Seasonal study of contamination by metal in water and sediment in a sub-basin in the Southeast of Brazil

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(With 4 figures)

Abstract

The spatial and temporal occurrence of heavy metals (Al, Cd, Pb, Zn, Cr, Co, Cu, Fe, Mn and Ni) in water and sediment samples was investigated in a sub-basin in the southeast of Brazil (São Carlos, SP). All samples were analysed using the USEPA adapted metal method and processed in an atomic absorption spectrophotometer. The discriminant analysis demonstrated that there are significant seasonal differences of metal distribution in the water data, but there are no differences to sediment. The basin studied has high levels of contamination by toxic metals in superficial water and sediment. The superficial water, in the rainy season, presented high levels of Cr, Ni, Pb and Cd, while in the dry season it presented high levels of Zn and Ni. The Principal Component Analysis demonstrated that the season has a huge influence on the levels, types and distribution of metals found in water. The source of contamination was probably diffuse, due to products such as batteries and fluorescent lamps, whose dump discharge can contaminate the bodies of water in the region in the rainy season. Due to fires from the harvest of sugar cane, high levels of Zn were found into the environment, in the dry season.

Keywords: heavy metal, water pollution, sediment pollution.

Estudo sazonal da contaminação por metais na água e sedimentos em uma sub-bacia na região sudeste do Brasil

Resumo

A ocorrência espacial e temporal de metais pesados (Al, Cd, Pb, Zn, Cr, Co, Cu, Fe, Mn e Ni) nas amostras de água e sedimento foram investigadas em uma sub-bacia do sudeste do Brasil (São Carlos, SP). Todas as amostras foram analisadas através do método de metal USEPA, adaptado e processado por espectrofotômetro de absorção atômica. A análise de Discriminante demonstrou que existem diferenças sazonais significantes na distribuição dos metais na água, mas não existem diferenças para o sedimento. A água superficial, na estação chuvosa, apresentou altos índices de Cr, Ni, Pb e Cd, enquanto na estação seca apresentou altos índices de Zn e Ni. A Análise de Componente Principal demonstrou que as estações do ano têm uma enorme influência no nível, no tipo e na distribuição dos metais encontrados na água. A fonte de contaminação foi provavelmente difusa devido a produtos como baterias e lâmpadas fluorescentes, cuja descarga nos lixões pode contaminar os corpos de água da região na estação chuvosa. Devido a queimadas provenientes da colheita de cana-de-açúcar, altos níveis de Zn foram encontrados no ambiente na estação de seca.

Palavras-chave: metal pesado, poluição da água, poluição do sedimento.

1. Introduction

Water is a vital element to living organisms and its inadequate use for different purposes has caused several problems both to quality and amount of this resource. Also, due to exponential increase in water demand and water quality deterioration because of lack of domestic and industrial effluent treatment, water started to be considered a limited resource, being the main cause for concern in different scales, from local to global (Tundisi, 2003).

Pollutants, when introduced to an aquatic system, present a heterogeneous behaviour, and they can be toxic just by their presence or by degradation process. Pollutants can release compounds, which assimilated by organisms, can interfere in physiologic processes, such as reproductive aspects, survival and, consequently, changing the population structure (Boudou and Ribeyre, 1989; Doi et al., 2007). Although adverse health effects of heavy metals have been known for a long time, exposure to heavy metals continues and is even increasing in some areas (Järup, 2003).

Metals in natural water can play an important role in the biological functioning of many organisms. Some metals, depending on the way they are distributed in water, can present a high toxicity level to living organisms, while others are considered essential, such as Fe, Al, Zn. However, even essential metal can be toxic if in large concentration (Templeton et al., 2000).

Industrial activities refine metallic minerals, use metals as raw material for their products or dispose sub-products in their processes. Foundries, electroplating, automobile and paper industry, use and discard high amount of metals such as cadmium, lead, copper, nickel and zinc (Peláez-Rodríguez, 2001; Järup, 2003). Pesticides and fertilisers used in agricultural areas have large amounts of Cu. Fires from the harvest of sugar cane release high levels of Zn into the environment (Ziolli, 1995). The deposit of household, industrial and health care waste, without a prior geological and hydrological study, emphasizes the possibility of soil, aquifers and surface water contamination.

According to IPT (1995), solid waste disposal can be done in three ways: in dumps (simply dumping of waste on the ground), at controlled landfills (disposal of waste on the ground with a degree of control, compression and coating) and landfills (waste placement associated with engineering works, independently and safely in the least space as possible). Velozo (2006) showed environmental pollution in the city of São Carlos because of the presence of a closed dump, located in the basin of the Feijão river.

The characteristics of rivers vary not only according to the basin in which they are located. These features are consequences of the geology that makes up basin drainage, slope, vegetation, rainwater characteristics, various types of human activities, in addition to their variation over time and space (Goldman and Horne, 1983; Pedroso et al., 1988). This fact requires that quality assessments of water bodies should be made in the course of a year, with periods of drought and rainfall. Thus, the analysis of variables on water quality, associated with indicators of chemical and the study of the area in an integrated way, provide relevant information for the spatial characterisation of bodies of water in river basins (Goldman and Horne, 1983).

