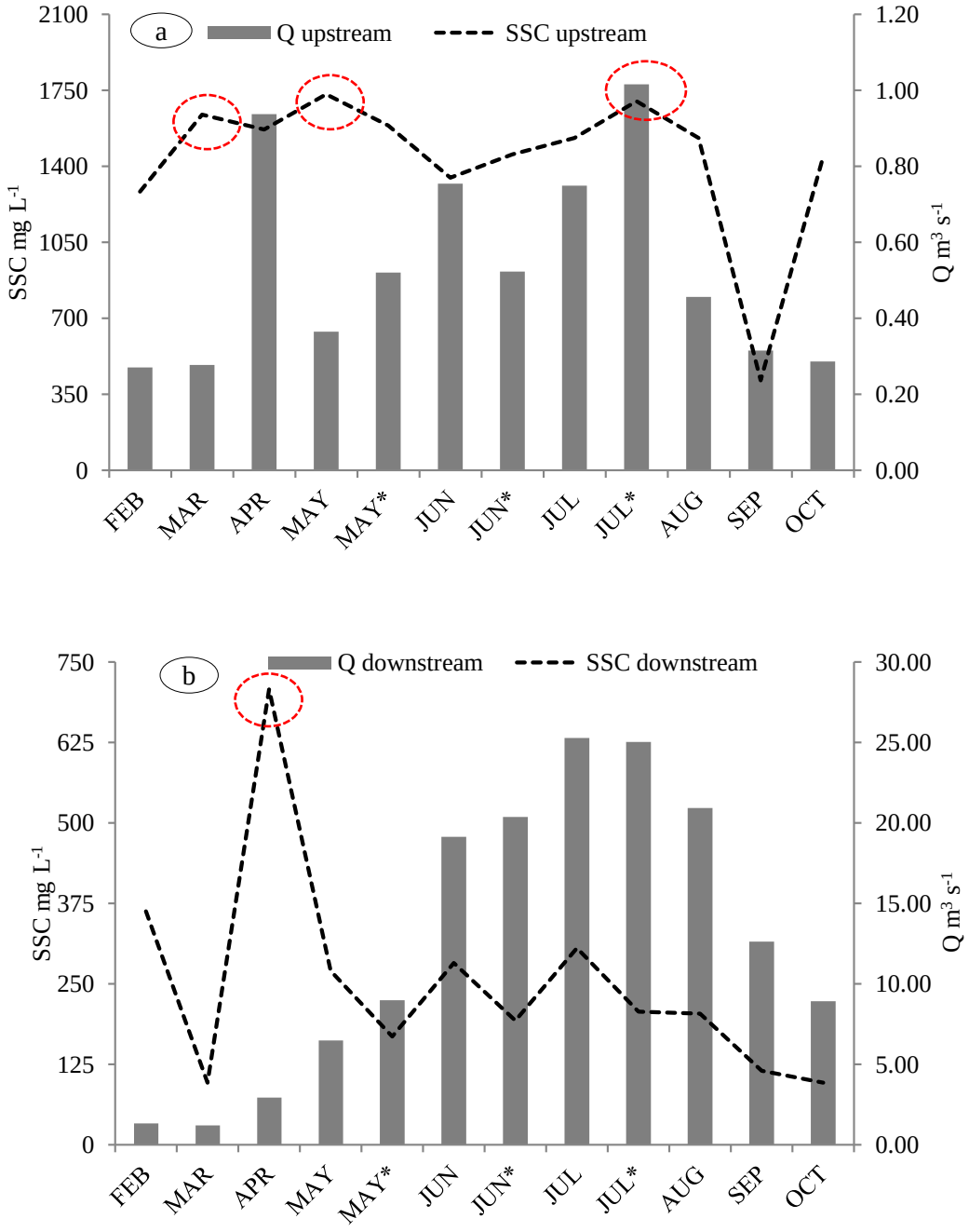

Figure 5 (a and b). Hydrographs and Sedigraphs at the studied sites of Ipojuca River. *second measurement in month.

The flow depth showed a standard deviation equal to 0.08 and 0.49 with a mean flow velocity equal to 0.15 m s^{-1} and 0.26 m s^{-1}, upstream and downstream, respectively (Table 2). In the upstream cross section the suspended sediment discharge ranged from

29.91 t day^{-1} for the period with the lowest water discharge (0.27 m^3 s^{-1}) to 150.35 t day^{-1} for the period with the highest water discharge (1.02 m^3 s^{-1}), whereas in the downstream cross section the suspended sediment discharge ranged from 7.67 t day^{-1} for the period with the lowest water discharge (1.21 m^3 s^{-1}) to 669.18 t day^{-1} for the period with the highest water discharge (25.26 m^3 s^{-1}). The mean coefficient box showed values equal to 1 at both sites, which comprise the ideal range of 0.9 to 1.2 (Gray, 2005). Thereby, the suspended sediment sampling was regarded accurate.

