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Research Article

Determination of the concentration of heavy metals in waters from lower São Francisco River basin, Brazil

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Abstract

In this study we determined the concentration of metals Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the water lower São Francisco River basin, to evaluate the influence of urbanization and industrialization on environmental changes in the water resource. The sampling stations located near the industrial areas were influenced by industrialization because they presented higher concentrations of Cd, Cr, Ni and Cu. The other sampled locations showed changes with regard to metals probably originating in the soil, like Fe, Zn and Pb. There was a gradual increase in the concentrations of metals, in general, in the period of highest rainfall of the hydrographic network. Overall, except for Zn and Mn, the trace elements exceeded the maximum allowed value established by national legislation (CONAMA). Lower São Francisco River basin has suffered interference from urbanization and industrialization, so awareness programs should be developed so as to control and lessen future problems.

Keywords: elements, industrialization, urbanization, environment

INTRODUCTION

The impacts of human activity on aquatic systems have been reported for over 200 years. However, coupled to fast population growth, industrialization, as well as some agricultural activities, increased the risks of pollution in natural environments like water, soil and the atmosphere in the last one hundred and fifty (150) years (Santoyo et al., 2000). The problems of contamination with toxic metals started in the Middle Age, with the mining activities, but were accelerated in the beginning of the nineteen century, with the processing of metals in chemical and foundry plants (Vink et al., 1999).

Heavy metals are toxic elements released by some types of industrial effluents (Tarley et al*.*, 2003). Many metals form stable complexes with biomolecules, and their presence, even at low quantities, can be harmful to plants and animals. The free metal ion is the most toxic form to aquatic life (Florence and Batley, 1980). The bioavailability and toxicity, as well as the dependence of the species upon transport phenomena, are related to the chemical form of the substance. Thus, determining the total concentration of a heavy metal in a water sample provides relative information about its toxicity. Contaminant metals can be controlled through sorption systems (Evans, 1989). Discussions on the metallic uptake in river basins cannot be performed without considering the routes through which metals are removed from the solution, be it by precipitation as insoluble salt and/or by adsorption on the surface of solids (Stumm and Wiley, 1992).

When present in an aquatic system, heavy metals are a threat to human health due to their impacts on the quality of the water, foods and ecosystems (Ernst, 1996). Metals such as Cu, Pb and Zn are components of household garbage. Based on material-flow studies, a contribution of 50-80% of these metals may come from urban sewage (Boller, 1997).

The quality of surface waters will depend on the type of waste released by many industrial processes. Tanneries generate a load potentially contaminating formed by Ca, free sulfides, high pH, organic matter, total Cr has high toxicity, and suspended solids.

Another source of contamination by metals are metallurgical industries (Sell, 1992). For many decades, production of Pb, Cu, Zn and Fe ranged around 200,000 tons per year in Brazil, so these were classified as dangerous disposals (Hajdú and Licskó, 1999). A variety of aquatic systems has been contaminated by metals generated from the oxidation of mineral sulfite, which is accelerated by the exposure of metal sulfites to air as a result of the mining activity (Paulson, 1997). Adsorption of heavy metals at the surface of the suspended particulate matter and river sediment has been shown as a geochemical process of removal of metals in solution (Stumm and Morgan, 1981).

The great industrial development is one of the main factors responsible for the contamination of our waters, due to both the negligence in treating industrial waste before dumping it in the rivers, and the accidents and increasingly often carelessness, which causes the release of many pollutants in the aquatic environments, contributing for the natural waters to become residuary. Thus, the industrial sector is the mostly diversified source of introduction of heavy metals in the aquatic environment.

The cities of Petrolina-PE and Juazeiro-BA, located in the Brazilian semi-arid region, together, form a metropolis. They are divided by the São Francisco River lower basin portion, and are connected by the Presidente Dutra bridge. Medium-sized cities have together a population of approximately six hundred thousand inhabitants (IBGE, 2013). The presence of several industries close to the São Francisco River, which intersects both cities, raises concern about the uptake of contaminant metals in these waters, which serve the population in many ways. The rampant growth of urban centers is oblivious to the difficulties that arise from the installation of industries. Their implantation, which in earlier times had not yet been studied or had its environmental impacts reported, currently requires supervision over compliance with the contaminants rates established by legislation, even if they are not reasoned as to their applicability and consequences to the environment and living beings.

