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Influence of the Rainfall Regime on the Mobility of Zn, Cd, Ni, Cu, Mn and Fe in the Surface Sediments of the Contas River Located in the Brazilian Semi-Arid Region

José S. dos Santos,* Marcio J. S. dos Santos and Maria L. P. dos Santos

Departamento de Ciências Naturais, Universidade Estadual do Sudoeste da Bahia,
Estrada do Bem Querer km 4, CP 95, 45083-900 Vitória da Conquista-BA, Brazil

Neste estudo foram avaliadas as influências do regime de chuva e do uso do solo na mobilidade de Zn, Cd, Ni, Cu, Mn e Fe no sedimento do Rio de Contas (Estado da Bahia, Brasil), com base no método de fracionamento utilizando a extração sequencial em três etapas. O estudo foi realizado no curso médio do Rio de Contas, em uma área que engloba o perímetro urbano e parte da zona rural da cidade de Jequié, influenciada pelas atividades agrícola, urbana e industrial. As determinações dos metais foram realizadas por espectrometria de absorção atômica por chama (FAAS). Os resultados deste estudo mostraram que as concentrações dos metais nas frações solúveis dos sedimentos estão diretamente associadas aos índices pluviométricos ocorridos na região. O estudo indica também que, dos elementos avaliados, o Zn, Cu, Cd e Ni apresentam maiores enriquecimentos no sedimento dentro do perímetro urbano.

In this study, the influences of the rainfall regimes and of the land use in the mobility of Zn, Cd, Ni, Cu, Mn and Fe in the surface sediment of the Contas River (Bahia State, Brazil) was evaluated with basis on the fractionation method that uses a three-step sequential extraction. The study was conducted in the middle of the Contas River, in an area that encompasses the urban perimeter and part of the rural zone of Jequié City that is influenced by agricultural, urban and industrial activities. The determinations of metals were conducted by flame atomic absorption spectrometry (FAAS). The result obtained from this study indicates that the concentrations of the metals in the soluble fractions of the sediments are directly associated with rainfall indices in the region. The study also indicated that the metals Zn, Cu, Cd and Ni exhibit higher concentrations in the sediments within the city.

Keywords: toxic element, availability of metals, sediment samples, urban zone

Introduction

Pollution sources for rivers and streams that run through urban and semi-urban areas are associated with the type and use of soil, and each pollutant that reaches natural water sources exhibits its own characteristics. Domestic sewage is composed of biodegradable organic compounds, nutrients and bacteria. In addition, industries release an even wider range of contaminants that are related to the types of raw materials and processes used.[1-5]

In addition to point sources, there are also urban and agricultural surface runoffs from diffuse sources. Urban surface runoff contains all of the pollutants that deposit on the soil surface as a result of urban activities, whereas agricultural surface runoff exhibits characteristics that are influenced by the agricultural practices used in each region. The composition of this runoff varies according to the time of year in which the soil is prepared for planting, the time of harvest and the processes by which fertilizers and pesticides are applied.[6-10]

River sediments are important compartments for the accumulation or release of metals to aquatic systems because they exhibit a high capacity for the retention and accumulation of trace elements released into the water column. As a result, studies of metals in these compartments are relevant to the assessment of pollution and contamination of water resources. The metals retained in sediments can return to the water column because of changes in their physicochemical properties (temperature, pH, alkalinity and redox potential) or through biological and

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*e-mail: zesoares@uesb.edu.br

microbiological activities. The release of these elements may cause undesirable changes in the water quality.[11-15]

One of the tools used to evaluate the behavior of trace metals in river sediments is the sequential extraction method.[16] Fractionation by sequential extraction provides valuable information regarding the relationship between metals and sediments. In this procedure, the sample is treated with a succession of extraction reagents with the specific intention of dissolving the different phases (or fractions) of sediment and thereby allowing the determination of the associated metals. The concentrations of metals determined in each of the extractions can provide information on the origin, mode of occurrence, biological and physicochemical availabilities, mobilization and transport of the metal.[17-28]

The Contas River (Bahia State, Brazil) bisects the Jequié City from West to East and provides perennial drainage of great regional importance. In the early 1970s, the Pedras Dam was constructed upstream of the urban perimeter of Jequié. This dam formed a large lake, whose waters are used for irrigation, agriculture and recreation as well as for a public water supply.[29]

Because of the typical climate of the semi-arid region, the city is included in the "Brazil's Drought Polygon", which is composed of the region subjected to frequent periods of prolonged drought. Rainfall predominance occurs during the summer rainy season (November/December/January), with peaks in the months from December to January and a dry period in the winter (June/July/August).

