HEAVY METAL CONTAMINATION IN SUSPENDED SEDIMENTS OF AN ENVIRONMENTALLY IMPACTED RIVER

Yuri Jacques Agra Bezerra da Silva [1], José Ramon Barros Cantalice[2], Vijay P. Singh[3], Clístenes Williams Araújo do Nascimento[4], Ygor Jacques Agra Bezerra da Silva[5], Sérgio M. S. Guerra[6], Cinthia Maria Cordeiro Atanázio Cruz Silva[7]

ABSTRACT --- The objectives of this study were to (1) determine the status of heavy metal concentrations in suspended sediments, (2) distinguish between natural and anthropogenic sources of metals, and (3) evaluate the risk, to the environment, posed by the heavy metals in the river system (by comparison with SQGs).Suspended sediment samples were obtained using a depth-integrated and isokinetic sampling. 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. 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 Zn, Pb, and As.

Keywords: Sediment quality, Multivariate statistical techniques, Enrichment factor.

1 PhD of Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: yuriufrpe@yahoo.com.br

2 Professor of Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: cantalice21@hotmail.com

3 Professor of Biological and Agricultural Engineering, Department of Civil Engineering, Texas A&M University, College Station, Texas - (EUA). Email: vsingh@tamu.edu

4 Professor of Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: cwanascimento@hotmail.com

5 PhD of Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: ygorufrpe@yahoo.com.br

6 Professor of Rural Technology Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: smsguerra@hotmail.com

7 Undergraduate Student of Agronomy Engineering, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: cinthia.ufrpe@yahoo.com.br

1. INTRODUCTION

Heavy metal contamination is a particular concern given the toxicity, abundance, and persistence of these elements in aquatic environments. 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, both in Brazil and other countries (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 in order 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 take into account 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 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). This study, therefore, has as its objectives to (1) determine the status of heavy metal concentrations in suspended sediments, (2) distinguish between natural and anthropogenic sources of metals in suspended sediments, and (3) evaluate 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 sediment pollution in the 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 and ranges from 2 m^3 $s^{-1}$to 35 m^3 s^{-1} in dry and rainy seasons, respectively.

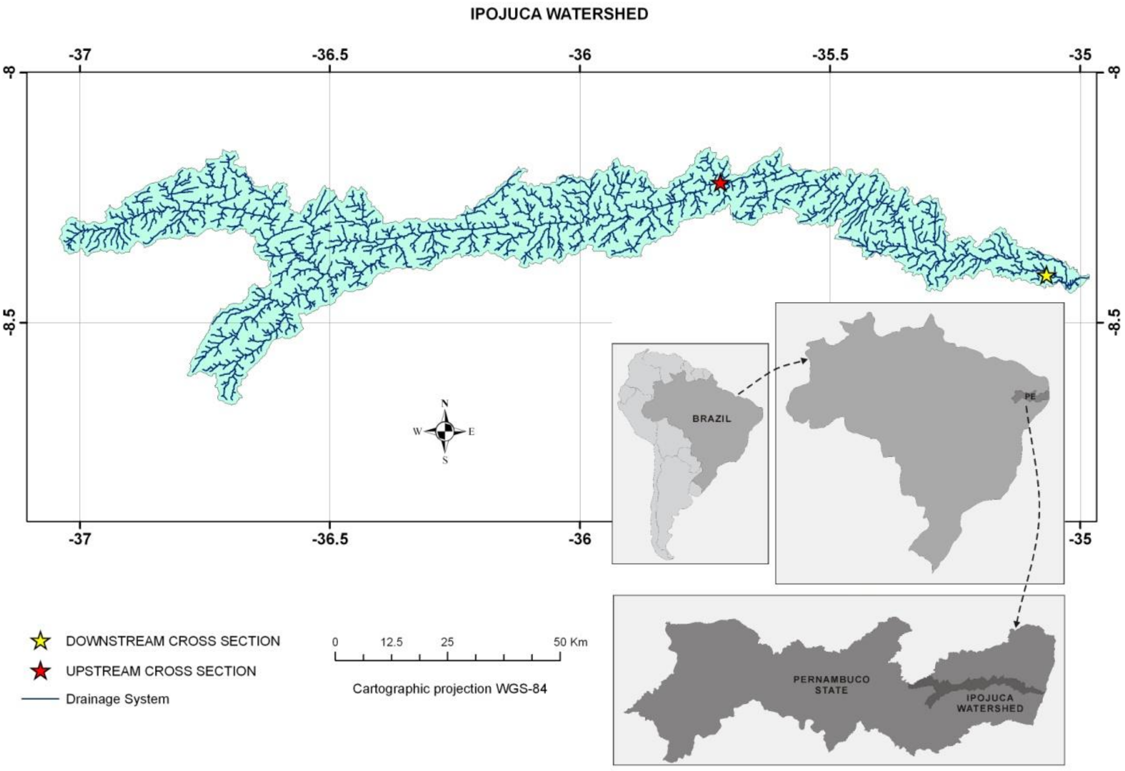

Figure 1 – Location of the Ipojuca River watershed.