The main objective of this study is to evaluate the presence and average concentration total of heavy metals in the water of lower São Francisco River basin, in the Petrolina-PE and Juazeiro-BA section, investigating the possible natural sources and influences of anthropogenic activities on the water quality.

MATERIALS AND METHODS

Geographical location

The area to be studied is located in the West region of the states of Pernambuco and Bahia, Brazil, comprising the municipalities of Petrolina-PE and Juazeiro-BA. These municipalities are on the course of São Franciso River basin, which is responsible for all the water supply to the region. The areas under study are specifically located at strategic points of the river (Figure 1).

Two periods of the hydrological year were sampled: September to December 2013 and January to March 2014, which characterized the collection periods 1 and 2, respectively. These periods in previous years occurred in the seasonality of rainfall collection points, these epochs were determined in order to observe its effect on metal concentrations (IBGE, 2013).

Three different areas of the river course were sampled: the urban area (UA) (9°24’25” South latitude - 40°30’7” West longitude) located within the central perimeter that divides both cities; and Balneário de Pedrinhas (BP) (9°16’84” South latitude - 40°19’11” West longitude) and Ilha do Massangano (IM) (9°27’24” South latitude - 40°35’49” West longitude), located 30 and 10 km away from the metropolis, respectively. Water samples from 5 points of each location were collected, shown in Figure 1 the 15 sampling points, adopting the distance of 500 meters for each point, comprising a total water course of 50 km of studied area.

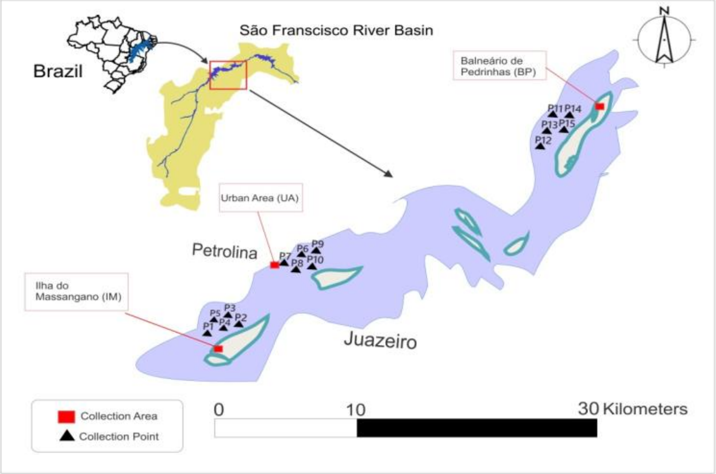

Figure 1. Panoramic view of the lower São Francisco River basin, showing the areas in red and black collection points

Preparation of the samples

The water samples were collected using 1L polyethylene bottles attached to an aluminum support. The containers had a pressure valve connected to a string; when the string was pulled, the restrained air would escape, so the water would have access by pressure. The sampling was performed in the deep part, at around 3m of depth, at a distance of 50m from the margin (Greenberg et al., 1992). The samples were then acidulated with two hundred microliters nitric acid P.A. to reach pH 2.0 in a ratio of 1 for 3 ml and kept refrigerated at 4ºC. Afterwards, the samples were pre-concentrated 10times through convective heating on a hot plate, at approximate temperature of 60ºC, to ensure sufficient metal concentration for the determination, due to the detection limit imposed by the Atomic Absorption Spectrometry technique (Ribeiro et al., 2012). The analyses were performed in triplicate.

Physicochemical analysis of the water from the river

During the collections, the physicochemical parameters of the water (temperature, dissolved oxygen, pH, conductivity, ammonia and turbidity) were measured using a Hanna Oxy-Chek portable probe and calorimetric test kits.