The purpose of the present study is to assess (*i*) the distribution of Zn, Cd, Ni, Cu, Mn and Fe in the surface sediment of the urban and semi-urban flows of the Contas River in Jequié City, which is influenced by agricultural, urban and industrial activities, and (*ii*) the influence of rainfall regimes on the mobility of metals in the sediment through a fractionation method that uses a three-step sequential extraction.

Experimental

Description of the study area

The study was conducted in the middle of the Contas River in an area that encompasses the urban perimeter and part of the rural zone of Jequié City, which is located in the Southwest region of Bahia State (Brazil). The region is located at the boundary between the Caatinga and the Atlantic Forest and is defined by the following geographical coordinates: (13°51'51" South latitude), (40°04'54" West longitude) (see Figure S1 in the Supplementary Information section).

Sampling

The sampling sites of sediments (as shown in Figure 1) were distributed to obtain a better strategy for studying the dynamics of the retention and mobilization of metals in the system based on the geomorphological aspects of the water bodies.

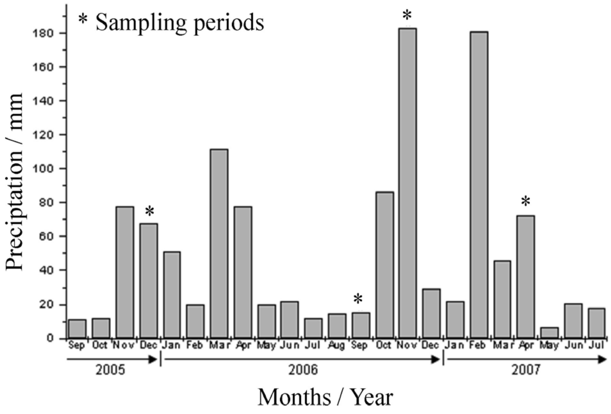

Figure 1. Average monthly distribution of rainfall in the region during the sampling period.

Points P1 and P2 are located in the main body and the spillway, respectively, of the Pedras Reservoir. Points P3, P4 and P5 along the Contas River were selected to evaluate the variations in the metal concentrations along the river that were caused by the different mobilities of the chemical species in the dissolved, sedimented or suspended phases along the stretch between the Pedras Reservoir and the perimeter of the Jequié City. Point P6 is located approximately 6 km downstream of the urban area of Jequié. Each of the sampling sites was georeferenced based on a global positioning system (GPS).

The sampling of sediment samples from the river bottom was performed in accordance with the dates of the annual rainfall distribution. The sampling was performed in the rainy season (December 2005), later in the dry season (September 2006), at the beginning of the rainy season (November 2006) and at the end of the rainy season (April 2007).

The sediments were collected according to Branco *et al.*[30] in accordance with the official protocols Guide for Collection and Preservation of Water Samples from the Environmental Control Agency of São Paulo State (CETESB, Brazil)[31] and Standard Methods for the Examination of Water and Wastewater from American Public Health Association (APHA, AWWA and WEF).[32] The samples were collected 1.5-2.0 m from the riverbank at an average depth of 2 m using a PVC collector measuring 50 mm in diameter that was constructed in our laboratory.

Soon after the collection, the samples were placed in plastic bags and immediately frozen and transported under refrigeration for drying and sieving. In the sieving process, a 63 µm nylon sieve was used because many studies have indicated that higher concentrations of metals occur in the fine sediment fractions.[28,29]

Meteorological conditions during the collection period

Because the rainfall regime exhibits a significant influence on the level and quality of rivers and reservoirs, it is important to report meteorological data for the region during the collection period.[25] Figure 1 shows the average monthly distribution of rainfall in the region during the sampling period.

Climatologically, the month of November is the beginning of the rainy season in the Southwest region of Bahia State. In November 2005, the precipitation total amount approximately 78 mm in the study area. In December 2005, the period in which the first sample was taken, the total rainfall recorded was 68 mm.

In May 2006, a drought in the region occurred and the average rainfall was of only 20 mm. Between the months of June and August (dry season), the average rainfall remained constant at approximately 15 mm. The drought continued into September 2006, the period in which the second sample was taken, and the total rainfall recorded was 15 mm.

