Metal contamination in benthic macroinvertebrates in a sub-basin in the southeast of Brazil

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(With 7 figures)

Abstract

Benthic macroinvertebrates have many useful properties that make possible the use of these organisms as sentinel in biomonitoring programmes in freshwater. Combined with the characteristics of the water and sediment, benthic macroinvertebrates are potential indicators of environmental quality. Thus, the spatial occurrence of potentially toxic metals (Al, Zn, Cr, Co, Cu, Fe, Mn and Ni) in the water, sediment and benthic macroinvertebrates samples were investigated in a sub-basin in the southeast of Brazil in the city of São Carlos, São Paulo state, with the aim of verifying the metals and environment interaction with benthic communities regarding bioaccumulation. Hypothetically, there can be contamination by metals in the aquatic environment in the city due to lack of industrial effluent treatment. All samples were analysed by the USEPA adapted method and processed in an atomic absorption spectrophotometer. The sub-basin studied is contaminated by toxic metals in superficial water, sediment and benthic macroinvertebrates. The Bioaccumulation Factor showed a tendency for metal bioaccumulation by the benthic organisms for almost all the metal species. The results show a potential human and ecosystem health risk, contributing to metal contamination studies in aquatic environments in urban areas.

Keywords: heavy metal, benthic macroinvertebrates, water pollution, sediment pollution.

Estudo da contaminação por metal em macroinvertebrados bentônicos em uma sub-bacia do sudeste do Brasil

Resumo

Os organismos bentônicos têm muitas propriedades úteis que os fazem organismos sentinelas em programas de biomonitoramento em ecossistemas de água doce. Analisando em conjunto com as características da água e do sedimento, são potenciais indicadores da qualidade ambiental. Neste contexto, a ocorrência espacial de metais pesados (Al, Zn, Cr, Co, Cu, Fe, Mn e Ni) na água, sedimentos e amostras de macroinvertebrados bentônicos foi investigada em uma sub-bacia no sudeste do Brasil, na cidade de São Carlos, SP, com o objetivo de verificar a interação dos metais do ambiente com a comunidade bentônica quanto à bioacumulação. Por hipótese, admite-se que haja contaminação por metais nos ambientes aquáticos do município devido à ausência de tratamento de efluentes industriais. Todas as amostras foram analisadas pelo método USEPA adaptado e processado por espectrofotômetro de absorção atômica. A bacia estudada apresenta contaminação por metais tóxicos em águas superficiais, sedimentos e macroinvertebrados bentônicos. O Fator de Bioacumulação mostrou uma tendência para a bioacumulação de metais por organismos bentônicos para quase todas as espécies de metal. Os resultados demonstram um potencial risco à saúde humana e ao ecossistema, contribuindo com o estudo de contaminação por metais em ambientes aquáticos de áreas urbanas.

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

1. Introduction

Throughout the twentieth century, aquatic ecosystems have been suffering incremental impact due to their inadequate use for different purposes (Muniz et al., 2004). Contaminants can enter freshwaters via several key routes, especially direct by pipeline discharges from cities, atmospheric deposition, and nonpoint source runoff from land. Urban development, agriculture and industrialisation have promoted a continuous increase in metal contamination in aquatic ecosystems (Mertz, 1986).

Metals in natural waters can play an important role in the biological function of many organisms. Some metals are considered essential, such as Fe, Al, Zn, while others, such as Cr and Ni, can present a high toxicity level to living organisms. However, even essential metals can be toxic if high in concentration (Templeton et al., 2000).

Pollutants, when introduced into an aquatic system, can be greatly modified by interaction with natural variables of water, and they can be toxic just by their presence or by degradation processes (Pettersen et al., 1993). Pollutants can release compounds, which assimilated by organisms, can interfere in physiologic processes, such as reproductive aspects, survival and consequently, change the population structure and the community structure (Boudou and Ribeyre, 1989). Metals accumulated in benthic organisms can also be bioconcentrated in food webs (Klavinš et al., 1998).