Instrumentation

The concentration of metals total was determined using a flame atomic absorption spectrophotometer, AAS. The operating conditions varied for each studied metal (Table 1). The optimal conditions for multi-element determination were established according to recommendations of the manufacturer. The limit of detection (DL) and limit of quantification practicable (PQL) were calculated according to the norms of IUPAC (The International Union of Pure and Apllied Chemistry).

Table 1. Operating conditions of the atomic absorption spectrophotometer, detection limits and parameters of the calibration curve for each element

Element	WL[1] / (nm)	Gas flow / (L min^{-1})	Gas type	DL[2] / (mg L^{-1})	PQL[3] / (mg L^{-1})	X	Y	r^2
Ni	233.0	2.3	Air-C_2H_2	0.0016	0.0786	0.030	0.003	0.9945
Cd	227.2	1.8	Air-C_2H_2	0.0017	0.0849	0.389	–0.015	0.9949
Zn	214.9	2.0	Air-C_2H_2	0.0114	0.5725	0.038	0.023	0.9998
Pb	218.0	2.1	Air-C_2H_2	0.0001	0.0069	0.017	–0.010	0.9994
Fe	249.3	2.3	Air-C_2H_2	0.0058	1.2919	0.082	0.008	0.9959
Mn	278.5	1.9	Air-C_2H_2	0.0015	0.0773	0.172	0.012	0.9979
Cr	356.9	2.9	Air-Ar[4]	0.0220	1.1023	0.018	0.006	0.9992
Cu	323.7	1.7	Air-C_2H_2	0.0002	0.0098	0.037	0.050	0.9994

1- WL: wavelength. 2- DL: detection limit. (DL = 3 RSD/α), RSD (relative standard deviation) for 10 measures of the analytic white solution and α is angular coefficient of the calibration curve. 3- PQL: Practical quantitation limit. (PQL= DL/DF), DF (Factor de dilution). 4-Ar: Argon.

Chemical reagents and standards

All the reagents employed in the development of this study were of analytical grade, and the water was highly pure (deionized). The stock solutions were prepared with high purity standards, in HNO_3 1 % (Merck). Next, the solutions were conditioned in pre-washed polyethylene bottles and decontaminated with HNO_3 10 %. A blank was prepared and stored in the same manner.

Statistical treatment of the data

For the analysis of the results obtained, the Resolution no. 357 of CONAMA (National Council for the Environment), of March 17, 2005, was consulted. This resolution addresses the classification of water bodies and environmental guidelines for this nature, as well as establishes the conditions and standards for effluent release, among other measures. Resolution 344 of CONAMA, from March 25, 2004 was also consulted; this resolution establishes general guidelines and minimum procedures for the evaluation of the material to be dredged in Brazilian waters, and other measures.

The statistical tests were conducted using the Assistat-7.5 statistical software (Silva, 2010). Data were compared between the different sites of samples. Correlations between the analyzed parameters were made by applying Spearman's r test. The probability of 0.05 or less was considered significant.

RESULTS

The water physicochemical parameters are described in Table 2. They were within the levels established by Resolution no. 357/2005 of CONAMA.

Table 2. Means of the physicochemical parameters of the water from lower São Francisco River basin, in Petrolina-PE and Juazeiro-BA section

Parameters	**UA^{5}**		**IM^{6}**		**BP^{7}**	
	P1^{8}	**P2^{9}**	**P1**	**P2**	**P1**	**P2**
Temp.^{1} / (° C)	25.6	24.4	25.7	24.3	25.4	24.5
O_2D^{2} / (mg L^{-1})	7.32	5.87	7.76	5.94	7.97	5.89
Conduct.^{3} / (µS cm^{-1})	90	103	83	94	81	99
pH^{4}	7.14	8.01	7.32	8.34	7.21	8.03
Turbidity / (NTU)^{10}	20	47	26	43	29	45
Ammonia / (mg L^{-1})	0.010	0.013	0.009	0.011	0.008	0.012

1- Temp.: temperature. 2- O_2D: dissolved oxygen. 3- Conduct.: conductivity. 4- pH: potential hydrogen. 5- UA: urbanarea. 6- IM: Ilha do Massangano. 7- BP: Balneário de Pedrinhas. 8-P1: Period 1. 9- P2: Period 2. 10- NTU: Nephelometric Turbidity Units.

