HEAVY METAL CONTAMINATION IN WATER OF THE IPOJUCA RIVER – BRAZIL

Yuri Jacques Agra Bezerra da Silva[1], José Ramon Barros Cantalice[2], Clístenes Williams Araújo do Nascimento[3], Cinthia Maria Cordeiro Atanázio Cruz Silva[4], Wagner Luís da Silva Souza[5], Hermon Augusto da Costa Braga Junior[6]

ABSTRACT --- Heavy metal concentrations in water of the Ipojuca River were determined to assess the level of contamination. Samples were obtained using a depth-integrated and isokinetic sampling. Contamination assessment of mercury (Hg), lead (Pb), cadmium (Cd), nickel (Ni), copper (Cu), chromium (Cr), zinc (Zn), arsenic (As), iron (Fe) and manganese (Mn) was studied using water quality guidelines and cluster analysis. The mean metal concentrations in 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. For both the upstream and downstream sites, the highest heavy metals concentrations in water were observed during the summer.The highest heavy metal concentration in water under low water discharge conditions depicts the highest threat for aquatic life. Despite this scenario, the water of Ipojuca River has been widely used for fishing and water irrigation.

Keywords: Water quality, Cluster analysis, Environmentally available metals.

[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 Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: cwanascimento@hotmail.com
[4] 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
[5] PhD of Soil Science Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: wagneragro@yahoo.com.br
[6] PhD of Environmental Engineering Department, Federal Rural University of Pernambuco (UFRPE), Dom Manuel de Medeiros street, s/n. Recife - (PE). Email: hermon.junior@gmail.com

1. INTRODUCTION

Heavy metal contamination in water 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.

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. 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 its objective to determine the status of heavy metal concentrations in water.

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 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.

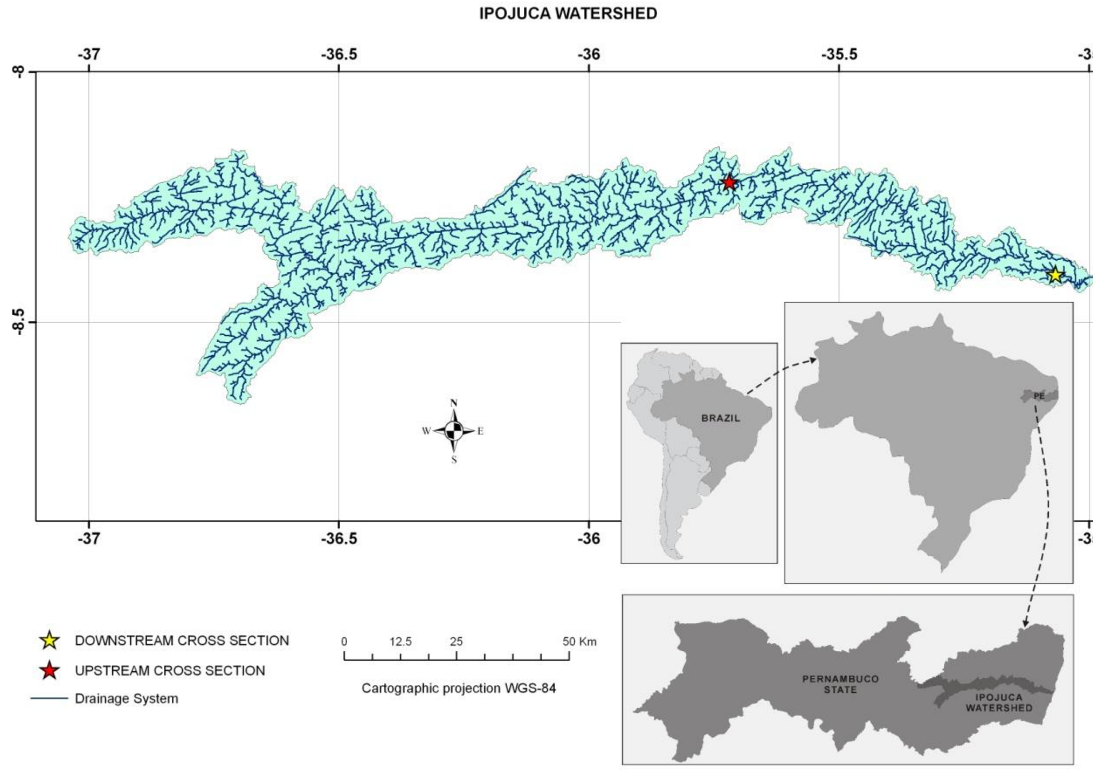

Figure 1 – Location of the Ipojuca River watershed.