Benthic organisms may be directly and/or indirectly impacted by metals in water (Kiffney and Clements, 1996), substratum (Chapman et al., 1998), and food resources (Hare, 1992; Kiffney and Clements, 1993; Farag et al., 1998). Direct toxic effects of metals reduce diversity and abundance of benthic invertebrates (Clements, 1994). Indirect effects include modifications of species interactions (Clements, 1999) and reductions in food quality (Carlisle, 2000).

The quantification and identification of environmental consequences of a particular pollutant are difficult, even when found in high concentrations and for a long period of exposure. Thus, benthic organisms have many useful properties that make possible the utilisation of these organisms as sentinels in biomonitoring programmes in freshwater and may indicate the implications of this pollutant for the environment (Lorenzi et al., 2008). Jara (2002) noted that stocks of fish and invertebrates found in the waters of a particular river system spend most of their life there, combining the characteristics of the water and sediment and thus they are potential indicators of environmental quality.

In recent years, many studies have been developed in concentrations of metals in aquatic macroinvertebrate populations through the establishment of bioindicators (Moreno and Callisto, 2006; Santoro et al., 2008; Corbi et al., 2008). This approach reflects a new trend in conservation worldwide, because it uses a methodology that integrates low cost and high efficiency and accuracy (Phillips and Rainbow, 1993). These populations summarise the recent history of their living environment, reflecting the effects of different environmental stressors.

In the region of São Carlos, some studies have been conducted to evaluate the environmental conditions of lotic systems, for example, Sé (1992), Rios (1993), Santos (1993), and Teixeira (1993). Specifically for the Monjolinho river basin, several studies have been conducted on various aspects, including those developed by Povinelli (1972), Gomes (1981), Salami (1996) and Peláez-Rodríguez (2001). Corbi et al. (2006, 2008) characterised metals in streams and aquatic biota near sugarcane cultures. However, there is a lack of studies on metals in urban area streams. Hypothetically, there can be contamination by metals in the aquatic environment in the city due to the municipality having a developed industrial sector around bodies of water and a lack of industrial effluent treatment.

Given the importance of metals as pollutants of aquatic ecosystems and the absence of behavioural studies of this pollutant in organisms in the watershed from São Carlos, Brazil, the aim of this study was to determine potentially toxics metals (Al, Zn, Cr, Co, Cu, Fe, Mn and Ni) concentrations in the water, sediments and benthic macroinvertebrates and to determine the bioaccumulation factors in the organisms.

2. Material and Methods

2.1. Study area

The municipality of São Carlos is located in central São Paulo state, between coordinates 47° 30' and 48° 30' Longitude and 21° 30' and 22° 30' Latitude, covering an area of 1,140.90 km^2 (Oliveira, 1996). The city has a population of about 219,000 inhabitants, with 93.6% living in the urban area. The climate is classified as 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 lot of drainage systems that drain into the Monjolinho River.

2.2. Sampling design

Samples were collected in September 2008 (dry season) in six sites of the city of São Carlos (SP, Brazil), in urban areas, for water, sediment and benthic macroinvertebrates (Figure 1). The samples were collected in the following bodies of water: Espraiado stream, Gregório stream, Água Quente stream, Maria Madalena stream and Monjolinho River.

2.3. Benthic macroinvertebrates sampling

Macroinvertebrates were collected using Surber sampler of 30 × 30 cm, 500 µm, in the selected sites. The samples were stored in refrigeration for live sorting. In the laboratory, the samples were then depurated for 48 hours, sorted and lyophilised with dry weight of 2 g per sample. For metal quantification analysis, USEPA 3050B (1998)