Tables 3 and 4 show the concentration range of the metals evaluated in the lower São Francisco River basin, in the Petrolina-PE and Juazeiro-BA section in the two times of the hydrological year, as well as the standard deviation, maximum value and coefficient of variation of the determinations. It also summarized the maximum allowed value (MAV) established in Resolution no. 357/2005 of CONAMA.

Table 3. Mean concentrations of heavy metals (mg L^{-1}), standard deviation and coefficient of variation of the different water collection sites of lower São Francisco River basin in Period 1

Metal	**MAV^{1}**	**----------(UA)^{5}----------**			**---------(IM)^{6}---------**			**---------(BP)^{7}---------**			**CV^{4} / (%)**
		Mean	Max.v.^{2}	SD^{3}	Mean	Max.v.	SD	Mean	Max.v.	SD	
Nickel	0.025	0.009^{ab}	0.020	0.005	0.011^{a}	0.022	0.005	0.007^{b}	0.016	0.005	53.20
Cadmium*	0.001	0.006	0.015	0.004	0.007	0.016	0.003	0.008	0.029	0.009	89.58
Zinc*	0.180	0.019	0.033	0.008	0.017	0.029	0.006	0.016	0.064	0.016	64.20
Lead*	0.010	0.023	0.048	0.014	0.017	0.042	0.010	0.016	0.028	0.006	56.38
Iron*	0.300	0.285	0.872	0.294	0.337	0.917	0.277	0.370	1.098	0.279	88.76
Manganese	0.100	0.040^{b}	0.064	0.016	0.060^{a}	0.159	0.033	0.028^{c}	0.060	0.019	57.52
Chromium	0.050	0.076^{a}	0.089	0.020	0.036^{b}	0.075	0.023	0.032^{b}	0.058	0.015	65.10
Copper*	0.009	0.004	0.014	0.003	0.004	0.009	0.002	0.005	0.011	0.002	64.20

1- MAV: maximum allowed value (Conama). 2- Max. v.: maximum value. 3- SD: standard deviation. 4- CV:coefficientofvariation. 5- UA: urbanarea. 6- IM: Ilha do Massangano. 7- BP: Balneário de Pedrinhas.
*Mean values followed by the same letter in the same row do not differ according to Tukey's test ($p>0.05$).

Table 4. Mean concentrations of heavy metals (mg L^{-1}), standard deviation and coefficient of variation of the different water-collection sites in lower São Francisco River basin in Period 2

Metal	**MAV^{1}**	**----------(UA)^{5}----------**			**---------(IM)^{6}---------**			**---------(BP)^{7}---------**			**CV^{4} / (%)**
		Mean	Max. v.^{2}	SD^{3}	Mean	Max. v.	SD	Mean	Max. v.	SD	
Nickel*	0.025	0.028	0.054	0.018	0.041	0.096	0.032	0.028	0.053	0.021	76.94
Cadmium	0.001	0.012^{b}	0.021	0.007	0.020^{ab}	0.035	0.011	0.023^{a}	0.029	0.005	44.12
Zinc	0.180	0.008^{ab}	0.017	0.007	0.003^{b}	0.008	0.003	0.013^{a}	0.019	0.004	60.73
Lead*	0.010	0.004	0.006	0.014	0.021	0.049	0.025	0.003	0.010	0.04	96.74
Iron*	0.300	0.596	0.821	0.130	1.129	2.090	0.671	0.749	1.162	0.351	53.80
Manganese	0.100	0.016^{a}	0.026	0.006	0.020	0.025	0.004	0.005^{b}	0.011	0.005	37.32
Chromium*	0.050	0.011	0.042	0.018	0.030	0.077	0.031	0.033	0.038	0.016	82.73
Copper*	0.009	0.018	0.596	0.013	0.006	0.017	0.007	0.013	0.020	0.007	75.44

1- MAV: maximum allowed value (Conama). 2- Max. v.: maximum value. 3- SD: standard deviation. 4- CV:coefficientofvariation. 5- UA: urbanarea. 6- IM: Ilha do Massangano. 7- BP: Balneário de Pedrinhas.
*Mean values followed by the same letter in the same row do not differ according to Tukey's test ($P>0.05$).