In 2006, the rainy season began in October, a period in which the recorded precipitation was approximately 86.7 mm. In November 2006, the month in which the third sample was taken, the precipitation in the region was extremely high, totaling 182.7 mm of rain. The Pedras Reservoir showed an increase in volume when compared to previous months.

February 2007 was the period with one of the greatest rainfall in the region, with a total recorded of 180.9 mm. This rainfall, when summed with the precipitations recorded in the months of March and April, totaled 320 mm of rain in the quarter, which caused a major flooding in the region. In April 2007, when the fourth sample was taken, a total rainfall of approximately 72.7 mm was recorded for the region.

Preparation of the sediment samples

After plant material and small rocks were removed from the sediment samples, the samples were dried at 60 °C, gently crushed and homogenized. Because of the affinity of metals for the finer sediment fraction, samples were sieved to a particle size of 63 µm. A selective extraction procedure was then applied to evaluate the availability of the metals.

Because of the environmental importance, extractions of metals in the soluble, available and residual fractions were performed on the collected sediment samples. To obtain the soluble fraction of metals, 1.0 g of sediment was treated with 10 mL of ultrapure H_2O and subjected to agitation for 1 h. The exchangeable fraction was obtained by adding 10 mL of 1 mol L^{-1} CH_3COONH_4 to 1.0 g of sediment and the mixture subjected to agitation for 30 min. For the acquisition of the residual fraction, 10 mL of aqua regia (HCl/HNO_3, 3:1 v/v) were added to 1.0 g of sediment and subjected to cold digestion for 16 h (without agitation), the solution was then heated in a block digester at 90 ± 5 °C for 2 h.

Reagents and solutions

For the determination of metals, stock solutions were prepared from standard solutions (Accustandart/SpecSol) with concentrations of 1000 mg mL^{-1} in deionized water purified with a Milli-Q system (Millipore) to high purity (resistivity of 18 MΩ cm^{-1}). The stock solutions were stored in polyethylene bottles that were pre-washed with 10% HNO_3. The working solutions were obtained by diluting the stock solutions. A blank was prepared with 1% HNO_3 in deionized water and stored in the same manner. To obtain the analytical curves, reference solutions were prepared by serial dilution of the 1000 mg mL^{-1} stock solutions of each metal in deionized water.

Analytical procedures

The determinations of the elements Zn, Cd, Ni, Cu, Mn and Fe in the sediment samples were performed using a flame atomic absorption spectrometer (FAAS), model AAnalyst 200 (USA) equipped with deuterium lamp for background correction using air-acetylene flame. The response of the instrument was periodically checked with standard solutions of known concentration. The data acquisition system was managed by a microcomputer coupled to the flame atomic absorption spectrometer, and a hollow cathode lamp of the respective metals was used as radiation source.

Results and Discussion

Quality control for the extraction/analysis procedures

The analytical performance for the sequential extraction and analysis procedures of Zn, Cd, Ni, Cu, Mn and Fe in sediment are summarized in Table 1. The intermediary precision was evaluated in terms of repeatability (inter-day) and reproducibility (intra-day), and it was determined using the relative standard deviations (RSDs) for five successive analyses of extracted fractions of each of the extraction steps. Linear regression curves of the individual elements gave correlation coefficients of at least 0.9985. Limits of quantification (LOQs) were calculated as ten times the standard deviation of 12 blank extractions of each extraction step divided by the slope of each calibration graph.

Accuracy was carried out according to Silva *et al.*[28] With base in this procedure, the results for the sum of the three extraction step method (including the residual phase) were compared with those obtained for the extraction using the microwave-assisted acid digestion procedure. The results showed a good recovery of the sediments of the six collection points, ranged from 92 to 102%.

Distribution pattern of the total metals in the sediments

Figure 2 shows variations in the concentrations of Zn, Cd, Ni, Cu, Mn and Fe in the residual fraction of the sediment collected in the urban and semi-urban waterways of the Contas River. The values for Zn, Cu, Cd and Ni exhibited the highest average concentrations within the urban perimeter. The highest concentrations recorded for Zn and Cu were at collection points P3 and P4 and for Cd and Ni at point P5. This phenomenon may be attributed to anthropogenic activities because the Contas River begins to receive sewage and stormwater downstream of P3. The sewage and stormwater are drained by a combined collection system composed of galleries and emissaries from the urban area of Jequié.