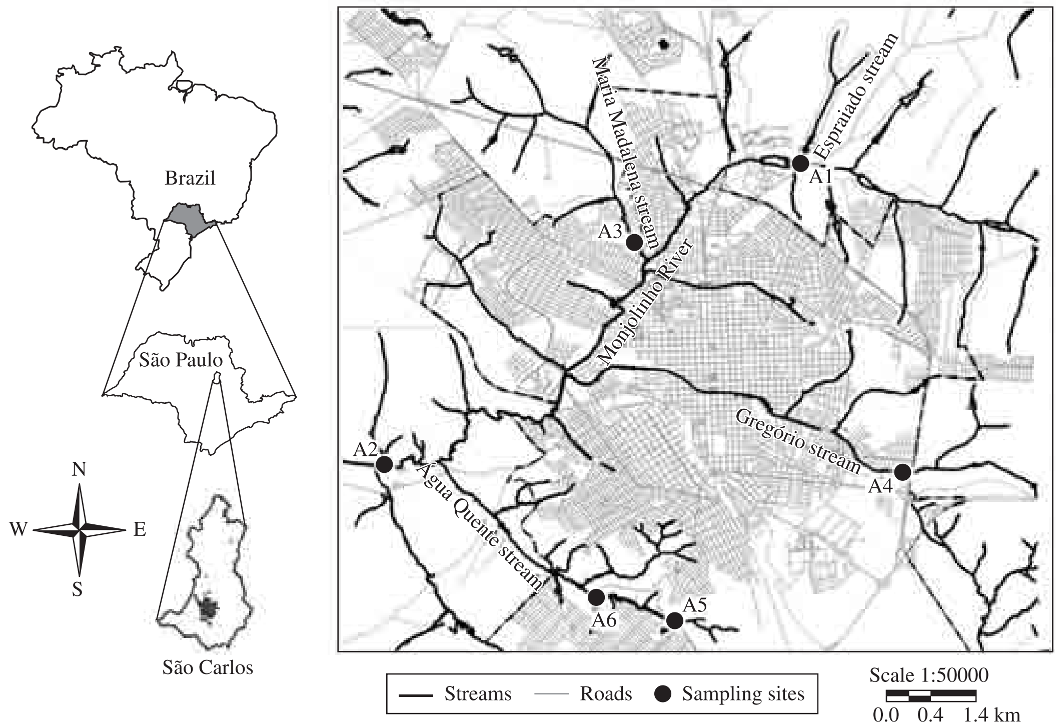

Figure 1. Study area: city of São Carlos.

methods, modified accordingly, were used. This adaptation consists of the use of 2 g of dry weight for each sample.

2.4. Analysis of sediment and water sampling

The sediment was collected with the aid of plastic collectors and stored at 4 °C. The content of metals in sediment samples was assessed according to USEPA 3050B (1998). The water was collected in acid cleaned plastic bottles of 500 mL and stored at 4 °C. In the laboratory, samples were filtered in Whatman paper Nº 41, being collected quantitatively in flasks of 100 mL.

All samples were analysed with an atomic absorption spectrophotometer Varian, AA240 FS (Fast Sequential).

2.5. Data analysis

Simpson Diversity Index was performed on benthic macroinvertebrates family data.

The ability of benthic macroinvertebrates to accumulate pollutants was quantified through the bioaccumulation factors (BAF) performed by Klavinš et al. (1998) (Equation 1):

$$BAF = \frac{M_{TISSUE}}{M_{SED}} \quad (1)$$

where M_{TISSUE} is the metal concentrations in the tissues of macroinvertebrates and M_{SED} is the metal amount in the sediment.

Bioaccumulation is recognised when the concentrations of metals in the organisms are higher than the concentrations of metals in the sediment. Thus, for values ≥ 1, bioaccumulation is considered.

3. Results

3.1. Benthic macroinvertebrate community structure

A total of nine families of benthic macroinvertebrates were identified according to Costa et al. (2006), distributed among the six sites: Baetidae, Hydrobiosidae, Libellulidae, Gomphidae, Ceratopogonidae, Chironomidae, Elmidae, Glossiphoniidae and Tubificidae were found. Richness/relative abundance and the Simpson Diversity Index of the benthic macroinvertebrate families are shown in Figures 2 and 3 respectively.

Sites A2 and A6 presented lowest richness among the sites collected. Sites A1 and A5 presented the highest richness. Sites A2, A3 and A6 presented lower diversity than A1, A4 and A5. The families with greatest abundance were Chironomidae and Tubificidae, whose high frequency is indicative of ecosystem deterioration.

3.2. Chemical water variables

Table 1 presents the values of chemical variables of water at the sampled sites.