Table 5. Mean correlation matrix of the analyzed elements of the water from lower São Francisco River basin

	Ni	Cd	Zn	Pb	Fe	Mn	Cr	Cu
Ni	**1**							
Cd	–0.43	**1**						
Zn	0.41	–0.12	**1**					
Pb	–0.26	0.76**	0.06	**1**				
Fe	0.75**	–0.48	0.27	–0.53*	**1**			
Mn	0.07	–0.08	0.15	–0.51*	–0.17	**1**		
Cr	0.61*	–0.35	0.43	–0.53*	0.51*	0.79**	**1**	
Cu	–0.08	0.31	0.24	0.30	–0.03	0.23	0.18	**1**

* significant at 5% of probability (P < 0.05).
** significant at 1% of probability (P < 0.01).

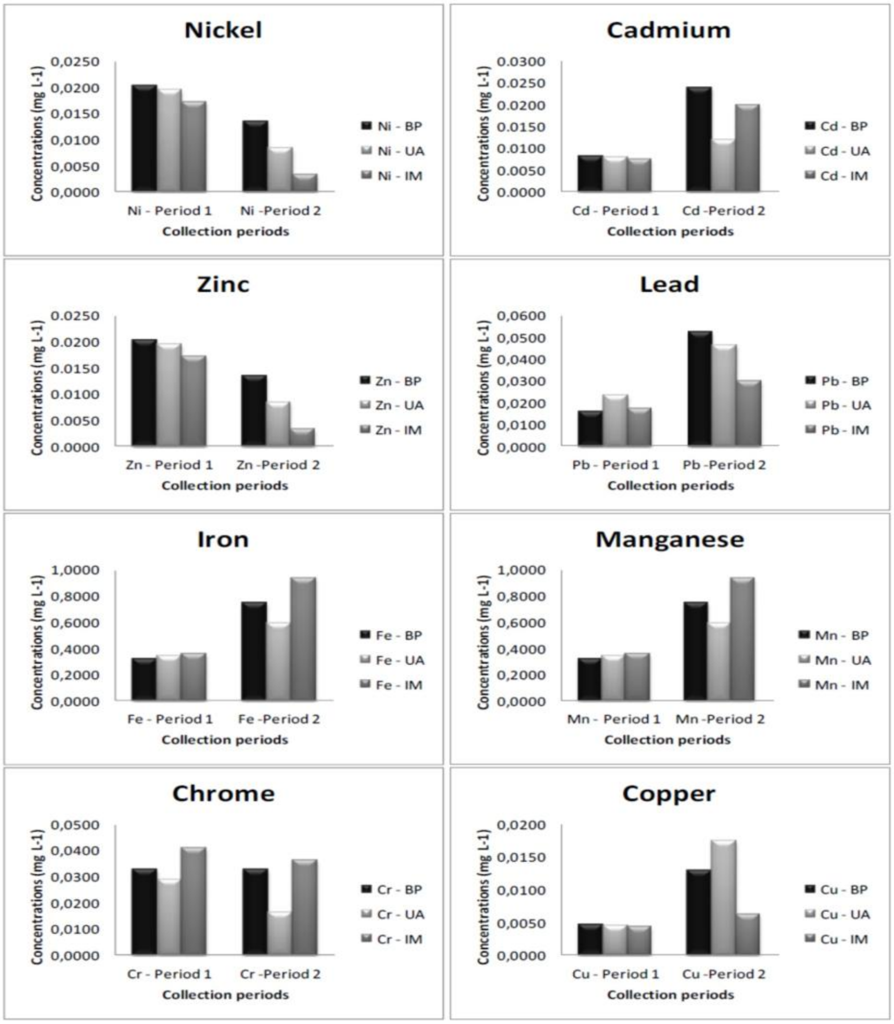

Figure 2. Graph of the concentrations (mg L-1) of metals in different points and periods of sampling

DISCUSSION

The metals that characterize aquatic environments in urban and industrial areas can originate in specific or diffuse sources, e.g., Ni, Cd, Zn, Pb, Fe, Mn, Cr and Cu, deeply transforming the characteristics of these aquatic environments.