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

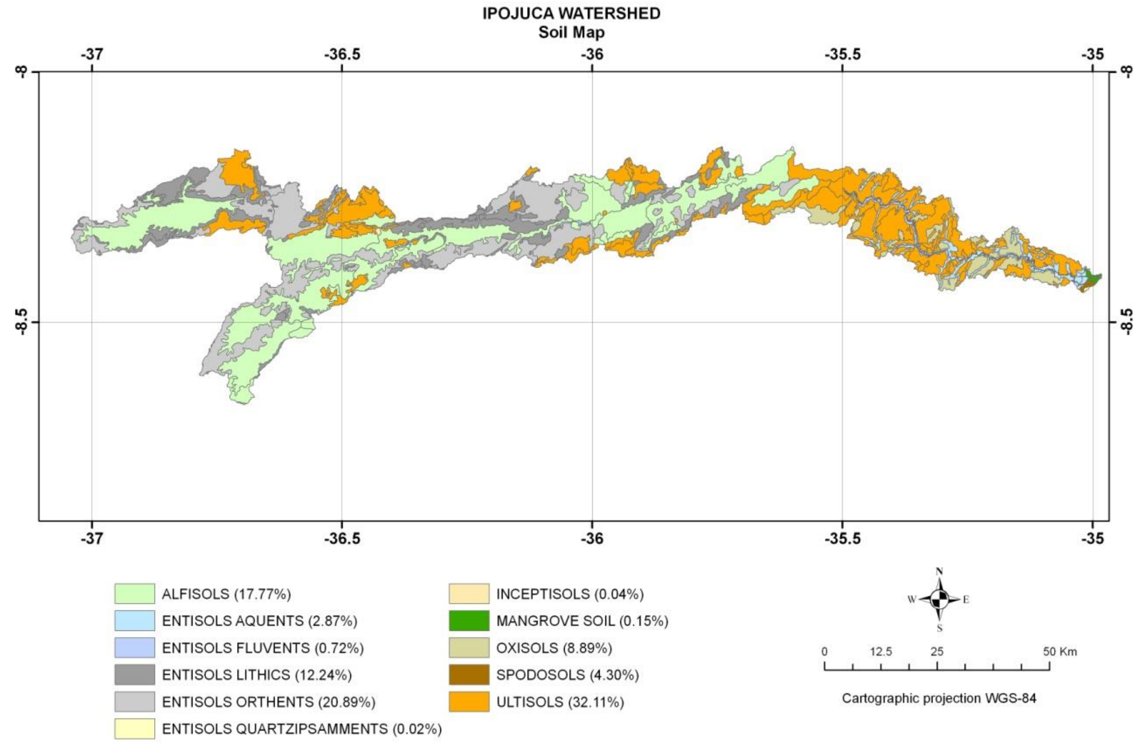

Figure 2 – Distribution of soils in the Ipojuca watershed.

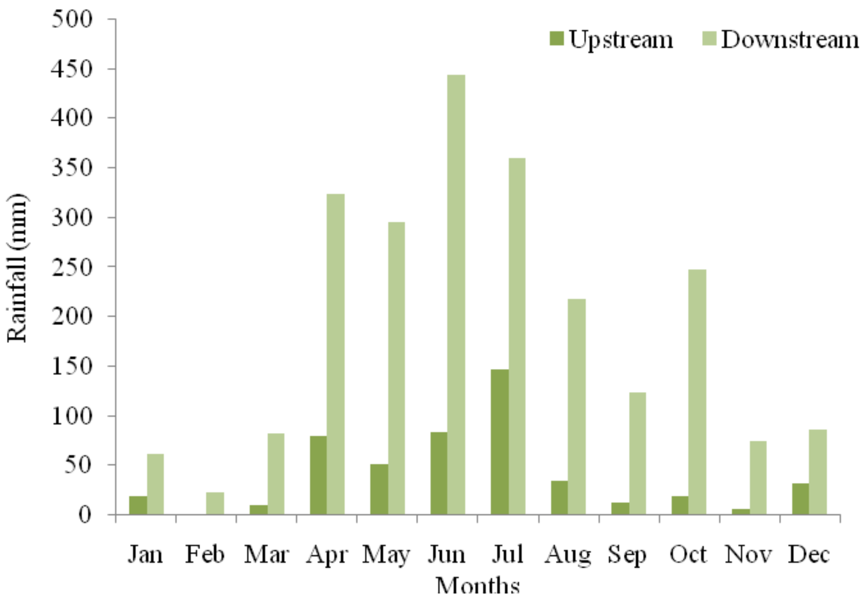

Figure 3 – Monthly rainfall of studied cross sections of Ipojuca River during 2013.

2.2 Sampling sites and measurements

We collected samples of 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 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.