3.3. Metals analysis

Table 2 presents the blank values and the detection limits of metal analysis in water, sediment and macroinvertebrates.

3.4. Metals in surface water

Metal concentrations in water samples from São Carlos streams are shown in Figure 4. Sites A2, A5 and A6 presented the highest concentrations of metals in water. Sites A3 and A4 had lower concentrations of metals. The metal Ni showed concentrations above the limit established for Brazilian waters (CONAMA, 2005).

3.5. Metals in sediment

Metals found in sediment samples from São Carlos streams are shown in Figure 5. Sites A1 and A3 presented the highest metal concentration among the sampling sites.

3.6. Metals in organisms

Metals found in benthic macroinvertebrate samples from São Carlos streams are shown in Figure 6. Benthic macroinvertebrates showed high levels of metals in their tissues, especially for the metals zinc, chromium and nickel.

3.7. Bioaccumulation Factors (BAF)

Bioaccumulation Factors for benthic macroinvertebrate samples from São Carlos streams are shown in Figure 7.

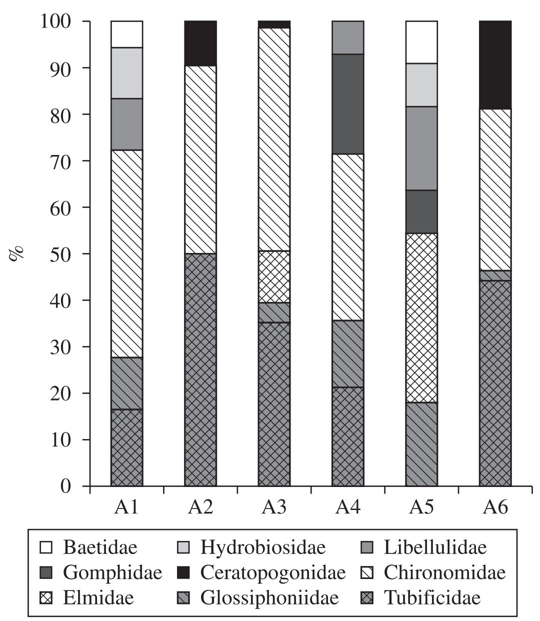

Figure 2. Richness/relative abundance (%) of benthic macroinvertebrates family in the six sampling sites.

Bioaccumulation was verified in all sites. The main accumulation rates occurred in A2, A5 and A6.

4. Discussion

According to Calmano et al. (1993), redox potential affects the mobility of metals in sediment to the water column with pH being the main mobilization factor. Acid water and sediment pH leads to greater metal mobilization (Chaillou et al, 2002). According to the data collected (Table 1), pH values did not promote the mobilisation of metals in the water column sediment since the pH was generally neutral. In addition, the high levels of oxygen in the water support this. Therefore, the high levels of metals in the water cannot be explained by the sediment-water metal mobilisation.

São Carlos watershed is contaminated by toxic metals, mainly related with Cr, Ni, and Zn (Figures 4 and 5). High concentrations of iron, manganese and aluminium are associated with the matrix composition of the sediment (Peláez-Rodríguez, 2001). However, these metals, also found in high concentrations in biota, did not represent high toxicity (Mertz, 1986).

Chromium, nickel and zinc were found in high concentrations in biota (Figure 6). Due to their high toxicity, these metals represent a risk to the ecosystem. Kiffney and Clements (1994) observed significant changes in benthic macroinvertebrate communities when exposed to Cu, and Zn at critical concentrations. Sites A2, A3 and A6 presented the lowest richness and diversity (Figures 2 and 3) among

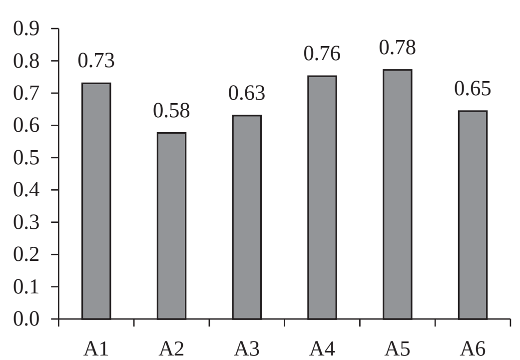

Figure 3. Simpson Diversity Index of the six sampling sites.