At both the upstream and downstream cross sections the bedload/suspended sediment ratio was lower than 5%. According to Yang (1996), the bedload transport rate of a river is about 5-25% of the suspended sediment transport. Nevertheless, the low rates might be related to the presence of dams which are known to have a strong effect on sediment transport (Walling, 2006; Preciso et al., 2012). Besides this possibility, the median grain diameter (D50) ranging from 0.252 mm to 0.736 mm may have triggered the suspension of bedload into flow due to turbulent motions (Powell, 2009). Based on bedload suspension criterion the bedload movement can occur between 0.07 to 4 mm of grain size (Bagnold, 1966).

Table 2. Hydraulic and sediment transport variables studied in Ipojuca River

Upstream						
Months	h	V	Q	SSQ	QB	(QB/SSQ)x100
FEB	0.27	0.12	0.27	29.91	0.03	0.11
MAR	0.29	0.13	0.28	32.40	0.01	0.03
APR	0.48	0.14	0.94	113.68	0.13	0.11
MAY	0.34	0.10	0.36	50.85	0.01	0.02
MAY*	0.37	0.13	0.52	74.18	0.10	0.13
JUN	0.43	0.18	0.75	85.18	0.04	0.04
JUN*	0.40	0.14	0.52	65.41	0.01	0.01
JUL	0.43	0.18	0.75	97.83	0.01	0.01
JUL*	0.56	0.19	1.02	150.35	1.98	1.32
AUG	0.40	0.16	0.46	60.97	0.39	0.65
SEP	0.32	0.14	0.31	11.26	0.01	0.07
OCT	0.38	0.12	0.29	35.72	0.04	0.12
Mean	0.39	0.15	0.54	67.31	0.23	0.22
SD	0.08	0.03	0.26	39.79	0.56	0.39
Downstream						
Months	h	V	Q	SSQ	QB	(QB/SSQ)x100
FEB	0.80	0.07	1.32	26.41	0.07	0.27
MAR	1.02	0.04	1.21	7.67	0.01	0.14
APR	1.90	0.15	2.94	195.77	0.03	0.02
MAY	1.27	0.18	6.49	131.61	0.05	0.03
MAY*	1.44	0.25	8.98	152.45	0.11	0.08
JUN	1.98	0.33	19.13	463.63	0.38	0.08
JUN*	2.04	0.35	20.38	341.29	0.05	0.01
JUL	2.43	0.38	25.26	669.18	0.22	0.03
JUL*	2.06	0.42	25.01	506.52	0.08	0.02
AUG	1.98	0.38	20.94	335.22	0.09	0.03
SEP	1.66	0.28	12.63	146.71	0.06	0.04
OCT	1.36	0.25	8.92	73.81	0.28	0.37
Mean	1.66	0.26	12.77	254.19	0.12	0.09
SD	0.49	0.12	9.05	208.77	0.11	0.12

(QB/SSQ)*100 = ratio between bedload and suspended sediment discharge (%); SD = standard deviation; * means the second measurement at month.

3.2 Metal concentration in water, suspended sediment and bedload

Despite the lack of spatial variation (cluster analysis not shown), temporal variation was observed in heavy metal concentration in water (Figure 6). Therefore, the monthly average between the water concentration upstream and downstream was calculated considering high and low water discharge conditions. In the first period, ranging from February to April, the mean metal concentration followed the order (mg L^{-}

[1]): Zn (10) > Fe (0.88) > Ni (0.46) > Pb (0.45) > Mn (0.34) > Cu (0.2) > Cr (0.02) > Cd = As (0.01) > Hg (<DL = below detection limit), while in second period, ranging from May to October, followed the order (mg L^{-1}): Zn (0.73) > Fe (0.17) > Mn (0.04) > Cu (0.04) > As (0.01) > Pb = Cd = Cr = Ni = Hg (<DL). The water standard levels of Brazilian National Environment Council (CONAMA, 2006) comprise the following values in mg L^{-1}: Fe (0.3), Mn (0.1), Pb (0.01), Cd (0.001), Zn (0.18), Cr (0.05), Cu (0.009), Ni (0.025), Hg (0.0002) and As (0.01). During the low water discharge period all heavy metals exceeded the CONAMA values, except for Cr and As; whereas no heavy metal exceeded the same thresholds during the high water discharge period as a consequence of the dilution effect (Seyler and Boaventura, 2003; Thorslund et al. 2012). In addition, the concentrations of Fe, Pb, Cr, and As were lower than the permitted level in the irrigation water standard (WHO, 2006), but the other metals exceeded the WHO guidelines as follows, in terms of number of samples: Cd 3 (FEB, MAR, and APR); Ni 3 (FEB, MAR, and APR); Zn 3 (FEB, MAR, and APR); Cu 1 (APR); Mn 1 (FEB). Despite this scenario, the water of Ipojuca River has still been widely used for fishing and water irrigation (Pimentel, 2003).