The São Francisco River is a freshwater body belonging to the class I; waters of this class can be intended for navigation and landscape harmony. This class adopts the same heavy metals standards established for class-3 water bodies (water that can be intended for human consumption, after conventional or advanced treatment; irrigation of tree, cereal and forage cultures; recreational fishing; secondary contact recreation; and watering animals).

The sampling areas named UA, whose urban and industrial activities are highly intense, presented higher concentrations of metals Ni, Cd, Pb, Fe, Cr and Cu (Figure 2.). There was also increase in the concentration of the other metals studied in these locations. At IM, however, there was increase in the average concentration of metals Ni, Cd, Pb and Fe, whose values were far above the allowed. Ilha do Massangano (IM) is characterized by having an area of approximately 250 hectares, centered at the middle of the river. People who live there depend on fishing and subsistence farming. The elevation in the level of these metals might have been caused by the chemicals utilized in these plantations, which are usually disposed without previous treatment directly in the river.

According to Santos et al. (2012) agriculture is one of the most important sources of metals in soils, as in the cases of Pb and Ni, through the application of pesticides and fertilizers, sewage sludge or irrigation water. To suppress some possible deficiencies of micronutrients like Zn and Cu in soils, farmers use fertilizers that in addition to the already mentioned heavy metals, contain others, namely Cr and Pb (Santos et al., 2012).

The analysis showed that there was no significant statistical difference for Cd, Zn, Pb, Fe and Cu in collection Period 1 in the different locations (Table 3). The mean concentrations of Ni, Mn and Cr, however, presented statistically significant differences ($P<0.05$), and the mean contents of Zn, Pb and Cr were higher in Period 1, and the concentrations of Ni, Cd, Fe, Mn and Cu were higher in Period 2. Yet, the elements Cd, Zn and Mn differed statistically ($P<0.05$) in the same period, attributing the occasionality of leaching to the rainfall during collection Period 2, affecting the elevation of the metals Ni, Cd, Fe, Mn and Cu seen in Figure 2.

The important volume of rainfall in the previous months and on the collection days of Period 2 should be considered a determining factor of the concentration of heavy metals present in lower São Francisco River basin observed in Figure 2. The average precipitation values during the 30 days prior to the collections of Period 2 were approximately 187 mm, and there was precipitation of 3 mm in collection Period 1 (CPTEC, 2013), demonstrating patterns in the rainfall with large differences between the collection periods.

These rains during collection period 2 are usually concentrated in a short period, with maximum precipitation in the hydrological year. However, several anthropic factors may be involved, fostering increase in the average concentration of metals, like leaching of the chemical products utilized in the cultivation of fruits from the semi-arid region and disposal of chemicals used in the industry sector, whose production peak is during this period. Similar to the results Santos et al. (2012). Observed increasing concentrations of Cd, Ni, Mn and Fe in the total fraction after precipitation of 299.3 mm of rainfall in the river Accounts in an area that encompasses the urban area and part of rural Jequie City, which is located in southwest region of the state of Bahia (Brazil).

Table 5 shows a negative, strong correlation between Pb and the other elements, which leads us to confirm the inexistence of heavy mineral residues, which have other metals in their structure. Good correlations between a few elements like Fe and Cr and nickel can also be observed, thus showing the mineralogical affinities with existing mineral assemblages in the river, where, according to Ivo and Figueiredo (1996), opaque minerals (magnetite, ilmenite, hydrated oxides), hornblende, hypersthene, augite, and others can be found; these are easily degraded by the intense physical processes in the region. Silva et al. (2012), reported that the coarser sediments of São Francisco River are characterized by being immature, subarkosic and by having a high content of unstable heavy minerals (1 to 8%).