Soils in the Ipojuca watershed range from Entisols to Oxisols (ZAPE 2002; EMBRAPA 2006). 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.

2.2 Sampling sites and measurements

Suspended sediment samples were collected 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 upstream cross section is affected by both domestic sewage and wastewater from industrial and agricultural production, whereas the downstream cross section is mainly affected by sugarcane farming and processing.

Suspended sediments were collected by means of 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 provides representative samples of 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 toUSEPA 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).

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. It was 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 means of 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 on the basis of the enrichment factor (EF) and comparison with background samples and SQGs. Four composite uncontaminated soil samples from each site were used as background values. 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 2013). To address and minimize this problem, we limited the 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, geochemical normalization with Fe as a conservative element was employed (Varol and Şen, 2012; Thuong *et al.*, 2013). Other elements could be used—such as Al or Li (see detailed discussion in Dung 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, it was 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 1 and 2.

2.5 Statistical analysis

Descriptive and multivariate statistical analysis methods were used. First, principal component analysis (PCA) of the data set was applied 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, Varimax rotation was employed (Kaiser, 1958). Second, cluster analysis (CA), using Ward's method (Euclidean distance as a measure of similarity) was carried out. We have chosen 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). Standardized data for both the PCA and CA analyses was used to avoid misclassification due to differences in data dimensionality (Webster 2001).

3. RESULTS AND DISCUSSION

3.1 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) (Figure 2); 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) (Figure 3). According to Sakan *et al.* (2009), the enrichment factors for the metals 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).

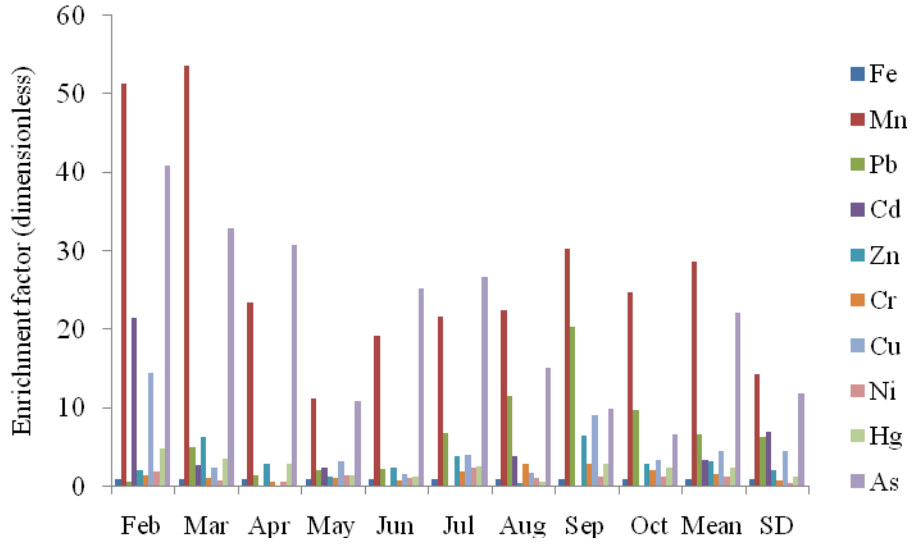

Figure 2 – Enrichment factors for heavy metals found in suspended sediments from the upstream cross section of the Ipojuca River. Note: SD = standard deviation.

The highest EF observed in all the suspended sediments was for Mn at the upstream site (53.71—see Figure 2); Mn has also been reported as one of the elements showing the highest EF relative to the upper crust (Viers 2009). The lowest EF observed was for Cd at the downstream cross section (0.0), 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—Figure 3). 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).