To collect 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 water for the depth profile of the river. The samples were stored in polyethylene bottles until analysis.

2.3 Chemical analysis for heavy metals

The water samples, 5 mL each, 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).

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 materials2710a 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 Statistical Analysis

Descriptive and cluster analysis were used in this study. 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 CA analyses, we used standardized data to avoid misclassification due to differences in data dimensionality (Webster 2001).

3. RESULTS AND DISCUSSION

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 4).

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

Month	Metal concentrations in water – upstream ($mg\ L^{-1}$)									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	0.80	0.81	0.49	0.020	11.76	0.03	0.14	0.45	0.003	0.01
MAR	0.75	0.07	0.42	0.020	9.92	0.02	0.29	0.43	0.002	0.00
APR	0.34	0.29	0.38	0.010	4.52	0.02	0.34	0.51	0.002	0.00
MAY	0.00	0.47	0.00	0.000	1.06	0.00	0.06	0.00	0.002	0.01
MAY*	0.00	0.00	0.00	0.000	0.90	0.00	0.05	0.00	0.002	0.00
JUN	0.00	0.00	0.00	0.000	0.63	0.01	0.06	0.00	0.002	0.01
JUN*	4.01	0.22	0.01	0.000	0.88	0.00	0.06	0.00	0.002	0.01
JUL	0.00	0.00	0.00	0.000	0.60	0.11	0.04	0.00	0.002	0.01
JUL*	0.00	0.07	0.00	0.000	0.69	0.00	0.00	0.00	0.002	0.01
AUG	0.00	0.00	0.00	0.000	0.65	0.11	0.00	0.00	0.002	0.01
SEP	0.00	0.00	0.13	0.000	0.60	0.00	0.04	0.00	0.002	0.02
OCT	0.00	0.00	0.06	0.000	0.14	0.00	0.00	0.00	0.004	0.02
Month	**Metal concentrations in water – downstream ($mg\ L^{-1}$)**									
	Fe	Mn	Pb	Cd	Zn	Cr	Cu	Ni	Hg	As
FEB	2.24	0.61	0.45	0.020	14.43	0.03	0.17	0.53	0.000	0.00
MAR	0.44	0.28	0.50	0.010	8.19	0.03	0.07	0.49	0.002	0.00
APR	0.72	0.01	0.49	0.010	11.23	0.01	0.10	0.37	0.001	0.02
MAY	0.00	0.02	0.00	0.000	1.14	0.00	0.05	0.00	0.002	0.00
MAY*	0.00	0.00	0.00	0.000	0.83	0.00	0.06	0.00	0.002	0.01
JUN	0.00	0.00	0.00	0.000	0.83	0.00	0.07	0.00	0.002	0.02
JUN*	0.00	0.00	0.00	0.000	0.64	0.00	0.06	0.00	0.002	0.00
JUL	0.00	0.00	0.00	0.000	0.59	0.00	0.06	0.00	0.002	0.01
JUL*	0.00	0.00	0.00	0.000	0.82	0.00	0.05	0.00	0.002	0.01
AUG	0.00	0.24	0.00	0.000	1.51	0.00	0.05	0.00	0.001	0.01
SEP	0.00	0.00	0.20	0.000	0.52	0.00	0.02	0.01	0.002	0.02
OCT	0.00	0.00	0.04	0.000	0.17	0.00	0.00	0.00	0.003	0.02
WHO**	5.00	0.20	5.00	0.01	2.00	0.10	0.20	0.20	na	0.10
USEPA***	na	na	na	0.002	0.12	na	0.01	0.47	0.001	0.34

na data not available; *second measurement in the same month; **Irrigation water standard (WHO 2006) ***Acute values for protection of freshwater aquatic life (USEPA 2006).