More or less significant correlations appear between Fe and trace elements: 0.75 (Fe-Ni) and 0.51 (Fe-Cr). Such values suggest that these metals were associated with clay minerals and stable-to-ultrastable primary minerals. More or less significant values, in turn, suggest strong associations with oxyhydroxides and Fe hydroxides.

Chromium had its highest concentration in Period 1, reaching an average value of 0.076 mg L^{-1} in UA and exceeding the maximum allowed value established in Resolution no. 357/2005 of CONAMA, which is 0.050 mg L^{-1}. The UA is located within the central perimeter that divides the two cities under study, which have an active industrial sector in leather processing.

The pollution generated in tanneries originates in the hides themselves and in the incompletely absorbed chemicals during tanning. Several chemical substances can be added to the hides until their transformation into leather, and they are present in the main wastes generated by tanneries. According to Schunemann et al. (1983), the mixture of residuary waters resulting from the tanning steps presents particular properties, such as presence of potentially toxic substances (heavy metals, lime and sulfides). The trivalent chromium, commonly employed in tanning in the form of basic sulfate, precipitates as hydroxide of the effluents from the primary treatment; it is concentrated in silt and suspended material from wastewater from tanneries.

The use of chromium salts as tanning agents and their possible toxicity has been widely discussed, especially in the last three decades (Aravindham et al., 2004; Armienta et al., 2001). Currently, the technique of chromium tanning is utilized in over 80% of the global leather population, and in Brazil, this number exceeds 90%. The wide use of chromium is due to the beneficial characteristics it provides to the leather, in relation to the other tanning agents. In view of this, no change in this scenario is expected for a near future, so measures that promote better understanding and a more effective control of the potentially pollutant activities involved in the industrial processing of hides and skins should be fostered.

Excess Cr becomes toxic, as a result of its exposure through inhalation and ingestion, producing toxicity in the lungs and stomach, because it is absorbed through cellular membranes and then infiltrates the interior of the cells. Dermal exposure to chromic acid causes skin damage, allowing rapid absorption of hexavalent chromium ions and leading to a potential acute chromium intoxication. Cr (VI) is considered a powerful carcinogen (Callender, 2005).

Metals like Mn and Pb, at concentrations above the maximum allowed, are considered neurotoxicants, capable of inducing neural dysfunctions or causing damage to the central or peripheral nervous system. Exposure to these elements triggers a wide range of clinical manifestations from motor dysfunction and behavioral changes to psychosis (Candurra et al., 2000; Muñoz et al., 2003). Zinc can cause irritation and corrosion of the intestinal tract, and may also lead to renal necrosis or nephritis, in the most severe cases (Barceloux, 1999). The high levels of Zn, Mn and Pb observed in the shallow water of the stream highlight the need for periodically monitoring this body of water, considering the toxic and bioaccumulative effects of these metals.

Ribeiro et al. (2012), conducted a study on heavy metals and water quality in the river segment between San Francisco Três Marias and Pirapora - MG, found clearly the influence of metals on the health of coastal fishermen, who used the river water without any treatment for consumption.

The Cu concentrations recorded in the water, especially in collection period 2, may cause deleterious effects on human beings if measures for decontamination of the water are not taken and if there is chronic human exposure to this environment. Copper is another essential element that at high concentrations can produce toxicity to human beings. For instance, patients with Wilson's disease, individuals with deficient levels of glucose-6-phosphate dehydrogenase, and children, especially those under 12 months of age in this study area, might have a greater risk of chronic overexposure to copper, probably due to their low capacity to excrete metals. At elevated concentrations, Cu can also cause great biochemical alterations in the body and affect the central nervous system (Laurent et al., 2010).

Normal concentrations of Ni were found in collection period 1. However, they were high in all the collection sites from Period 2. In Table 4, we can observe maximum values reaching 0.096 mg L^{-1} in IM, which is well above the allowed, so preventive measures for decontamination of these sites should be taken.