Table 1. Chemical variables of water.

Sites	pH	Conductivity (mS)	OD (mg.L^{-1})	ORP (mV)
A1	6.67	0.038	7.3	319
A2	7.70	0.193	7.3	148
A3	6.78	0.030	9.2	208
A4	6.43	0.039	7.9	106
A5	6.72	0.021	9.6	57
A6	6.85	0.331	8.8	14

Table 2. Blank values and deviation limits for water, sediment and benthic macroinvertebrates for the metal analysis.

	Water (mg.L^{-1})							
	Al	**Mn**	**Ni**	**Zn**	**Cr**	**Co**	**Cu**	**Fe**
BV1w	-0.188	0.002	0.026	0.011	0.013	0.06	0.011	0.003
BV2w	-0.175	0.003	0.026	0.009	0.017	0.066	0.009	0.001
BV3w	-0.184	0.004	0.025	0.008	0.024	0.062	0.011	0.008
DL (mg.L^{-1})	**0.02**	**0.002**	**0.003**	**0.004**	**0.018**	**0.009**	**0.004**	**0.01**
	Sediment and benthic macroinvertebrates (mg.L^{-1})							
BV1s	0.169	0.002	0.017	0.014	0.006	0.007	0.001	0.174
BV2s	0.173	0.002	0.03	0.012	0.002	0.002	0.000	0.203
BV3s	0.145	-0.012	0.039	0.013	0.003	0.013	0.000	0.179
BV4s	0.151	-0.02	0.033	0.011	0.004	0.008	0.001	0.185
BV5s	0.168	0.002	0.029	0.013	0.000	0.017	0.001	0.243
BV6s	0.161	0.056	0.036	0.013	0.001	0.006	0.000	0.195
DL (mg.kg^{-1})	**3.288**	**7.952**	**2.349**	**0.303**	**0.591**	**1.612**	**0.151**	**7.513**