On the other hand, the contents of organic matter (OM) in the sediments from urban area (P3, P4 and P5) were high in comparison with those from rural areas (P1, P2 and P6). The amounts of OM ranged from 5.12 to 7.13% in the urban area and from 2.62 to 3.51% in the rural area. The pH values were observed to be in the range of 7.1-8.2 in the dry season and of 6.8-7.2 in the rainy season. The high level of OM in the sediments from urban perimeter can also explain the high values of concentrations of Zn, Cu, Cd and Ni observed in the three collection sites (P3, P4 and P5).

It is known that metals in the oxidizable phase may be bound to active sites of organic molecules or precipitated as sulfides. With the depletion of the dissolved oxygen content in the sedimentary environment as a result of microbiological activity, sulfate is the major electron acceptor driving OM oxidation in anaerobic sediments. The generated sulfide that may be represented by acid volatile sulfide (AVS) in the process of OM oxidation is an important ligand, which can form stable metal sulfide precipitates in sediments, and thereby governs the behavior of divalent metals. This can also explain the high values of concentrations of Zn, Cu, Cd and Ni in the urban perimeter.

Table 1. Limit of quantification (LOQ) and precision of method

Element	Extractions	Soluble fraction	Available fraction	Residual fraction
Zn	LOQ / (mg kg^{-1})	0.060	0.067	0.060
	repeatability / (% RSD)	2.8	1.8	2.0
	reproducibility / (% RSD)	3.0	2.5	2.5
Cd	LOQ / (mg kg^{-1})	0.010	0.013	0.010
	repeatability / (% RSD)	3.8	4.2	2.1
	reproducibility / (% RSD)	4.0	4.5	2.5
Ni	LOQ / (mg kg^{-1})	0.047	0.047	0.047
	repeatability / (% RSD)	3.4	2.8	2.5
	reproducibility / (% RSD)	3.8	3.0	2.5
Cu	LOQ / (mg kg^{-1})	0.023	0.033	0.027
	repeatability / (% RSD)	3.7	3.3	2.8
	reproducibility / (% RSD)	4.0	3.5	3.0
Mn	LOQ / (mg kg^{-1})	0.17	0.20	0.17
	repeatability / (% RSD)	4.6	1.7	3.7
	reproducibility / (% RSD)	4.7	2.2	3.7
Fe	LOQ / (mg kg^{-1})	0.033	0.033	0.033
	repeatability / (% RSD)	3.4	4.8	1.9
	reproducibility / (% RSD)	4.3	4.8	2.0

RSD: relative standard deviation.