The deleterious effects on public health regarding the elevated concentrations of Ni were caused mainly by inhalation through the respiratory tract and ingestion of contaminated water, containing ultrafine particles of nickel metal, at one dose. This can normally result in greater inflammatory response, probably because the extremely small size of the particle and the large corresponding surface area can change several mechanisms of the organism, e.g. inhibit phagocytosis, increase oxidative stress, and increase inflammation in the lung epithelium, allowing the ultrafine particles to diffuse more rapidly within the lung interstitium and increasing the risk of lung cancer (Plumlee and Ziegler, 2005). Nickel can be carcinogen, participating in specific stages of carcinogenesis, and may play a role in more than one, or all of its three phases (Plumlee and Ziegler, 2005).

The concentrations of Fe verified in the water, especially during collection period 2, showed high levels, in accordance with the legislation. According to Richter and Neto (1991), in Brazil, it is common to find water with high iron contents, especially from old lands and alluvia.

According to Feitosa and Filho (1997) in the human body, iron acts in the formation of hemoglobin (pigment of the red blood cell that carries oxygen from the lungs to the tissues). Its deficiency can cause anemia and excess can increase the incidence of heart disease and diabetes. The evaluation of iron in groundwater for human consumption is because of its organoleptic properties. Delvin (1998) states that accumulation of iron in the liver, pancreas and heart can lead to cirrhosis and liver tumors, diabetes mellitus and heart failure, respectively. Also, Mahan (2000) states that excess iron can help generate excessive amounts of free radicals that attack cellular molecules, thereby increasing the number of potentially carcinogenic molecules within them.

Cadmium was above the MAV in all sites and collection periods, according to the national legislation. Exposure to this metal causes symptoms similar to food poisoning. Accumulation of this metal in man results in the itai-itai disease, which causes problems in calcium metabolism, followed by decalcification, rheumatism, neuralgia and cardiovascular problems (Train, 1979). High concentrations accumulated in organisms destroy the testicular tissue and red blood cells and can lead to mutagenic and teratogenic effects (Manaham, 1994). In Taubaté, SP (Brazil) a very high level of cadmium was found in 58 samples of human colostrum (Nascimento, 2005), and speciation of trace elements in breast milk has been the subject of research with increasing frequency and complexity (Michalke, 2006).

Recent studies have shown significant concern of doctors and scientists about the chronic and subclinical toxicity by metals in the environment, as reported by a review of Brazilian pediatricians that emphasizes the deleterious effects to the nervous system of children by lead and mercury (Silva and Fruchtengarten, 2005) and a study in Bangladesh, which suggests that there is association between mortality and ingestion of water containing manganese (Hafeman, 2007).

Similarly, in Europe, a multicenter study involving children of France, Poland and the Czech Republic accuses subclinical effects of exposure to heavy metals (Burbure, 2006). Specifically on the neurotoxicity of lead, mercury and manganese, scientists from twenty seven (27) nations, meeting in the International Commission on Occupational Health, in June 2006, formulated guidelines to ten countries around the world, in a document known as Declaration of Brescia on Prevention of Neurotoxicity of Metals (Landrigan, 2007). However, data show the importance of detecting concentrations of metals in freshwater reservoirs, for characterizing the local situation in order to make decisions for greater environmental control.

CONCLUSIONS

Throughout the course of the sampled lower São Francisco River basin, Petrolina-PE and Juazeiro-BA section, there was regular presence of metals Cd, Cr, Ni and Cu with probable origin in urbanization and industrialization, these sources being broken down by similarity analysis. There was also systematic presence of Fe, Zn and Pb, probably from the soil.

The period of higher rainfall showed increased concentrations of metals typical of the soil due to heavy particle entrainment into the aquatic system. This impact may be related to irregular occupation along the banks and agricultural activity on islands in the river. Much soil has been removed, silting the river, which is kept exposed without vegetation cover.

It is thus concluded that the lower São Francisco River basin, Petrolina-PE and Juazeiro-BA section has been influenced by urbanization and industrialization, and awareness programs can be established to monitor and mitigate future problems.

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