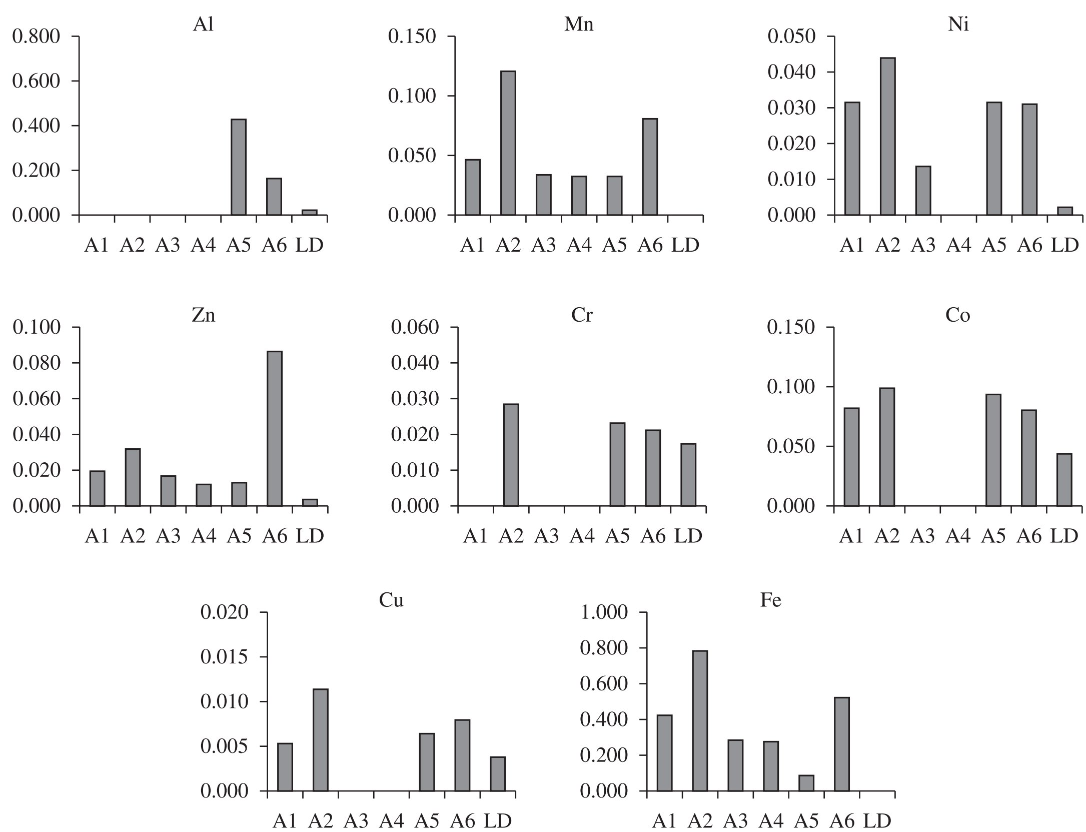

Figure 4. Metal concentration determined in water (mg.L^{-1}) from the six sampling sites.

the sampled points. This may be associated with high concentrations of Ni and Cu in water samples observed at sites A2 and A6 and high sediment concentration of Zn observed at site A3. According to Angelotti-Netto et al. (2004), chromium, nickel and zinc are metals found in high concentrations in fertilisers used in agricultural crops, which is an intensive practice in the study area. These metals are also widely used in industrial processes and products present at the city, as metal coatings, industrial textiles, industrial technology and metallurgy.

Zn was found in high concentrations in organisms and sediment. This can be attributed to the high zinc

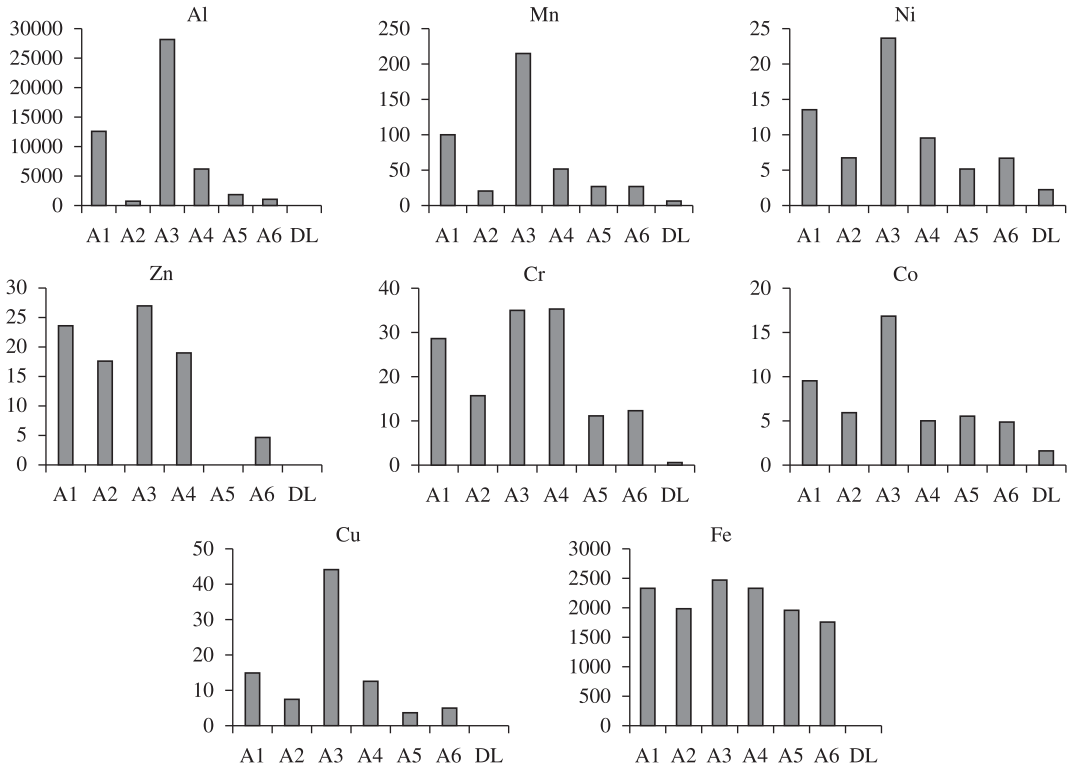

Figure 5. Metal concentration determined in sediment (mg.kg^{-1}) at the six sampling sites.