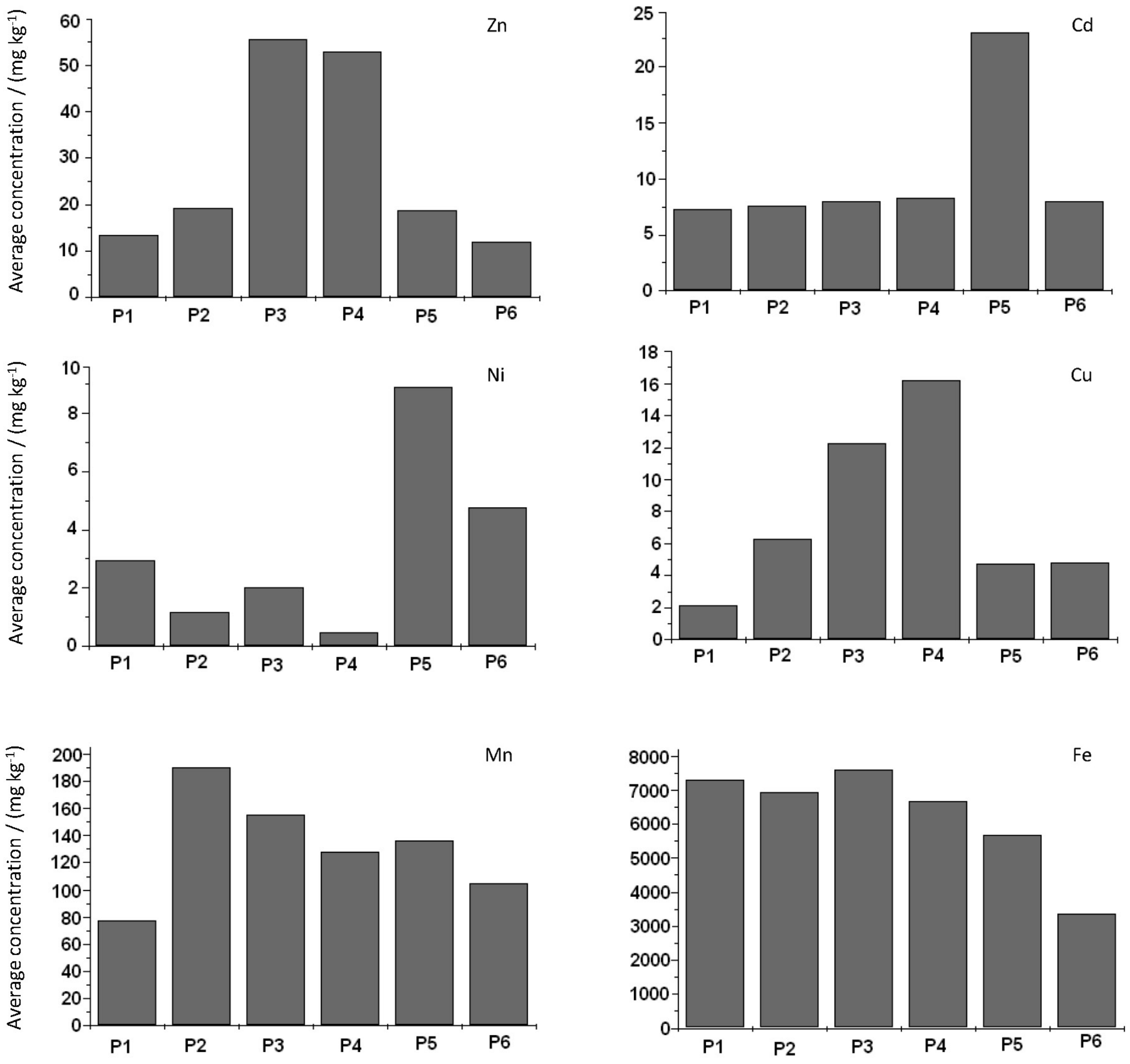

Figure 2. Average concentrations of Zn, Cd, Ni, Cu, Mn and Fe in the residual fractions of the sediments.

Although the levels of these four metals were relatively high within the urban perimeter, the cadmium was the only one presenting concentration values that exceeded TEC (threshold effect concentration) and PEC (probable effect concentration) in the residual fraction of the sediment, mainly in the sampling point P5. According to Sediment Quality Criteria (SQC) that was established by Brazilian National Council on the Environment (CONAMA 344/04), the greatest certainty in predicting the absence or presence of sediment toxicity occurs at sediment contaminant concentrations that are lower than the threshold effect concentration or greater than the probable effect concentration values, respectively.[25-28]

Considering the metals tested, only Mn exhibited a higher concentration in the sediments collected outside of the urban area, at sampling point P2. This high Mn concentration may be attributed to contributions from agricultural activities because of an irrigated agricultural area in the vicinity of the sampling point. However, Fe exhibited very similar levels at most of the sampling points, with a progressive reduction in its concentration starting at point P4.

Levels of Zn, Cd, Ni, Cu, Mn and Fe in the sediment fractions

The sequential extraction used in this study is useful to indirectly assess the potential mobility and bio-availability of metals in the sediment. The water soluble and exchangeable phases are leachable under neutral conditions, while the residual phase is difficult to leach under natural conditions. The residual phase contains the metals with the strongest association with the crystalline structures of the minerals, and which are therefore the most difficult to separate from the sediments.[33-35] In this phase, Zn, Cu, Cd and Ni exhibited concentration levels relatively high within the urban perimeter. Due to the existing microorganisms, the metal bound to organic matter might be decomposed and become a potential pollutant. This indicates that the metals Ni, Cd, Zn, and Cu are potentially leachable in the natural environment. These four metals retained in sediments of the Contas River can return to the water column due to changes in their physicochemical properties or through biological and microbiological activities. The release of these elements may cause undesirable changes in water quality.

Table 2 presents the average, minimum and maximum concentrations of Zn, Cd, Ni, Cu, Mn and Fe determined in each one of the three sediment fractions (soluble, exchangeable and residual).