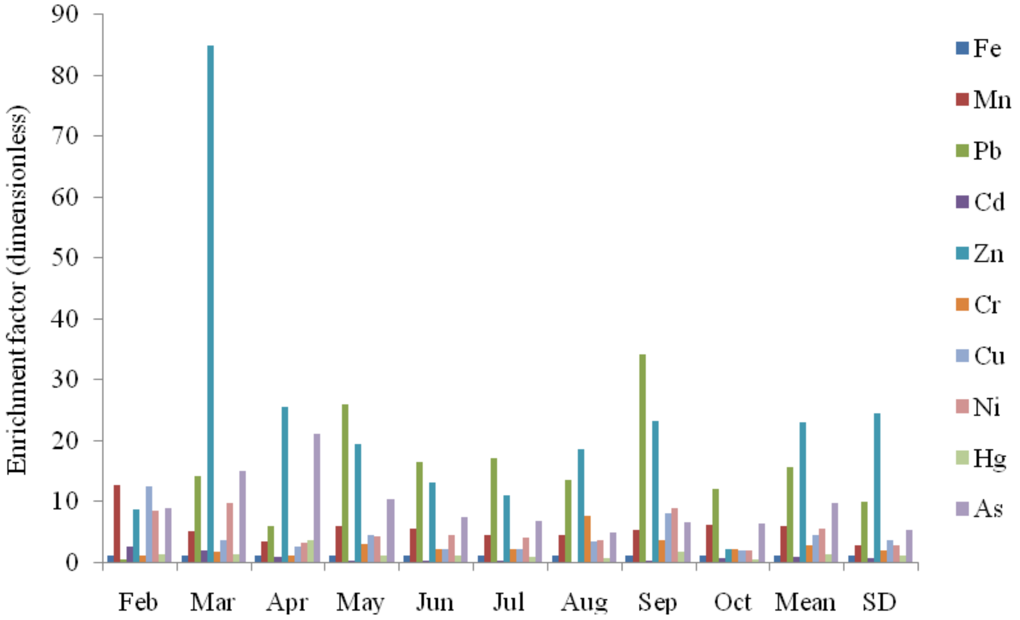

Figure 3 – Enrichment factors for heavy metals found in suspended sediments from the downstream cross section of the Ipojuca River. Note: SD = standard deviation.

3.2 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 of Fe > Mn > Zn > Pb > Cr > Cu > Ni > As > Cd > Hg (Table 1). According to the SQGs, only Mn and Pb show concentrations potentially having harmful effects on sediment-dwelling organisms.

Table 1 – 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	0.00	47.08	2.25	0.00	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	0.00	45.80	3.75	1.03	2.18	0.02	1.08
JUN*	3,700	1,996	19.79	0.00	92.87	6.76	3.86	3.19	0.02	2.30
JUL	1,164	518.43	19.84	0.00	42.25	5.45	2.08	2.55	0.01	0.65
JUL*	1,091	575.43	10.29	0.00	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	0.00	154.13	14.11	10.76	2.55	0.03	0.55
OCT	2,991	1,656	56.84	0.00	77.01	11.42	4.53	3.03	0.03	0.41
Mean	3,002	1,482	36.27	0.07	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; 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 2). 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 2). 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 2 – 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. 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.

It was used cluster analysis to confirm the higher levels of heavy metal contamination in suspended sediments at the downstream cross section (Figure 4). On the basis of 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).