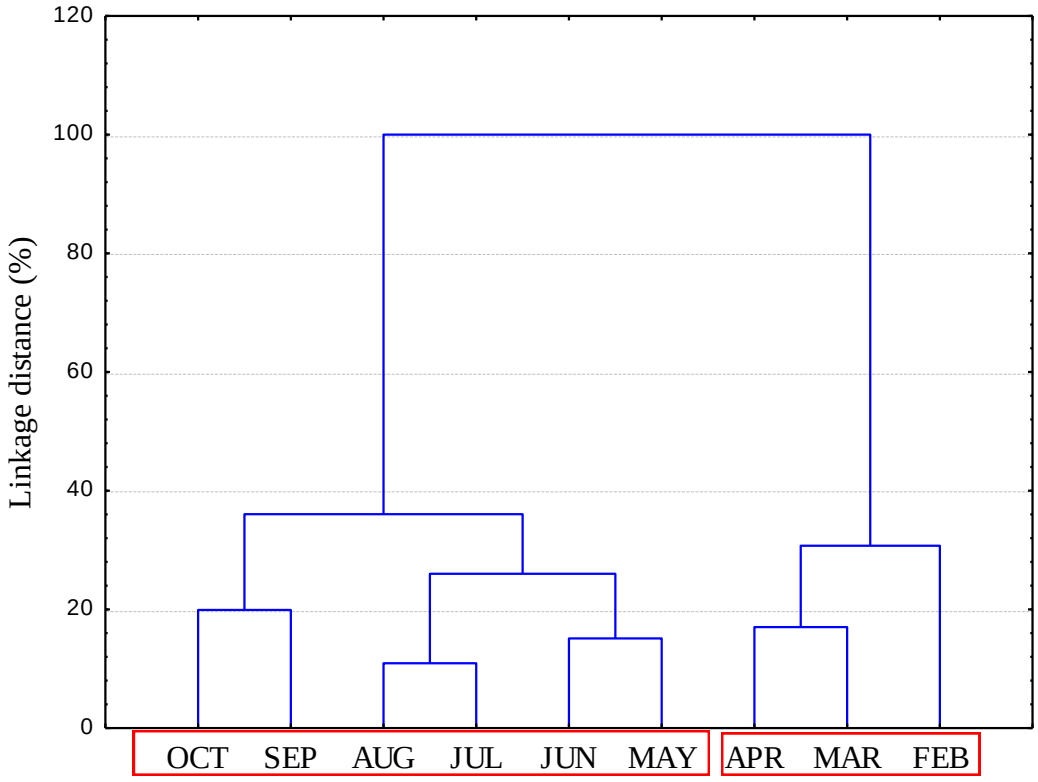

Figure 6. Cluster analysis of heavy metal concentrations in water, according to Ward's method.

The mean heavy metal concentrations in suspended sediments were predominantly higher than in the bedload (Table 3). These values were used to compute the percentage of heavy metal flux associated with each fraction at both sites. The background values followed the order (mg kg^{-1}): Fe (10682.9) > Mn (238.9) > Zn (93.1) > Pb (20.7) > Cr (19.4) > Ni (8.2) > Cu (4.6) > As (0.2) > Cd (0.1) > Hg (0.05) and Fe (24454.1) > Mn (113.9) > Cr (27.4) > Pb (15) > Zn (12.1) > Cu (8.7) > Ni (3.1) > As (1) > Cd (0.3) > Hg (0.06), upstream and downstream, respectively. In the suspended sediment the concentrations of Fe, Ni and Hg were lower than the background values. However, Mn, Pb, Cd, Zn, Cr, Cu and As exceeded the background values in 100%, 33%, 25%, 25%, 8%, 33% and 100% of samples. In the downstream cross section Fe, (Mn, Zn, Cu, Ni and As), Pb, Cd, Cr and Hg exceeded the background values in 75%, 100%, 92%, 17%, 75% and 50% of samples, respectively.