According to Boyd (2010) there is the need to explore ecosystem studies on metals in larger-scale than toxicological studies. Despite being more difficult to implement, the study involving the collection of information about presence, distribution, quality and quantity of contaminants in different matrices such as water and sediment, provides useful information for assessing environmental risks and therefore for ecological monitoring and human health (Zimmer and Zimmer, 2008).

In recent years, many studies have been conducted on the evaluation of metals in freshwater environments (Sanei et al., 2010; Mdegela et al., 2009; Kikuchi et al., 2009; Brahimpour and Mushrifah, 2008; Mastoi et al., 2008). However, there are few studies involving the influence of seasonality as a key factor in determining the sources of pollutants.

In the region of São Carlos, some studies were conducted to evaluate the environmental conditions of lotic bodies, as Rios (1993), Santos (1993) and Teixeira (1993). Specifically for the Monjolinho river basin, several studies have been carried out on various aspects, including those developed by Povinelli (1972), Gomes (1981), Santos (1990), Sé (1992), Salami (1996) and Pelaez-Rodriguez (2001). Only Pelaez-Rodriguez (2001) focused on the analysis of metals in bodies of water of the Jacaré-Guaçú basin.

Given the importance of studying metals as pollutants of aquatic ecosystems and the absence of behavioural studies of this pollutant, considering the watershed as a whole, from the southeast of Brazil, this project aimed to evaluate the concentration of metal in the basins of Monjolinho and Feijão rivers. The study aimed to evaluate the concentrations of the metals Al, Cd, Pb, Zn, Cr, Co, Cu, Fe, Mn and Ni in the water and sediment, to quantify and investigate the routes of intake of these metals for the watershed.

2. Methods

2.1. Study area

The city of São Carlos is located in central São Paulo State, between coordinates 47° 30' and 48° 30' Longitude, 21° 30' and 22° 30' Latitude. The area of the city is 1.132 km^2, with a population of about 219,000 inhabitants, of whom 93.6% are of an urban settlement. The climate is classified as humid subtropical (Tolentino, 1967) or mild mesothermal (Nimer, 1972), with hot and humid summer from October to March, and cold and dry winter from April to September. The draining of the city has a dendritic pattern, reflecting the regional geology. The city has a rich water supply and the Monjolinho river is responsible for major urban drainage, crossing the city from east to west. The streams of Gregório, St. Maria Madalena and Tijuco Preto, which are Monjolinho tributaries, are located in the centre and north of São Carlos. They all have small flow and stabilised profiles. The Feijão river, the main surface water source that supplies the city of São Carlos, is 13 km from the centre of the city. The other surface water catchment is the Espraiado, near Monjolinho river. Figure 1 shows the sampling sites and Table 1 shows the rivers and corresponding sampling sites.

2.1.1. Sampling methodology and procedures

Samples were collected in February and March 2008 (rainfall) and September 2008 (dry) in twenty-six sites of the city of São Carlos (SP, Brazil), in urban, agricultural and natural areas, for water and sediment. The surface water samples were collected in 500 mL polyethylene gallon and kept away from the sun and heat in styrofoam boxes with ice for laboratory analysis. The collected water was filtered through a glass fiber filter Whatman GF/C with a porosity of 1.2 mm. The samples were preserved in polyethylene bottles of 150 mL with 2 mL of HNO_3 and then frozen (APHA, 2005).

2.1.2. Sediment methodology

The sediment was collected with the aid of plastic spatulas and stored at 4 °C. The content of metals in sediment samples was assessed according to USEPA 3050B.

A reference material from Ultra Scientific - Catalog IRM-008 and lot J408 – was used to check if the methodology used was appropriate for determination of metals in the sediment. Five tests were performed using standard synthetic sediment, which proved the effectiveness of the method.

Table 1. Rivers and corresponding sampling sites.

Sites	Water bodies	Sites	Water bodies
A1	Monjolinho river	A12	Espraiado stream
A8		A13	
A9		A14	
A10		A11	Sta. Maria Madalena stream
A19		A15	
A20		A16	Tijuco Preto stream
A21		A17	
A22		A18	
A2	Gregório stream	A23	Água Quente stream
A3		A24	
A4		A25	Laranja Azeda stream
A5			
A6		A26	Feijão river
A7			

Figure 1. Study area: city of São Carlos. Sites A25 and A26, not represented, are located southeast of the city.

2.1.3. Superficial water methodology

Physic chemistry parameters (pH, conductivity, turbidity, dissolved oxygen, temperature, TDS and ORP), were verified with a Horiba multiparameter probe. All products collected were analysed with an atomic absorption spectrophotometer Varian, AA240 FS (Fast Sequential). The blanks were treated in the same way as the samples, ie, they received the reagents and they were read in triplicate. The detection limits of the analyses of metals were calculated according to INMETRO (2009).

2.1.4. Climatological data

Data on monthly rainfall compared with the climatological normal (1961-1990) were obtained for the city of São Carlos from the Instituto Nacional de Meteorologia (INMET, 2008) (Figure 2).

2.1.5. Statistical analysis

The values of metals concentration from water and sediment were normalised. There were two Discriminant analyses to verify if there were significant differences between the data from the rainy season and dry season for water and sediment. To analyse the spatial and temporal distribution of metals in the water, Principal Components Analysis (PCA) was performed. The PCA and the Discriminant analyses were performed using the software PAST v.1.95.