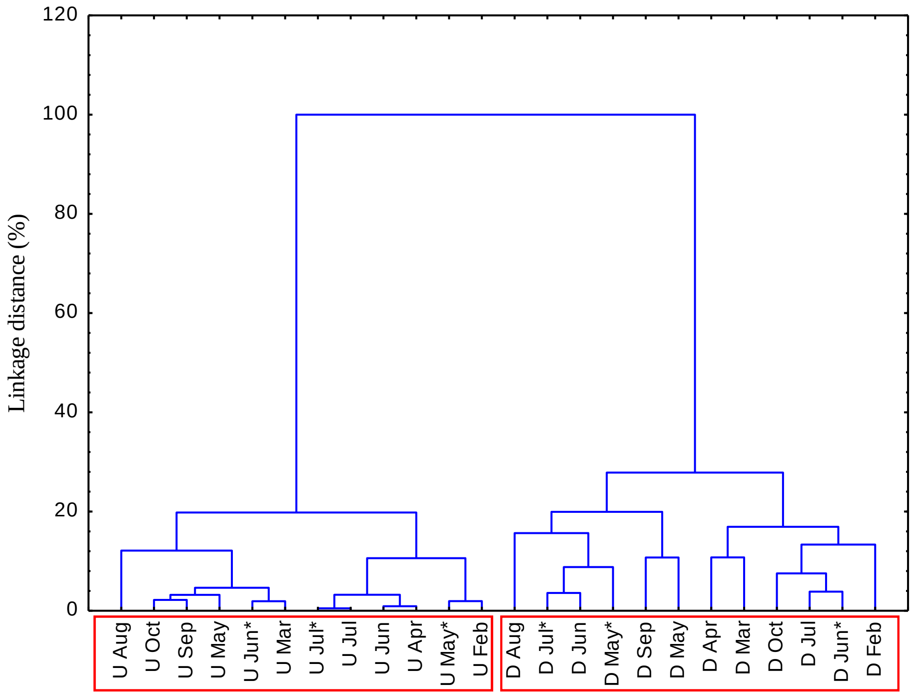

Figure 4 – Cluster analysis of metal concentrations in suspended sediment, according to Ward's method. U = Upstream; D = Downstream; * = second measurement in the same month.

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.

3.3 Principal component analysis

Principal component analysis (PCA) of standardized data was applied to discern patterns among sediment samples and to identify the contribution of each heavy metal to each PC (Table 3). 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 1 and Figure 2). 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 3 – 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 3). 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 2 and Figure 3).

Of all the heavy metals, the highest concentrations found were of Mn and As in suspended sediments at the upstream cross section. 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). Pb has a long half-life in soils and sediments, which may be another possible explanation for the high levels in suspended sediment. According to Horowitz (2009), Pb is usually linked with petroleum and coal combustion products, such as tires and oil. Martínez & 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

The results of the combined methods employed 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. Principal component analysis distinguished natural from anthropogenic sources of metals and also explained roughly 80% and 74% of the total variance in suspended sediment quality in the upstream and downstream cross sections, respectively. 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. Pb might be related to petroleum and coal combustion products, such as tires and oil. Furthermore, 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. 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 danger for sediment-dwelling organisms, and for the downstream portion the most dangerous metals are Pb and Zn. However, it is important to note that 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, strategies for future remediation to protect aquatic life and human health, must be based primarily on analysis of sediments and comparison with background values.

ACKNOWLEDGEMENTS

This research was supported by Brazilian Government, MEC/MCTI/CAPES/CNPq/FAPs EDITAL Nº 61/2011-Science Without Borders Program, project number (402603/2012-5), and by FACEPE process number (IBPG-0889-5.01/11).

REFERENCES

ADAMO, P.; ARIENZO, M.; IMPERATO, M.; NAINMO, D.; NARDI, G.; STAZIONE, D. (2005). *Distribution and partition of heavy metals in surface and sub-surface sediments of Naples city port*. Chemosphere 61, 800–809.

ANDERSSON, P.S.; PORCELLI, D.; WASSERBURG, G.J.; INGRI, J. (1998). *Particle transport of ^{234}U–^{238}U in the Kalix River and in the Baltic Sea*. Geochimica et Cosmochimica Acta 62, 385–392.

BANERJEE, A.D.K. (2003). *Heavy metal levels and solid phase speciation in street dusts of Delhi, India*. Environmental Pollution 123, 95–105.

BARROS, A.M.L.; SOBRAL, M.C.; GUNKEL, G. (2013). *Modelling of point and diffuse pollution: application of the Moneris model in the Ipojuca river basin, Pernambuco State, Brazil*. Water Science & Technology 357–365, DOI: 10.2166/wst.2013.086.

CCME. (1995). Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life, Canadian Council of Ministers of the Environment, EPC- 98E, 35 pp.

Companhia Pernambucana do Meio Ambiente (CPRH). (2003). Diagnóstico Socioambiental do Litoral Sul de Pernambuco, 87 pp.

Conselho Nacional do Meio Ambiente (CONAMA). (2012). Estabelece as diretrizes gerais e os procedimentos referenciais para o gerenciamento do material a ser dragado em águas sob jurisdição nacional. Resolução Nº 454, de 01 de novembro. Disponível em: http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=693. pdf (acessado em 03.11.2013), 66 pp.

DAVUTLUOGLU, O.I.; SECKIN, G.; ERSU, C.B.; YILMAZ, T.; SARI, B. (2011). *Heavy metal content and distribution in surface sediments of the Seyhan River, Turkey.* Journal of Environmental Management 92, 2250–2259.