In general, the concentration of heavy metals in bedload was lower than in suspended sediment, but exceeded the background values in the following percentage order As (75%) > Mn (58%) > Cu (42%) > Pb, Cd, Zn, Cr and Ni (25%) > Hg (17%) and Zn (100%) > As and Ni (83%) > Cu and Mn (58%) > Pb (50%) > Hg (33%) > Cr (25%) > Fe (8%), upstream and downstream, respectively. Both the concentration of Fe at the upstream site and of Cd at the downstream site were lower than the background values.

Table 3 Heavy metals concentration in suspended sediment and bedload of studied sites (mg kg^{-1})

Months	Metal concentration in suspended sediment - upstream										Metal concentration in bedload - upstream									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	1171.50	1345.50	1.40	0.25	20.95	3.30	7.40	1.75	0.02	0.97	6665.00	147.05	31.35	0.40	15.00	21.85	19.15	10.10	0.03	0.39
MAR	1801.91	2164.47	17.43	0.05	99.73	3.85	1.93	1.20	0.03	1.21	5795.91	238.17	26.78	0.10	350.10	53.00	42.03	34.65	0.04	0.89
APR	1843.41	968.97	5.08	0.00	47.08	2.25	0.00	1.00	0.02	1.15	4637.91	210.32	8.03	0.00	59.88	8.25	3.78	2.95	0.03	0.40
MAY	5181.30	1483.42	27.48	0.05	95.51	11.14	11.38	6.75	0.05	1.23	10199.76	790.52	40.14	0.00	276.90	27.10	10.54	14.61	0.04	1.18
MAY*	5325.00	1172.72	17.13	0.20	18.23	10.05	3.40	4.55	0.02	1.11	3167.41	322.12	5.96	0.00	38.35	5.75	1.63	1.98	0.06	0.17
JUN	2686.03	867.43	10.21	0.00	45.80	3.75	1.03	2.18	0.02	1.08	3204.91	712.72	6.13	0.00	39.05	5.42	1.33	1.80	0.04	0.32
JUN*	3700.30	1996.90	19.79	0.00	92.87	6.76	3.86	3.19	0.02	2.30	4348.50	692.56	18.50	0.00	150.77	14.63	5.37	7.31	0.09	0.48
JUL	1164.78	518.43	19.84	0.00	42.25	5.45	2.08	2.55	0.01	0.65	2479.16	203.34	5.91	0.00	35.68	4.47	1.61	1.15	0.03	0.04
JUL*	1091.78	575.43	10.29	0.00	34.30	2.95	1.90	1.80	0.01	0.57	6822.69	725.36	12.80	0.03	85.55	10.78	5.83	4.67	0.03	0.35
AUG	6380.00	3216.47	142.90	0.25	31.45	34.15	4.80	5.60	0.02	1.96	3184.78	192.80	6.09	0.00	36.40	6.77	2.28	2.10	0.03	0.18
SEP	2693.85	1827.67	106.90	0.00	154.13	14.11	10.76	2.55	0.03	0.55	4604.41	622.97	8.93	0.00	58.53	6.42	3.66	2.95	0.03	0.30
OCT	2991.39	1656.02	56.84	0.00	77.01	11.42	4.53	3.03	0.03	0.41	6592.50	326.34	6.05	0.13	8.48	9.20	2.98	3.00	0.03	0.26
Mean	3002.61	1482.78	36.27	0.07	63.27	9.10	4.42	3.01	0.02	1.10	5141.91	432.02	14.72	0.05	96.22	14.47	8.35	7.27	0.04	0.41
SD	1793.84	762.45	44.38	0.10	40.87	8.82	3.67	1.77	0.01	0.56	2195.08	251.98	11.84	0.12	109.16	14.01	11.75	9.52	0.02	0.32