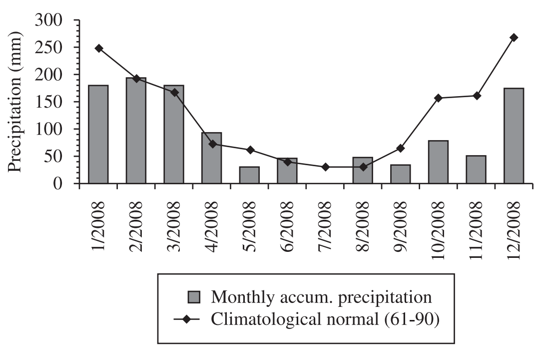

Figure 2. Accumulated precipitation x monthly climatological normal (1961-1990) for the municipality of São Carlos - SP, 2008. Source: INMET.

3. Results

3.1. Chemical water parameters

Table 2 presents the means, standard deviations and maximum and minimum values of chemical parameters of water conducted at sites for pH, conductivity (mS), dissolved oxygen (DO) (mg.L^{-1}) and redox potential (ORP) (mV).

3.2. Metals procedures

Table 3 presents the blank values and the detection limits of metal analysis in water and sediment.

3.3. Metals in surface water: rainy season

Metals found in water samples from São Carlos streams, in the collection conducted during the rainy season, are shown in Table 4, along with the limits established by Brazilian law for metals in water (Lgs. CONAMA 357/05, 2005).

It was found that the sites A19, A20, A21, A22, A23, A24, A25 and A26, have concentrations of cadmium, lead, copper and nickel above the permitted level for Class 3 waters and concentrations of cobalt and iron above the permitted level for Class 1 waters.

3.4. Metals in surface water: dry season

Metals found in water samples from streams in São Carlos, during the gathering held in the dry season, are shown in Table 5, together with the limits established by Brazilian law for metals in water (Lgs. CONAMA 357/05, 2005).

Cd values were above those provided for Class 1 waters in almost all sampling sites; the sites A21, A22, A23 and A24 presented the highest concentrations.

Pb presented values above the limits for Class 1 waters in A2, A4, A6, A13, A15, A16, A17, A18, A19, A20, A21, A22, A25 and A26.

Levels of iron above the limit for Class 1 were found in most sites; its highest concentration was found in A1.

Most of the sites presented above Ni level permitted for Class 3 waters, reaching their highest values in the sites A17, A19 and A21 and A22.

Copper levels were higher than those provided for Class 3 CONAMA in A6, A7 and A19.

3.5. Metals in sediment: the rainy and dry season

Metal concentrations found in sediment samples from São Carlos streams, in rainy and drought periods, can be

Table 2. Chemical parameters of water: average, maximum and minimum value in the two collection periods, rain and drought.

Parameter	Dry period			Rainfall period		
	Average	Minimum value	Maximum value	Average	Minimum value	Maximum value
pH	6.89	6.09	7.54	7.09	6.15	7.65
Condutivity (mS)	0.12	0.01	0.47	0.17	0	0.715
OD (mg.L^{-1})	8.27	7.2	9.6	5	0.73	9.77
ORP (mV)	163.16	14	380	94.23	12	250

Table 3. Blank values and deviation limits for water and sediment for the metal analysis

	Al	Cd	Pb	Zn	Cr	Co	Cu	Fe	Mn	Ni
Water ($mg.L^{-1}$)										
BV1w	–0.188	0.013	0.038	0.011	0.013	0.06	0.011	0.003	0.002	0.026
BV2w	–0.175	0.013	0.038	0.009	0.017	0.066	0.009	0.001	0.003	0.026
BV3w	–0.184	0.014	0.034	0.008	0.024	0.062	0.011	0.008	0.004	0.025
DL ($mg.L^{-1}$)	0.02	0.001	0.007	0.004	0.018	0.009	0.004	0.01	0.002	0.003
Sediment ($mg.L^{-1}$)										
BV1s	0.169	–0.001	0.106	0.014	0.006	0.007	0.001	0.174	0.002	0.017
BV2s	0.173	–0.002	0.081	0.012	0.002	0.002	0.000	0.203	0.002	0.03
BV3s	0.145	–0.002	0.096	0.013	0.003	0.013	0.000	0.179	–0.012	0.039
BV4s	0.151	–0.001	0.090	0.011	0.004	0.008	0.001	0.185	–0.02	0.033
BV5s	0.168	–0.002	0.080	0.013	0.000	0.017	0.001	0.243	0.002	0.029
BV6s	0.161	–0.002	0.054	0.013	0.001	0.006	0.000	0.195	0.056	0.036
DL ($mg.kg^{-1}$)	3.29	0.17	5.34	0.30	0.59	1.61	0.15	7.51	7.95	2.35

Table 4. Concentration of metals in the water during the rainy season ($mg.L^{-1}$).