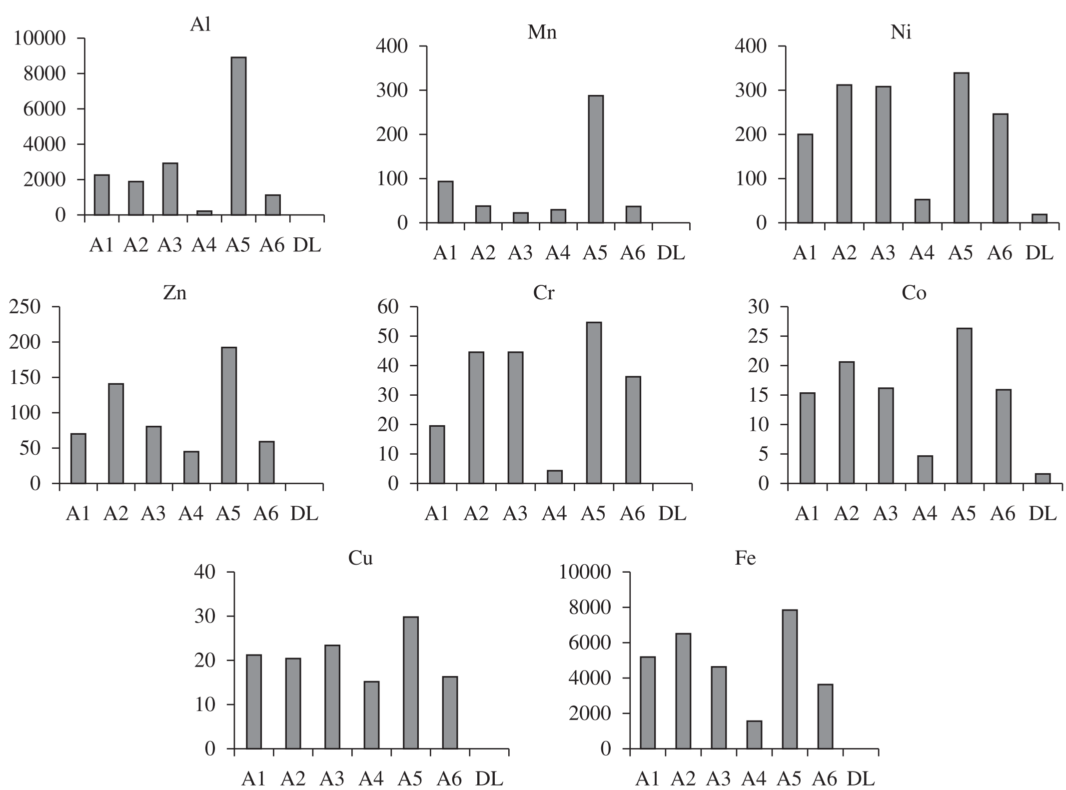

Figure 6. Metal concentration in benthic macroinvertebrate tissues (mg.kg^{-1}) from the six sampling sites.