Months	Metal concentration in suspended sediment - downstream										Metal concentration in bedload - downstream									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	16450.00	972.50	4.13	0.69	70.06	19.81	72.50	17.63	0.05	6.25	9360.00	98.30	11.55	0.35	29.35	44.35	41.65	14.00	0.05	2.96
MAR	10350.91	245.47	90.13	0.35	435.63	18.60	13.43	12.85	0.03	6.69	6495.91	51.22	41.53	0.00	475.45	57.45	16.48	40.35	0.08	2.74
APR	12565.91	200.52	45.58	0.20	158.83	15.15	10.83	5.15	0.12	11.37	9965.91	76.32	15.63	0.00	271.58	14.00	39.93	9.40	0.07	4.27
MAY	31122.73	959.03	320.20	0.17	534.27	60.63	77.22	19.58	0.11	15.07	3712.95	160.64	8.23	0.00	80.60	8.83	5.53	6.67	0.06	1.63
MAY*	31814.58	759.90	682.05	0.23	68.53	141.88	19.90	13.34	0.07	12.81	7460.91	115.59	8.91	0.00	70.25	9.55	8.01	6.00	0.09	2.61
JUN	25966.38	718.76	379.38	0.15	299.98	72.00	18.51	16.73	0.08	11.86	3230.91	66.92	4.68	0.00	33.20	15.60	3.38	1.00	0.04	0.33
JUN*	39845.70	939.48	223.26	0.32	56.16	81.94	33.13	19.69	0.08	7.40	14763.41	527.39	18.48	0.03	81.93	19.07	13.86	5.13	0.08	3.52
JUL	34504.69	656.95	123.30	0.28	50.19	58.52	25.69	15.14	0.06	9.01	5833.41	147.07	7.78	0.00	65.53	7.87	5.73	3.63	0.04	1.74
JUL*	28635.78	612.90	496.11	0.05	269.58	89.30	20.84	16.95	0.06	9.11	12945.91	941.97	19.66	0.00	103.30	15.25	16.06	5.53	0.04	2.96
AUG	39006.49	796.90	325.23	0.12	357.15	332.17	46.61	17.90	0.06	8.16	15487.78	308.58	25.56	0.05	111.75	21.17	18.08	8.48	0.05	2.58
SEP	31516.07	770.90	662.00	0.22	363.43	123.62	90.28	35.25	0.14	8.75	27683.41	426.92	34.51	0.18	143.88	34.50	19.93	12.25	0.06	2.95
OCT	37236.47	1049.74	275.23	0.51	38.58	88.31	24.97	9.17	0.04	10.08	3984.16	27.32	4.81	0.00	44.95	5.12	4.16	1.70	0.03	0.36
Mean	28251.31	723.59	302.22	0.27	225.20	91.83	37.83	16.62	0.08	9.71	10077.06	245.68	16.78	0.05	125.98	21.06	16.07	9.51	0.06	2.39
SD	10057.28	269.38	224.98	0.18	173.45	85.44	27.34	7.27	0.03	2.64	6955.38	270.14	11.87	0.11	127.79	16.17	12.91	10.46	0.02	1.18

* = second measurement in the same month; SD = standard deviation

3.3 Correlating hydrology and metals concentration

The water discharge was positively correlated with the concentration of Fe, Pb, Cr, Ni, Hg, and As in suspended sediment, whereas no correlation was observed for Mn, Cd,

Zn and Cu (Table 4). Except for Mn, the negative correlation between the suspended sediment concentration and heavy metals suggested that the amount of suspended sediment do not play an important role in the heavy metal concentration. These results were supported by measurements carried out upstream, where the highest suspended sediment resulted in the lowest metal concentration in comparison with the downstream measurements.

The strong positive correlation of Fe with Pb, Cr, Cu, Ni, Hg and As suggested that these metals in suspended sediments were likely transported and mediated by oxyhydroxydes. However, the same correlation was not observed for Mn, Cd and Zn. This behavior was also observed by Roussiez et al. (2013) who showed that particulate metals (except for Cd and Mn) usually depict a strong correlation with Fe. Not surprisingly, neither the bedload nor the bedload/suspended sediment ratio was correlated with the metal concentration in this fraction. The strong positive correlation of Pb with Zn, Cr, Cu, Ni, Hg and As in suspended sediment and Zn, Cr and Ni in bedload might be related to similar anthropogenic sources, being essential the comparison with the background values aforementioned. On the other hand, the lack of correlation between Pb and Cd not only in suspended sediment but also bedload highlights the high affinity of Pb to the solid phase, whereas Cd is often more soluble (Wong, 2006).

Table 4. 1: Pearson's correlation matrix for suspended sediment metal concentration (mg kg^{-1}). 2: correlation matrix for bedload metal concentration (mg kg^{-1}). Hydraulic and sediment transport variables were also included. Significant correlations at $p < 0.05$ are in bold.