DUNG, T.T.T.; CAPPUYNS, V.; SWENNEN, R.; PHUNG, N.K. (2013). *From geochemical background determination to pollution assessment of heavy metals in sediments and soils*. Reviews in Environmental Science and Bio/Technology 12, 335–353.

EDWARDS, T.K.; GLYSSON, G.D. (1999). *Field methods for measurement of fluvial sediment*. In Techniques of Water-Resources Investigations of the U.S. Geological Survey (USGS). Reston, Virginia, book 3, chapter C2, 97 pp.

Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA). (2006). Centro Nacional de Pesquisa de Solos. Sistema Brasileiro de Classificação de Solos. 2º ed. Rio de Janeiro, 306 pp.

FACCHINELLI, A.; AACCHI, E.; MALLEN, L. (2001). *Multivariate statistical and GIS-based approach to identify heavy metal courses in soils*. Environmental Pollution 114, 313–324.

GAO, X.; CHEN, C.T.A. (2012). *Heavy metal pollution status in surface sediments of the coastal Bohai Bay*. Water Research 46, 1901–1911.

GARCIA, C.A.B.; PASSOS, E.A.; ALVES, J.P.H. (2011). *Assessment of trace metals pollution in estuarine sediments using SEM-AVS and ERM–ERL predictions.* Environmental Monitoring and Assessment 181, 385–397.

GAWEL, J.E.; ASPLUND, J.A.; BURDICK, S.; MILLER, M.; PETERSON, S.M.; TOLLEFSON, A.; ZIEGLER, K. (2014). *Arsenic and lead distribution and mobility in lake sediments in the south-central Puget Sound watershed: The long-term impact of a metal smelter in Ruston, Washington, USA.* Science of the Total Environment 472, 530–537.

GUNKEL, G.; KOSMOL, J.; SOBRAL, M.; ROHN, H.; MONTENEGRO, S.; AURELIANO, J. (2007). *Sugar Cane Industry as a Source of Water Pollution – Case Study on the Situation in Ipojuca River, Pernambuco, Brazil*. Water, Air, & Soil Pollution 180, 261–269.

HOROWITZ, A.J. (2009). *Monitoring suspended sediments and associated chemical constituents in urban environments: lessons from the city of Atlanta, Georgia, USA Water Quality Monitoring Program*. Journal of Soils and Sediments 9: 342–363.

KAISER, H.F. (1958). *The Varimax criterion for analytic rotation in factor analysis.* Psychometrika 23, 187–200.

KOENING, M.L.; LEÇA, E.E.; LEITÃO, S.N.; MACÊDO, S.J. (2003). *Impacts of the construction of the Port of Suape on Phytoplankton in the Ipojuca River Estuary (Pernambuco-Brazil).* Brazilian Archives of Biology and Technology 46, 73–81.

KRČMOVÁ, K.; ROBERTSON, D.; CVECKOVÁ, V.; RAPANT, S. (2009). *Road-deposited sediment, soil and precipitation (RDS) in Bratislava, Slovakia: compositional and spatial assessment of contamination.* Journal of Soils and Sediments 9, 304–316.

MACDONALD, D.D.; INGERSOLL, C.G.; BERGER, T.A. (2000). *Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems.* Archives of Environmental Contamination and Toxicology 39, 20–31.

MACDONALD, D.D.; INGEROLL, C.G.; SMORONG, D.E.; LINDSKOOG, R.A.; SLOANE, G.; BIERNACKI, T. (2003). *Development and Evaluation of Numerical Sediment Quality Assessment Guidelines for Florida Inland Waters*. Technical Report. Prepared for: Florida Department of Environmental Protection, USA, 150 pp.

MARTÍNEZ, L.L.G.; POLETO, C. (2010). *Lead distribution by urban sediments on Impermeable areas of Porto Alegre – RS, Brazil*. Journal of Urban and Environmental Engineering 4, 1–8.

MICÓ, C.; RECATALÁ, L.; PERIS, M.; SÁNCHEZ, J. (2006). *Assessing heavy metal sources in agricultural soils of an European Mediterranean area by multivariate analysis.* Chemosphere 65, 863–872.

MUNIZ, K.; NETO, B.B.; MACÊDO, S.J.; FILHO, W.C.P. (2005). *Hydrological impact of the port complex of Suape on the Ipojuca River (Pernambuco-Brazil).* Journal of Coastal Research 215, 909–914.

NASEHI, F.; HASSANI, A.H.; MONAVVARI, M.; KARBASSI, A.R.; KHORASANI, N. (2013). *Evaluating the metallic pollution of riverine water and sediments: a case study of Aras River*. Environmental Monitoring and Assessment 185, 197–203.