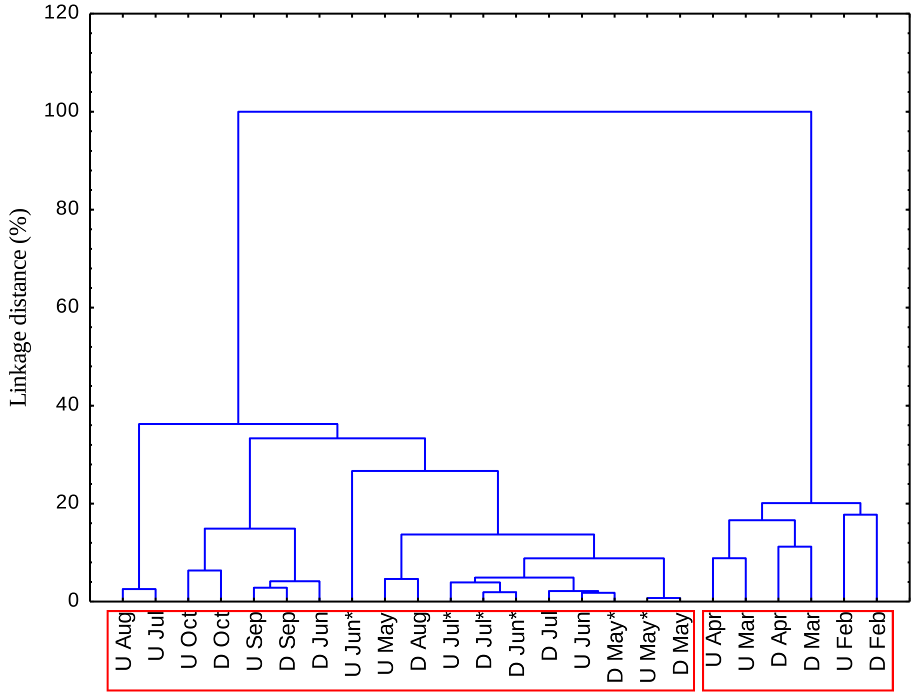

Figure 4 – Cluster analysis of metal concentrations in water, according to Ward's method. U = Upstream; D = Downstream; * = second measurement in the same month.

The mean metal concentrations in 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 the lack of spatial variation (Figure 4), temporal variation was observed in heavy metal concentration in water and therefore the monthly average between the water concentration upstream and downstream was calculated considering high and low water discharge conditions (Figure 5). In the first period, ranging from February to April, the metal concentration followed the order Zn > Fe > Cd > Pb = Ni > Mn > Cu > Cr > As > Hg, while in second period, ranging from May to October, followed the order Zn > Fe > Mn > Pb > Cu > Cr = As > Cd = Ni = Hg.

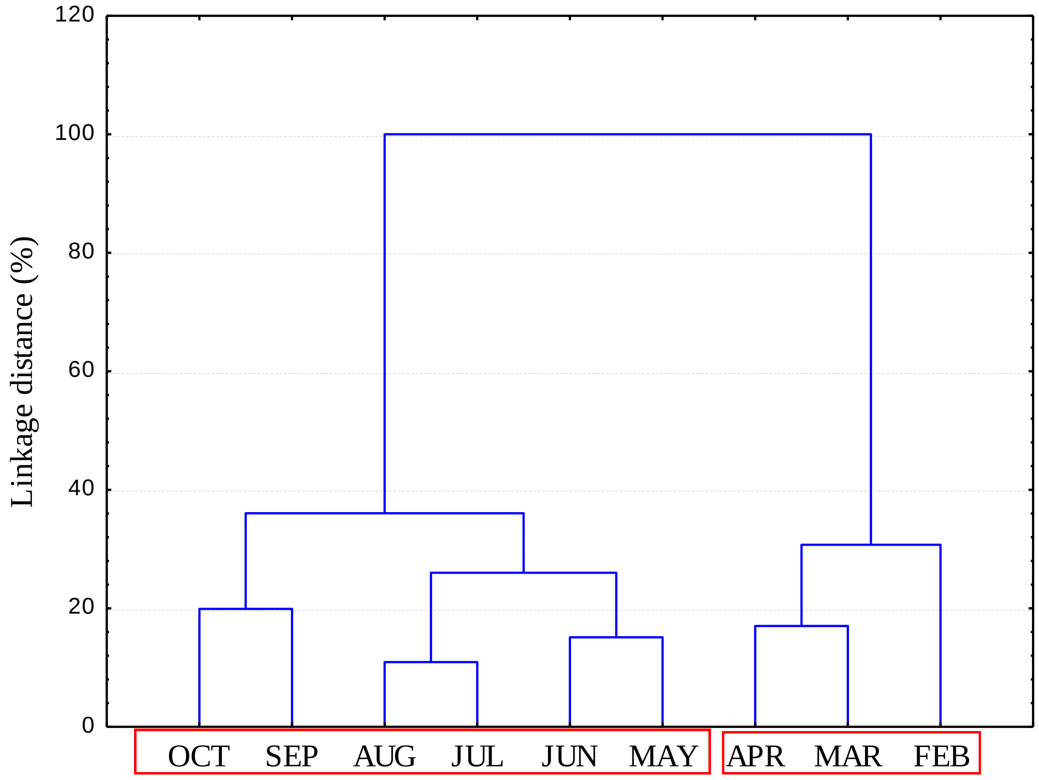

Figure 5 – Cluster analysis of heavy metal concentrations in water, according to Ward's method.

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 *et al*. 2003; Thorslund *et al*. 2012). 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.

4. 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.

Despite this scenario, the water of Ipojuca River has been widely used for fishing and water irrigation.

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).

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