1	Q	SSC	SSQ	QB	(QB/SSQ)	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
Q	1.00														
SSC	**-0.67**	1.00													
SSQ	**0.92**	-0.45	1.00												
QB	-0.04	0.22	0.09	1.00											
(QB/SSQ)	-0.24	0.28	-0.16	**0.92**	1.00										
Fe	**0.84**	**-0.84**	**0.63**	-0.12	-0.22	1.00									
Mn	-0.38	0.46	-0.40	-0.10	0.12	-0.37	1.00								
Pb	**0.63**	**-0.68**	0.40	-0.09	-0.18	**0.74**	-0.24	1.00							
Cd	0.16	**-0.53**	0.00	-0.12	0.06	0.46	-0.14	0.13	1.00						
Zn	0.32	**-0.57**	0.18	-0.18	-0.27	0.42	-0.32	**0.49**	0.01	1.00					
Cr	**0.66**	**-0.58**	0.43	-0.08	-0.17	**0.75**	-0.22	**0.67**	0.14	0.43	1.00				
Cu	0.39	**-0.65**	0.16	-0.16	-0.16	**0.65**	-0.25	**0.54**	**0.50**	**0.58**	**0.48**	1.00			
Ni	**0.67**	**-0.77**	0.45	-0.15	-0.23	**0.80**	-0.35	**0.75**	0.44	**0.62**	**0.59**	**0.87**	1.00		
Hg	**0.51**	**-0.66**	0.39	-0.22	-0.35	**0.67**	-0.41	**0.65**	0.26	**0.59**	0.43	**0.74**	**0.80**	1.00	
As	**0.63**	**-0.82**	**0.51**	-0.13	-0.24	**0.84**	**-0.48**	**0.71**	0.43	**0.59**	**0.53**	**0.61**	**0.71**	**0.78**	1.00

2	Q	SSC	SSQ	QB	(QB/SSQ)	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
Q	1.00														
SSC	**-0.67**	1.00													
SSQ	**0.92**	-0.45	1.00												
QB	-0.04	0.22	0.09	1.00											
(QB/SSQ)	-0.24	0.28	-0.16	**0.92**	1.00										
Fe	0.44	-0.41	0.22	-0.09	-0.16	1.00									
Mn	0.05	0.27	0.06	0.18	0.09	0.23	1.00								
Pb	-0.01	-0.06	-0.15	-0.18	-0.19	**0.56**	0.19	1.00							
Cd	-0.17	0.00	-0.26	-0.11	0.01	0.28	-0.21	0.29	1.00						
Zn	-0.15	-0.04	-0.17	-0.15	-0.16	0.18	-0.01	**0.72**	-0.17	1.00					
Cr	-0.08	-0.16	-0.21	-0.18	-0.13	0.37	-0.14	**0.74**	0.43	**0.72**	1.00				
Cu	-0.02	-0.17	-0.07	-0.19	-0.15	0.41	-0.21	0.45	**0.51**	**0.49**	**0.71**	1.00			
Ni	-0.21	-0.07	-0.29	-0.19	-0.13	0.17	-0.16	**0.74**	0.21	**0.88**	**0.92**	**0.61**	1.00		
Hg	0.12	-0.34	0.03	-0.27	-0.33	0.29	-0.01	0.27	-0.11	0.37	0.27	0.22	0.30	1.00	
As	0.46	**-0.64**	0.34	-0.23	-0.28	**0.67**	-0.07	0.39	0.09	0.39	0.41	**0.62**	0.33	**0.62**	1.00

The lack of correlation between discharge and/or suspended sediment concentration with metals makes it infeasible to estimate water, suspended and bedload chemical levels using rating curves. Therefore, the heavy metal flux was carried out through concurrent measurements of hydrologic features and metal concentrations in suspended and bedload sediments. Despite some studies having estimated heavy metal fluxes using rating curves,

this approach seems to be often inappropriate both in large and small rivers (Horowitz et al. 2008b).

3.4 Heavy metal fluxes in suspended sediment and bedload

Both upstream and downstream, the suspended sediment contributed more than 99% of the heavy metal fluxes (Table 5). According to Viers et al. (2009), the heavy metal flux of major rivers in the world was mainly associated with suspended sediments instead of water (bedload not studied). Based on 15 Gt year^{-1} for the world suspended flux (common accepted value) they observed that 96% of As, 88% of Cd, 99% of Cr, 95% of Cu, 99% of Fe, 95% of Mn, 97% Ni, 99% of Pb and 99% of Zn were transported by suspended sediment. Nicolau et al. (2012) also showed that Cu, Zn, Cd and Pb were predominantly transported by suspended sediment, 92%, 89% 96% and 97%, respectively.

The highest heavy metal fluxes in suspended sediment may be related to the pH, with 90% of values higher than 7.5 and 7, upstream and downstream, respectively (SRH, 2010). Although sorption reactions between water and sediments can be controlled by several parameters, the pH is regarded to have a major influence (Gundersen and Steinnes, 2003). As neutral pH constrains the transport in dissolved phase and the heavy metal flux in bedload of Ipojuca River accounted for less than 1%, the suspended sediment played the most important role in heavy metal fluxes. Studying the fluxes of heavy metals from a highly polluted watershed, Žák et al. (2009) pointed out that more than 99% of Pb and also the most heavy metals were transported by suspended particulate matter, the dissolved phase transport becoming negligible.