	Al	Cd	Pb	Zn	Cr	Co	Cu	Fe	Mn	Ni
A1	>DL	>DL	>DL	0.007	>DL	>DL	>DL	>DL	0.004	>DL
A2	>DL	>DL	>DL	0.009	0.018	>DL	>DL	>DL	0.023	>DL
A3	>DL	>DL	>DL	0.012	>DL	>DL	0.004	0.287	0.034	>DL
A4	>DL	>DL	>DL	0.009	0.049	>DL	0.006	0.218	0.023	>DL
A5	>DL	>DL	>DL	0.008	>DL	>DL	0.005	0.094	0.014	>DL
A6	>DL	>DL	>DL	0.034	0.021	>DL	0.006	0.280	0.021	>DL
A7	>DL	>DL	>DL	>DL	0.020	>DL	0.006	0.239	0.023	>DL
A8	>DL	>DL	>DL	>DL	>DL	>DL	>DL	0.068	0.010	>DL
A9	>DL	>DL	>DL	>DL	0.018	>DL	0.005	0.048	0.008	>DL
A10	>DL	>DL	>DL	0.013	>DL	>DL	0.007	0.059	0.007	>DL
A11	>DL	>DL	>DL	0.034	>DL	>DL	0.006	0.026	0.008	>DL
A12	>DL	>DL	>DL	>DL	>DL	>DL	0.004	0.023	0.013	>DL
A13	>DL	>DL	>DL	>DL	>DL	>DL	0.006	0.024	>DL	>DL
A14	>DL	>DL	>DL	>DL	>DL	>DL	0.005	0.022	>DL	>DL
A15	>DL	>DL	>DL	0.023	>DL	>DL	0.007	0.015	>DL	>DL
A16	>DL	>DL	>DL	0.005	0.019	>DL	0.009*	>DL	0.014	>DL
A17	>DL	>DL	>DL	>DL	0.019	>DL	0.008	>DL	0.022	>DL
A18	>DL	>DL	>DL	>DL	0.018	>DL	0.008	>DL	0.018	>DL
A19	>DL	0.015+	0.167+	0.031	0.028	0.090*	0.021+	0.341*	0.020	0.064+
A20	>DL	0.018+	0.198+	0.065	0.040	0.111*	0.024+	0.493*	0.026	0.069+
A21	>DL	0.016+	0.200+	0.051	0.031	0.102*	0.019+	0.699*	0.182*	0.069+
A22	>DL	0.017+	0.205+	0.043	0.038	0.096*	0.022+	0.850*	0.058	0.061+
A23	>DL	0.018+	0.201+	0.017	0.044	0.099*	0.021+	0.359*	0.018	0.066+
A24	>DL	0.019+	0.226+	0.122	0.046	0.092*	0.026+	0.577*	0.069	0.061+
A25	>DL	0.016+	0.134+	0.021	0.018	0.075*	0.014+	0.639*	0.009	0.040+
A26	>DL	0.013+	0.142+	0.021	0.020	0.098*	0.015+	0.398*	0.006	0.047+
DL	0.020	0.001	0.007	0.004	0.018	0.009	0.004	0.010	0.002	0.003

DL = Detection Limit; *Values above CONAMA 357/05 Class 1 to superficial waters; + Values above CONAMA 357/05 Class 3 to superficial waters. Legislative limits (Lgs. CONAMA 357/05 - Rating 1-3) of permitted metal amount in freshwater: Al 0.1-0.2 $mg.L^{-1}$; Cd 0.001-0.01 $mg.L^{-1}$; Pb 0.01-0.033 $mg.L^{-1}$; Zn 0.18-5.0 $mg.L^{-1}$; Cr 0.05-0.05 $mg.L^{-1}$; Co 0.05-0.2 $mg.L^{-1}$; Cu 0.009-0.013 $mg.L^{-1}$; Fe 0.3-5.0 $mg.L^{-1}$; Mn 0.1-0.5 $mg.L^{-1}$; Ni 0.025-0.025 $mg.L^{-1}$. Class 1 - Water which may be intended for supply for human consumption after treatment simplified Class 3 - water which may be intended for supply for human consumption after conventional treatment or advanced.

Table 5. Concentration of metals in the water during the dry season (mg.L^{-1}).