National Institute of Standards and Technology - NIST. Standard Reference Materials –SRM 2709, 2710 and 2711 Addendum Issue Date: 18 January 2002.

PONTER, C.; INGRI, J.; BOSTRÖM, K. (1992). *Geochemistry of manganese in the Kalix River, northern Sweden*. Geochimica et Cosmochimica Acta 56, 1485–1494.

RAJU, K.V.; SOMASHEKAR, R.K.; PRAKASH, K.L. (2012). *Heavy metal status of sediment in river Cauvery, Karnataka*. Environmental Monitoring and Assessment 184, 361–373.

SAKAN, S,M.; DJORDJEVIC, D.S.; MANOJLOVIC, D.D.; PREDRAG, P.S. (2009). *Assessment of heavy metal pollutants accumulation in the Tisza river sediments*. Journal of Environmental Management 90, 3382–3390.

Secretaria de Recursos Hídricos (SRH). (2010). Plano hidroambiental da bacia hidrográfica do rio Ipojuca: Tomo I - Diagnóstico Hidroambiental. Volume 1, 2 e 3, pp. 713.

SIN, S.N.; CHUA, H.; LO, W.; NG, L.M. (2001). *Assessment of heavy metal cations in sediments of Shing Mun River, Hong Kong*. Environment International l26, 297–301.

TAYLOR, K.G.; BOYD, N.A.; BOULT, S. (2003). *Sediments, porewaters and diagenesis in an urban water body, Salford, UK: Impacts of remediation*. Hydrological Processes 17, 2049–2061.

TEMPL, M.; FILZMOSER, P.; REIMANN, C. (2008). *Cluster analysis applied to regional geochemical data: Problems and possibilities*. Applied Geochemistry 23: 2198–2213.

THUONG, N.T.; YONEDA, M.; IKEGAMI, M.; TAKAKURA, M. (2013). *Source discrimination of heavy metals in sediment and water of To Lich River in Hanoi City using multivariate statistical approaches*. Environmental Monitoring and Assessment 185: 8065–8075.

USEPA. (1998). Method 3051a - microwave assisted acid digestion of sediments, sludges, soils, and oils.

USEPA. (2006). National recommended water quality criteria. United States Environmental Protection Agency. Office of Water, Office of Science and Technology.

USGS. (1973). Techniques of Water Resources Investigations. Washington.

VAREJÃO, E.V.V.; BELLATO, C.R.; FONTES, M.P.F.; MELLO, J.W.V. (2011). *Arsenic and trace metals in river water and sediments from the southeast portion of the Iron Quadrangle, Brazil*. Environmental Monitoring and Assessment 172, 631–642.

VAROL, M. (2011). *Assessment of heavy metal contamination in sediments of the Tigris River (Turkey) using pollution indices and multivariate statistical techniques*. Journal of Hazardous Materials 195, 355–364.

VAROL, M.; ŞEN, B. (2012). *Assessment of nutrient and heavy metal contamination in surface water and sediment of the upper Tigris River, Turkey*. Catena 92, 1–10.

VIERS, J.; DUPRÉ, B.; GAILLARDET, J. (2009). *Chemical composition of suspended sediments in World Rivers: New insights from a new database.* Science of the Total Environment 407, 853–868.

WEBER, P.; BEHR, E.R.; KNORR, C.L.; VENDRUSCOLO, D.S.; FLORES, E.M.M.; DRESSLER, V.L.; BALDISSEROTTO, B. (2013). *Metals in the water, sediment, and tissues of two fish species from different trophiclevels in a subtropical Brazilian river*. Microchemical Journal 106, 61–66.

WEBSTER, R. (2001). *Statistics to support soil research and their presentation*. European Journal of Soil Science 52, 331–340.

WONG, C.S.C.; LI, X.; THORNTON, I. (2006). *Urban environmental geochemistry of trace metals*. Environmental Pollution 142, 1–16.

XIAO, R.; BAI, J.; HUANG, L.; ZHANG, H.; CUI, B.; LIU, X. (2013). *Distribution and pollution, toxicity and risk assessment of heavy metals in sediments from urban and rural rivers of the Pearl River delta in southern China*. Ecotoxicology 22, 1564–1575.

Zoneamento Agroecológico do Estado de Pernambuco (ZAPE). (2002). Recife: Embrapa.