In the soluble fraction (extracted with ultrapure water), six of the investigated metals were detected, including the most toxic elements (Ni and Cd), whose concentrations were 11.3 and 4.41 mg kg^{-1}, respectively. Metals in this sediment fraction are encountered in the form of soluble ions that can be easily released into the water column. In the exchangeable fraction (extracted with CH_3COONH_4), the largest variations in concentrations relative to the soluble fraction were observed for Mn and Fe. The maximum concentrations in the soluble and exchangeable fractions ranged from 38.00 to 82.10 mg kg^{-1} for Mn and from 451.0 to 11.80 mg kg^{-1} for Fe. These results demonstrate an antagonistic behavior between the two elements, whereas the concentration of Mn increases more than two times in the available fraction while Fe decreases sharply.

The evaluation of the metal concentrations in the three sediment fractions based in the TEC and PEC values (Table 2) indicates that in the soluble and available fractions of the sediment the maximum concentration values for all metals were below of concerned level of TEC and PEC, except by cadmium that presented values of the maximum concentration in the two fractions (soluble and available), upper of the TEC value.

Spacial and temporal variations of the soluble and available metals in the sediments

The graphs in Figure 3 were obtained from the results of the percentages of soluble metals (portion extracted with ultrapure water) in the sediment relative to the residual levels (percentage extracted with aqua regia), calculus were based on the following equation:

$$\text{Metal\%} = \frac{\text{Soluble fraction}}{\text{Residual fraction}}\,100 \qquad (1)$$

Based on the graphs in Figure 3, in the November 2006 (rainy season) sample, a large discrepancy was observed in the distribution of Cu in the soluble fraction of the sediment when compared with the other sampling periods. At points P1, P4, P5 and P6, Cu was detected only in the soluble sediment fractions. At points P2 and P3, the levels of Cu in the soluble extract relative to the residual level were approximately 40 and 9%, respectively. This discrepancy may be attributed to the large volume of rainfall

Table 2. Metal concentrations (mg kg^{-1}) determined in the soluble, available and residual fractions of the sediments collected in all the points sampling in the period (from December 2005 to April 2007)

		Zn	Cd	Ni	Cu	Mn	Fe
Soluble fraction	average	0.30	0.91	1.36	0.37	4.81	121.8
	minimum	< 0.018	< 0.003	< 0.014	< 0.007	< 0.052	< 0.010
	maximum	4.68	4.41	11.30	1.80	38.00	451.0
	standard deviation	1.07	1.63	2.95	0.67	10.32	115.6
Exchangeable fraction	average	0.14	0.93	0.70	0.07	29.65	2.32
	minimum	< 0.020	< 0.004	< 0.014	< 0.010	0.84	< 0.010
	maximum	3.31	4.02	6.47	0.65	82.10	11.80
	standard deviation	0.68	1.65	1.92	0.17	24.53	4.05
Residual fraction	average	28.69	10.38	2.89	7.78	132.1	6263
	minimum	7.15	3.68	< 0.014	< 0.008	4.87	1019
	maximum	131.0	65.80	35.60	39.90	238.0	11259
	standard deviation	29.37	11.97	8.04	8.40	55.92	2661
Level 1	TEC / (mg kg^{-1})	120.0	0.99	23.00	32.00	460.0	20000
Level 2	PEC / (mg kg^{-1})	460.0	5.00	49.00	150.0	1100	40000

To calculate the average, all such values below the LOD were considered to be zero; TEC: threshold effect concentration; PEC: probable effect concentration.