	Al	Cd	Pb	Zn	Cr	Co	Cu	Fe	Mn	Ni
A1	>DL	0.001	>DL	0.022	>DL	0.010	>DL	3.039*	0.144*	0.020
A2	>DL	0.002*	0.016*	0.014	>DL	0.013	>DL	0.347*	0.112*	0.028+
A3	>DL	0.002*	>DL	0.027	>DL	0.015	0.004	0.503*	0.142*	0.028+
A4	>DL	0.002*	0.013*	0.038	>DL	0.019	0.006	0.262	0.146*	0.030+
A5	0.141*	0.001	0.010	0.075	>DL	0.011	0.005	0.421*	0.087	0.025
A6	0.160*	0.002*	0.036^{+}	0.412*	0.028	0.028	0.017+	0.283	0.098	0.036+
A7	>DL	0.001	0.010	0.029	0.019	0.015	0.014+	0.274	0.083	0.035+
A8	0.206^{+}	>DL	>DL	0.012	>DL	>DL	>DL	0.477*	0.043	0.009
A9	>DL	>DL	>DL	0.027	0.021	0.013	0.009	0.474*	0.104*	0.030+
A10	0.023	>DL	>DL	0.028	0.019	0.012	0.008	0.662*	0.100	0.034+
A11	>DL	>DL	>DL	0.017	>DL	>DL	>DL	0.293	0.035	0.014
A12	>DL	0.002*	>DL	0.020	0.018	0.017	0.005	0.432*	0.049	0.032+
A13	>DL	0.001	0.011*	0.013	>DL	>DL	>DL	0.089	0.006	0.021
A14	>DL	0.001	0.008	0.026	0.020	0.018	0.005	0.563*	0.023	0.034+
A15	0.115*	>DL	0.011*	0.019	>DL	>DL	>DL	0.062	0.003	0.014
A16	>DL	>DL	0.012*	0.015	>DL	0.011	0.005	0.104	0.053	0.024
A17	0.178*	0.002*	0.015*	0.022	0.025	0.024	0.008	0.120	0.065	0.038+
A18	0.035	0.001	0.011*	0.015	0.019	0.016	0.006	0.075	0.073	0.036+
A19	>DL	>DL	0.021*	0.232*	0.031	0.016	0.029+	0.449*	0.057	0.037+
A20	>DL	0.002*	0.017*	0.018	>DL	0.013	0.005	0.109	0.020	0.027+
A21	0.513^{+}	0.005*	0.012*	0.025	0.026	0.023	0.008	1.019*	0.227*	0.038+
A22	>DL	0.004*	0.015*	0.033	0.029	0.020	0.012*	0.792*	0.122*	0.044+
A23	0.429^{+}	0.003*	>DL	0.013	0.024	0.019	0.007	0.090	0.034	0.032+
A24	0.168*	0.003*	>DL	0.087	0.022	0.016	0.008	0.532*	0.082	0.032+
A25	>DL	0.002*	0.012*	0.013	>DL	0.013	>DL	0.540*	0.025	0.026+
A26	>DL	0.001	0.012*	0.013	>DL	0.013	>DL	0.348*	0.017	0.027+
DL	0.020	0.001	0.007	0.004	0.018	0.009	0.004	0.010	0.002	0.003

DL = Detection Limit; *Values above CONAMA 357/05 Class 1 to superficial waters; $^{+}$Values above CONAMA 357/05 Class 3 to superficial waters. Legislative limits (Lgs CONAMA 357/05 - Rating 1-3) of permitted metal amount in freshwater: Al 0.1-0.2 mg.L^{-1}; Cd 0.001-0.01 mg.L^{-1}; Pb 0.01-0.033 mg.L^{-1}; Zn 0.18-5.0 mg.L^{-1}; Cr 0.05-0.05 mg.L^{-1}; Co 0.05-0.2 mg.L^{-1}; Cu 0.009-0.013 mg.L^{-1}; Fe 0.3-5.0 mg.L^{-1}; Mn 0.1-0.5 mg.L^{-1}; Ni 0.025-0.025 mg.L^{-1}. Class 1 - Water which may be intended for supply for human consumption after treatment simplified Class 3 - water which may be intended for supply for human consumption after conventional treatment or advanced.

found in Tables 6 and 7, together with the limits established by Brazilian law for metal (Lgs. CONAMA 344/04, 2004).

Brazilian legislation does not provide a sediment maximum value for the metals Al, Co, Fe and Mn.

For Ni, the sites A1, A6, A7, A11, A14 and A20 in the dry season, showed concentrations above the level 1. In the rainy season, site A9 showed higher concentration than allowed for level 1, and A5 showed higher concentration than the permissible amount for level 2.

For Cu, the sites A1, A2, A6, A7, A11, A14, A18 and A20 in the dry season, showed concentrations above the level 1. In the rainy season, the sites A1, A8, A16 and A17 showed concentrations above level 1.

For Cr, the sites A1, A2, A14 and A20 in the dry season, showed concentrations above the level 1. Already in the rainy season, the sites A5 and A9 showed concentrations above level 1.

For Zn, only the point A20, in the dry season, has a concentration greater than that permitted for level 1.

3.6. Statistical analysis

The Discriminant analysis (Figure 3) performed for the data base of surface water shows significant differences between the two metal collections, rainy and drought, with p = 1.582E-21. Sediment was not significantly different between the collections of drought and rainy, with p = 0.7014.

The PCA analysis (Figure 4) revealed greater sites characterisation for the rainy season by Pb, Cd, Co, Cu and Cr, while in the dry season, the analysis showed further characterisation by the metals Al, Mn, Fe and Zn.

Table 6. Concentration of metals in the sediment during the rainy season ($mg.kg^{-1}$).