The bedload did not play an important role in heavy metal fluxes, but in polluted rivers with concurrent high bedload/suspended sediment ratio (not observed in Ipojuca River), this fraction may need to be considered in future studies. The values of ratio between bedload and suspended sediment ranging from 4% to 12% have been reported in semiarid streams (Cantalice et al., 2009). However, the heavy metal fluxes were not determined in this research. Furthermore, the total heavy metal flux in solid phase (suspended sediments + bedload) followed the order Fe > Mn > Zn > Pb > Cr > Cu > Ni > As > Cd = Hg and Fe > Mn > Pb > Zn > Cr > Cu > Ni > As > Cd > Hg, upstream and downstream, respectively (Table 5).

Table 5. Heavy metals fluxes in suspended sediment and bedload (t year^{-1})

Upstream	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
SS	69.36	31.34	0.65	0.001	1.30	0.19	0.078	0.070	0.001	0.028
B	0.50	0.050	0.001	0.000	0.006	0.001	0.0004	0.0003	0.000	0.000
Total	69.86	31.39	0.651	0.001	1.306	0.191	0.078	0.070	0.001	0.028
B/SS (%)	0.72	0.16	0.15	0	0.46	0.53	0.51	0.42	0	0
Downstream	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
SS	2875.78	65.69	28.21	0.018	18.82	2.92	2.92	1.53	0.006	0.892
B	0.316	0.0075	0.0004	0.000	0.003	0.0006	0.0004	0.0002	0.000	0.0001
Total	2876.09	65.697	28.21	0.018	18.823	2.9206	2.9204	1.53	0.006	0.892
B/SS (%)	0.01	0.01	0.001	0	0.01	0.02	0.01	0.01	0	0.01

Note: SS: suspended sediment and B: bedload.

The contamination in Ipojuca River is caused by a variety of sources, including inappropriate use of chemical substances, such as pesticides and insecticides, untreated sewage sludge and wastewater from industrial and agricultural activities. By far Pb and to a less extent Zn in suspended sediments at the downstream site represent a major concern. Both Pb and Zn showed the highest concentration in May, 682.05 mg kg^{-1} and 534.27 mg kg^{-1}, respectively (Table 3). These concentrations might be linked to petroleum and coal combustion products, such as tires and oil tire residues (Horowitz, 2009). Zn, found in high concentrations in the suspended sediments, is most likely due to the sugarcane industry, with its large-scale use of agrochemicals and fertilizers. In addition, municipal solid waste incineration may enhance the atmospheric deposition and consequently aerosol particles enriched with Pb and Zn (Le Floch et al., 2003).

The average fluxes of Pb and Zn in suspended sediment of Ipojuca River were 4.20 kg km^2 year^{-1} and 2.93 kg km^2 year^{-1}, respectively. Thorslund et al. (2012) observed in Tuul River, regarded highly impacted by mining activities, that its watercourse transported 1.60 kg km^2 year^{-1} and 1.30 kg km^2 year^{-1} of Pb and Zn (suspended + dissolved phase), respectively. Nicolau et al. (2012) calculated that the Pb flux (suspended + dissolved) to the sea of some Mediterranean rivers was equal to 3.4 kg km^2 year^{-1}. In their study were considered important rivers, such as Nilo, Rhône, Po, Axios, Aude, Hérault, Venice, Tet, Orb, Eygoutier and also small rivers. Therefore, the highest flux of Pb and Zn in Ipojuca River highlighted the importance to include also medium or small rivers in future estimation of world heavy metal fluxes.

3.5 Fate of heavy metals transported by suspended sediment

Understanding the fate and also the extent to which heavy metals in suspended sediment become bioavailable is acknowledged as a major question (Thorslund et al., 2012). Nevertheless, the values discussed herein depict only environmentally available concentrations. Whether related to exchangeable fraction (i.e. most associated with toxic effects) or iron and manganese oxides fraction, the metals become less or more available under specific conditions as discussed for the pH. As a result, it is fundamental to consider whether the heavy metals in suspended sediment settle down in estuarine environment or reach the ocean in order to provide insights regarding the adverse effects in aquatic systems. Although data analyzed here do not allow us to discuss this issue in the broadest sense, according to Windom (1990) the suspended material is often settled down nearshore. Martin and Whitfield (1983) observed that only 10% of suspended sediment reaches the sea. They studied twenty east coast North American rivers and concluded that the heavy metal particulate transport was not delivered to open ocean. Mechanisms related to suspended sediment and heavy metal deposition in estuarine zones are poorly understand, but based on the previous aforementioned studies and the slope predominantly flat (Figure 2) near the coast, we hypothesize that the major part of the suspended sediment has been deposited in estuarine zones, where the harmful impact to aquatic life seems to be greater.