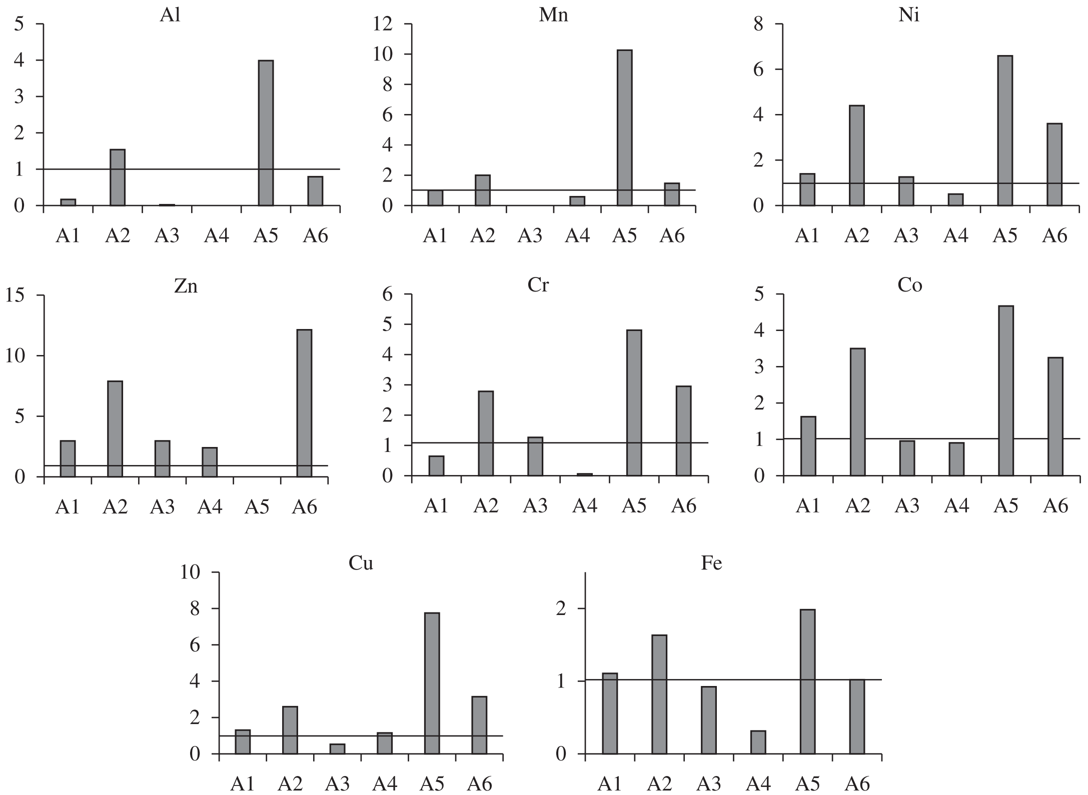

Figure 7. Bioacumulation Factor (BAF) for the six sampling sites. The solid line represents the limits of bioaccumulation.

concentrations in sugar cane cultures, both on the ground and plant biomass, due to application of zinc sulfate ($ZnSO_4$), widely used as fertiliser. Setting fire to land, a common practice in the dry season in São Paulo state, produces ash with high concentrations of zinc and due to the rainfall and wind action, the zinc contained in ashes reaches the water bodies (Ziolli et al., 1995).

Site A2 had the highest concentrations of metals in water. This can be attributed to its location in a region of Monjolinho River confluence of tributaries. Thus, any contribution of pollutant upstream converges to this point, characterising the high levels of metals in water. Moreover, the sediment at this site presented one of the lowest metal concentrations among the sampling sites. This can be explained by extreme turbulence of the water in this stretch of Monjolinho River that produces a large oxygenation of sediment per revolution, providing greater flow of these metals to the water column (Calmano et al., 1993). This also contributes to the high levels of metals found in water from this site.

Organisms showed evidence of bioaccumulation for all metals analysed, but at different rates. According to the values of BAF (Figure 7), the metal concentrations in organisms exceeded the concentrations of metals found in water and sediment of the corresponding sites, indicating bioaccumulation in this ecosystem (Klavinš et al. 1998).

There was no consistent relationship between the physical and chemical variables of water, metals in water and metals in the sediment with Bioaccumulation Factors presented. Probably, the patterns of accumulation are associated with complex relationships of the environment.

The high concentration of metals in water, sediment and organisms increases vulnerability to human health by this contamination and bioaccumulation. This vulnerability resulting from heavy metal contamination may be the result of two routes: contamination of drinking water due to deficient treatment, exposing the population to the ingestion of metal above tolerable doses, or ingestion through the food web by eating fish. The Espraiado stream, which showed levels of nickel in water above Brazilian law limits, is responsible for the supply of water to 50 thousand inhabitants in the municipality of São Carlos.

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