Sites	Al	Cd	Pb	Zn	Cr	Co	Cu	Fe	Mn	Ni
A1	11123.73	0.41	15.75	28.07	34.15	10.45	65.83*	1500.21	97.77	17.42
A2	12544.34	>DL	8.03	18.39	30.22	6.35	33.44	1467.13	101.69	10.29
A3	2799.26	>DL	>DL	34.12	19.99	>DL	6.23	1349.95	24.89	4.29
A4	3277.34	>DL	>DL	24.83	24.68	2.43	8.06	1414.17	46.43	11.41
A5	7685.32	>DL	7.33	58.95	76.88*	5.29	22.22	1436.69	85.58	43.04+
A6	3697.01	>DL	10.48	60.92	27.16	5.37	26.51	1448.33	94.31	7.62
A7	3505.16	>DL	6.42	63.24	16.49	2.90	20.46	1415.29	61.18	5.21
A8	8011.93	>DL	5.44	28.66	26.87	4.18	35.98*	1423.29	57.68	14.75
A9	13568.65	0.32	24.10	54.25	43.25*	11.52	28.44	1457.93	90.45	18.80*
A10	6391.35	0.18	14.54	31.39	23.80	7.66	14.97	1376.05	43.19	12.62
A11	2456.39	>DL	8.61	9.58	19.72	5.52	7.45	1344.23	19.32	9.03
A12	9012.72	0.19	18.32	30.25	20.33	6.76	12.88	1386.00	48.27	9.48
A13	5755.85	>DL	12.86	13.32	22.33	6.32	6.95	1412.30	31.29	8.77
A14	6419.05	>DL	12.47	14.97	17.71	7.69	6.96	1423.04	40.02	9.10
A15	4148.20	>DL	10.86	11.97	12.60	5.19	6.88	1275.80	>DL	6.75
A16	4405.36	>DL	20.95	50.73	25.88	12.07	63.35*	1348.03	75.50	13.83
A17	12033.96	0.21	28.29	105.71	26.69	9.19	79.61*	1414.08	93.96	16.50
A18	2777.68	>DL	13.75	30.30	23.48	6.94	17.96	1342.07	38.19	10.05
A19	7585.45	>DL	>DL	41.65	17.02	3.93	15.31	1431.70	76.19	4.90
A20	6621.15	>DL	>DL	50.61	19.75	4.32	16.17	1431.81	50.68	5.33
A21	1176.90	>DL	>DL	10.80	2.96	2.20	7.41	1320.67	40.26	>DL
A22	1467.67	>DL	>DL	23.73	9.12	2.55	8.91	1361.38	39.07	>DL
A23	702.74	>DL	>DL	3.89	4.10	>DL	2.91	1193.02	43.14	>DL
A24	907.86	>DL	>DL	3.20	1.89	>DL	2.74	1041.83	10.94	>DL
A25	2316.74	>DL	>DL	7.48	2.75	2.48	4.15	1361.04	71.52	>DL
A26	8956.23	>DL	>DL	6.45	0.83	>DL	2.34	10343.21	45.23	>DL
DL	3.29	0.17	5.34	0.30	0.59	1.61	0.15	7.51	7.95	2.35

DL = Detection Limit; *Values above CONAMA 344/04 Level 1 to sediments; + Values above CONAMA 344/04 Level 2 to sediments. Legislative limits (Lgs CONAMA 344/043- Rating 1-2) of permitted metal amount in sediment in freshwater: Cd 0.6-3.5 $mg.kg^{-1}$; Pb 35-91.3 $mg.kg^{-1}$; Zn 123-315 $mg.kg^{-1}$; Cr 37.3-90 $mg.kg^{-1}$; Cu 35.7-197 $mg.kg^{-1}$; Ni 18-35.9 $mg.kg^{-1}$. Level 1 - threshold below which provides a low probability of adverse effects to biota; Level 2 - threshold above which provides for a probable adverse effect on the biota.

4. Discussion

4.1. Chemical parameters of water

According to Calmano et al. (1993), the redox potential and pH affect the mobility of metals in sediment to the water column and the pH is the main mobilisation factor. Acid content of water and sediment in the environment lead to greater metal mobilisation (Chaillou et al., 2002). This mobility increases in oxygenated sediment. According to the data collected, despite high levels of oxygen, pH values did not promote mobilisation of metals in sediment to the water column. Therefore, the difference in concentrations of metals found in both periods and high levels of metals in water cannot be explained by the sediment-water metal mobilisation.

4.2. Metals in surface water and sediment

Sites A25 and A26, located on the Feijão river, show higher concentrations of Cd, Pb, Cu and Ni above the permitted level for Class 3 waters in the rainy season. This stream is responsible for supplying the municipalities of São Carlos and Itirapina – SP.

During the rainy season, the high contamination by cadmium, lead, copper and nickel can be related to the disposal of batteries in landfills located nearby bodies of water. These metals are considered "industrial metal", as they are found in low concentrations in nature, but used extensively in industrial processes (Järup, 2003).

Sites A19, A20 A21 and A22 located in downstream Monjolinho river, showed high levels of industrial metals Pb, Cd, Ni and Cu. However, sites upstream A5, A8, A9 and A10 whose environment is occupied by large urban

Table 7. Concentration of metals in the sediment during the dry season (mg.kg^{-1}).