4. Conclusions

This research sheds light on the importance of studying both metal concentrations in water/sediments and also the associated chemical fluxes. The highest heavy metal concentration in water under low water discharge conditions poses the highest threat for aquatic life as a consequence of the highest concentration in heavy metals. Despite this scenario, the water of Ipojuca River has been widely used for fishing and water irrigation.

The increase of metal flux associated with suspended sediment toward the downstream cross section suggests increased anthropogenic inputs. Suspended sediment is the major source responsible for metal transport along the river. Both upstream and downstream the suspended sediment contributed more than 99% of the heavy metal fluxes. The average fluxes of Pb and Zn in suspended sediment equal to 4.20 kg km^2 $year^{-1}$ and 2.93 kg km^2 $year^{-1}$ highlighted the importance to include also medium or small

polluted rivers in future estimation of world heavy metal fluxes in order to protect estuaries and coastal zones.

Bedload did not play an important role in heavy metal fluxes. Even after increasing the water discharge toward the downstream site, the metal flux in bedload remained low (< 1%). Not measuring metals in bedload can make the environmental monitoring more economically feasible and less time-consuming. Thus, the data showed herein represent an important contribution not only for future estimation of heavy metal fluxes from world rivers but also for developing countries, where financial resources for sediment field measurement and heavy metals analysis are scarce.

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Final conclusions

The highest heavy metal concentration in water under low water discharge conditions poses the highest threat for aquatic life as a consequence of the highest concentration in heavy metals. However, analysis of the water samples, although essential for the concurrent analysis of the sediments, would have been inconclusive by itself.

The results of the combined methods indicated that the suspended sediments of the upstream portion of the Ipojuca River are moderately contaminated, with higher contaminant levels for Mn and As; and that the sediments of the downstream portion are highly contaminated with heavy metals, mainly Zn, Pb, and As.

The comparison of our data with SQGs indicated that for the suspended sediments of upstream portion, it is the concentrations of Mn and Pb that are likely to pose a danger for sediment-dwelling organisms, and for the downstream portion the most dangerous metals are Pb and Zn. On the other hand, taking into account the mean heavy metal concentrations in bedload, harmful effects on sediment-dwelling organisms are not supposed to occur; nevertheless, the comparison with regional background seems to be more reliable than the comparison with Canadian SQGs.

Multiple lines of evidences observed by means of EF, comparison with background values, and PCA suggested that some metals, such as Zn, Pb, and As in suspended sediments and Ni, Zn, Cu and As in bedload at downstream site were mainly derived from anthropogenic sources and can be easily remobilized under natural conditions encountered in Ipojuca River.

Both upstream and downstream the suspended sediment contributed more than 99% of the heavy metal fluxes. The average fluxes of Pb and Zn in suspended sediment equal to 4.20 kg km^2 $year^{-1}$ and 2.93 kg km^2 $year^{-1}$ highlighted the importance to include also medium or small polluted rivers in future estimation of world heavy metal fluxes in order to protect estuaries and coastal zones.

Future challenges and recommendations

There is a poor comprehension of the pathways that sediments take from sources to input into rivers, being essential to understand better the urbans contributions (e.g., road-deposited sediment, deposition in gully pots, and so on), changing environmental conditions (i.e., physical and chemical changing during transport). The results discussed herein, raised the following question: what is the role of urban areas in controlling heavy metal fluxes? Sediment fingerprinting approach may be a feasible tool to highlight this issue. Therefore, we suggest that future works should be focussed on connecting urban areas to the rest of the Ipojuca River. In addition, redox conditions, pH, and sediment sampling should be measured concurrently in order to better understand the heavy metal fluxes.

There is also a need for better sampling and monitoring not only in Ipojuca River but also for other watersheds around the world due to the complex interactions among sediments, heavy metals, and water in such environments. We suggest that for contamination studies the number of cross sections (i.e., upstream and downstream) might be better addressed. Furthermore, we believe that the heavy metal fluxes monitoring should be based on water discharge behavior rather than calendar definition.

From here on out, we also strongly encourage studies regarding metal speciation based on sequential extraction analysis coupled with isotopes techniques which in turn has been widely used in environmental studies. A potential possibility might be to apply Lead isotopes as a fingerprint technique to determine sources of Pb – one of the most dangerous heavy metal observed in suspended sediments at downstream site.