Sites	Al	Cd	Pb	Zn	Cr	Co	Cu	Fe	Mn	Ni
A1	12103.70	>DL	>DL	34.81	46.95*	10.78	90.90*	2508.23	127.51	19.87*
A2	21598.26	>DL	>DL	22.37	43.39*	9.74	35.92*	2474.73	156.99	16.37
A3	6436.08	>DL	>DL	19.47	34.99	4.98	12.72	2330.92	52.47	9.51
A4	8439.46	>DL	7.36	63.23	30.21	7.02	18.70	2390.03	89.51	12.59
A5	9699.54	>DL	7.50	61.89	26.41	6.80	21.90	2343.18	60.19	11.09
A6	21432.26	>DL	13.46	110.97	29.19	12.68	47.58*	2489.99	134.75	22.45*
A7	22548.26	>DL	12.74	73.93	22.73	15.38	41.30*	2491.08	234.41	20.65*
A8	1710.36	>DL	>DL	3.81	15.43	5.34	5.62	2086.34	45.29	4.57
A9	8582.90	>DL	7.74	49.79	25.35	7.38	22.66	2234.50	29.67	10.91
A10	3721.94	>DL	>DL	20.25	27.97	6.40	15.08	2256.29	47.35	12.21
A11	28196.26	>DL	5.62	27.25	34.73	16.88	44.12*	2481.27	215.47	23.59*
A12	13027.36	>DL	20.02	23.85	28.67	9.48	14.86	2324.93	99.65	13.55
A13	3946.18	>DL	>DL	7.57	9.83	9.90	4.60	2260.92	275.53	10.05
A14	32728.26	>DL	26.58	63.57	53.61*	16.54	44.50*	2458.39	96.41	26.49*
A15	3536.96	>DL	>DL	>DL	14.09	7.32	3.88	1910.11	7.99	8.07
A16	1930.98	>DL	>DL	24.97	21.43	6.64	22.78	2202.37	37.95	10.35
A17	4495.58	>DL	8.22	65.43	21.03	6.78	33.54	2225.79	51.03	9.87
A18	4445.88	>DL	6.84	45.07	25.13	7.16	65.50*	2230.69	57.55	8.41
A19	3647.66	>DL	>DL	32.05	18.57	6.70	12.10	2208.36	30.35	8.35
A20	25508.26	>DL	15.72	190.65*	41.17*	17.50	55.38*	2454.58	175.03	25.79*
A21	5818.94	>DL	>DL	20.49	13.59	9.46	11.56	2208.90	72.37	8.43
A22	1252.60	>DL	>DL	17.97	15.79	5.90	7.72	2004.35	20.91	6.89
A23	2247.80	>DL	>DL	>DL	11.27	5.60	3.82	1964.86	28.27	5.15
A24	1485.28	>DL	>DL	4.97	12.25	4.86	5.22	1756.23	27.01	6.81
A25	5903.20	>DL	>DL	13.17	6.09	5.32	5.98	2373.41	264.71	5.83
A26	1015.62	>DL	>DL	9.40	2.54	2.25	3.23	1305.11	73.65	>DL
DL	3.29	0.17	5.34	0.30	0.59	1.61	0.15	7.51	7.95	2.35

DL = Detection Limit; *Values above CONAMA 344/04 Level 1 to sediments; $^{+}$Values above CONAMA 344/04 Level 2 to sediments. Legislative limits (Lgs CONAMA 344/043- Rating 1-2) of permitted metal amount in sediment in freshwater: Cd 0.6-3.5 mg.kg^{-1}; Pb 35-91.3 mg.kg^{-1}; Zn 123-315 mg.kg^{-1}; Cr 37.3-90 mg.kg^{-1}; Cu 35.7-197 mg.kg^{-1}; Ni 18-35.9 mg.kg^{-1}. Level 1 - threshold below which provides a low probability of adverse effects to biota; Level 2 - threshold above which provides for a probable adverse effect on the biota.

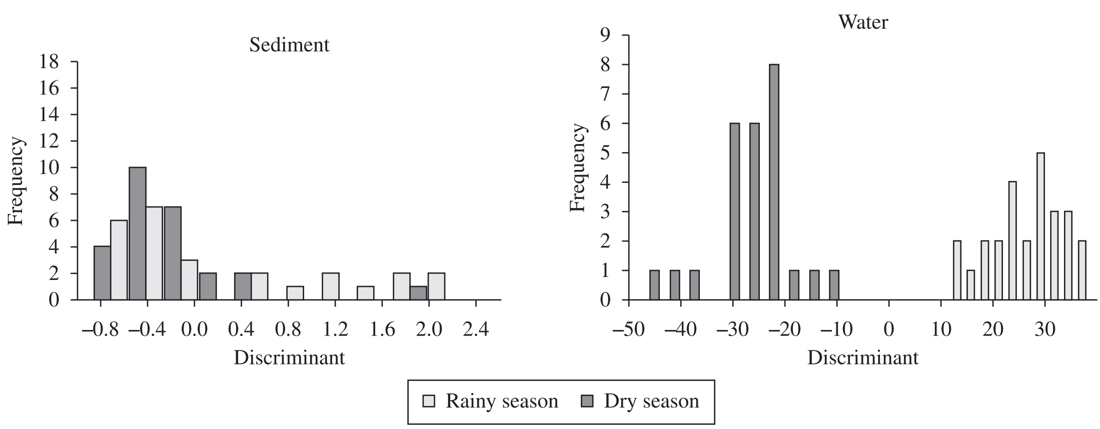

Figure 3. Discriminant analyses performed on water and sediment metals for rainy and dry season.

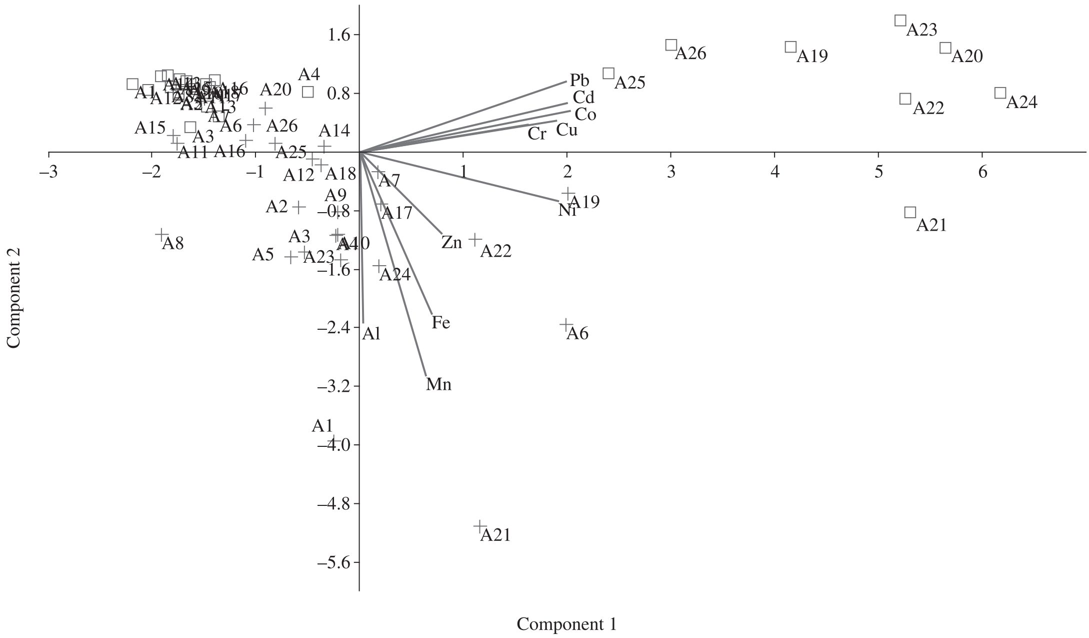

Figure 4. Principal Components Analysis for metals in water for the two collections □ = Rainy; + = Dry. Percentage of explanation = 69.28% for the first two axes.

density, did not show high levels of these metals. Thus the contamination of metals downstream Monjolinho river is not correlated with the presence of industries.

In the rainy season, there is a high leaching of the surrounding bodies of water. This causes the carrying of large quantities of particles and pollutants into rivers and streams, characterising the contribution of diffuse sources. Rietzler et al. (2001) related the elevated concentrations of metals recorded during the wet season to the landfill dump of the city and rain drainage. In addition, the riparian absence in streams is an aggravating factor for diffuse pollutants, as this vegetation is the main barrier to the uptake of leaching into water bodies.

São Carlos has a landfill located in the watershed the Feijão river. The landfill, in use between 1979 and 1996, has a high potential for contamination of groundwater, soil and surface water from its surroundings as it offers inadequate isolation of leached (Velozo, 2006). This landfill can be correlated with heavy metal contamination of industrial origin in the rainy season in sites of the Feijão river.

The city also has a dump still in use, located next to the Água Quente stream. This dump does not provide adequate isolation structure, characterising a high potential for contamination (Dimitriou et al., 2008) and may be correlated with high levels of heavy metals in the rainy season in sites A21, A23 and A24.

Kruskal-Wallis test between the concentrations of zinc at all sampling sites for periods of drought (average 0.0486) and rainy (average 0.0201), showed statistically significant differences ($p = 0.01126$). The highest concentration found in the dry season is probably due to fires to harvest cane sugar. High levels of zinc are found in this culture, both on the ground in plant biomass due to application of zinc sulfate ($ZnSO_4$), widely used fertilizer. The fires, common practice in the dry season in the study area, produce ash with high concentrations of zinc, which reaches the water bodies (Ziolli, 1995).

Discriminant analysis showed no significant seasonal differences related to the metallic composition of the sediment during the study period. This is due to the stochastic nature of the sediment, where changes are perceived over a wider range of time. Therefore, sediment can act as an environmental indicator for large time intervals. By contrast, water has an ephemeral nature, since specific changes in space-time are reflected in its composition. Thus, the seasonal differences in the influence of metal behaviour on the environment are perceived in the water by the Discriminant analysis.

The metal punctual contamination (industrial waste, for example) is more evident in the dry season. This type of contamination provides a constant supply of metals in water. Thus, during rainy periods, the levels of metals in water bodies should be less than metal levels in periods of drought, due to decreased concentration of metals by high flows of rivers and streams. However, contamination by Pb, Cd, Co, Cu and Cr, from industrial processes occurred mainly in the rainy season, as demonstrated by the PCA.

Thus, this contamination may have originated from diffuse sources via leaching associated with landfills; because these landfills are close to the most impacted regions (Feijão river and Água Quente stream).

The origin of high concentrations of metals Fe, Al and Mn, present in the dry season, is from natural sources, since this metal composition is characteristic of the morphology of the savanna soil in this sub-basin (Queiroz-Neto, 1982).

5. Conclusions

São Carlos basin has high levels of industrial metal contamination in water bodies during the rainy season and Zn contamination in the water during the dry season. So, the levels and types of metals found in water are related to seasonality.

Contamination comes from diffuse sources. Thus, there was no evidence that there is disposal of industrial metal effluents directly into the water.

The high level of Zn found in the dry season is probably due to the burning of sugar cane, which release high levels of metal into the environment.

A diffuse source of contamination during the rainy season was probably due to products such as batteries, fluorescent lamps and chrome, whose presence in landfills can contaminate not only the soil but also aquifers and springs supply in the region. These landfills are located near sources of supply (Feijão river) and poorer neighbourhoods with high population density (Água Quente stream), presenting a potential risk of exposure for the population to these contaminated waters.

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