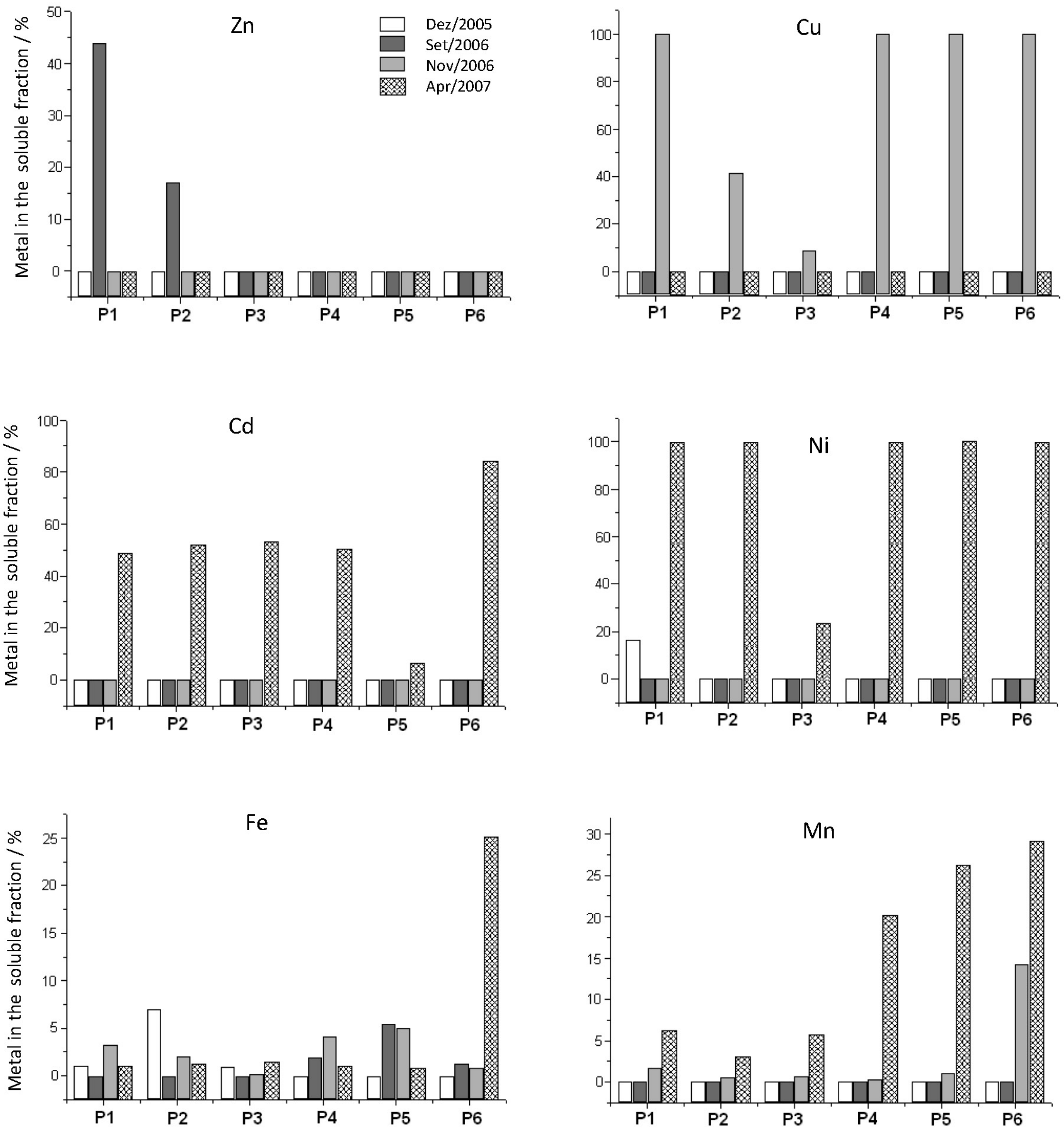

Figure 3. Graphs of the percentages of soluble Zn, Cd, Ni, Cu, Mn and Fe in the sediments.

that occurred in the region (approximately 182.7 mm), which may have provoked the draining of Cu introduced by anthropogenic actions, such as the use of inorganic fertilizers in agricultural activities and Cu residues from urban activities.

For the samples collected at the end of the rainy season (April 2007), the high levels of Cd, Ni, Mn and Fe observed in the soluble fraction of the sediments stand out, as seen in Figure 4. These results are probably also due to the large volume of rainfall in the region during the period prior to sampling (approximately 299.3 mm). This high volume of rain caused major flooding in the basin and contributed to the intensification of the existing drainage of soluble metals from urban and rural areas.

At the end of the rainy season, Ni exhibited a different behavior than the one exhibited during the other periods. It was detected only in the soluble fraction of the sediments collected at points P1, P2, P4, P5 and P6. At point P3, a significant portion of Ni was detected in the soluble fraction: approximately 24% compared to the total fraction. This large discrepancy, as previously mentioned, is due to the heavy rains during the period, which caused major flooding in the region. As for Cd, significant concentrations were detected in the soluble fraction: approximately 50% compared to the residual in the samples collected at points P1, P2, P3 and P4, as seen in Figure 3. In samples collected at site P6, Cd showed a relative concentration in the soluble fraction that was even higher than the soluble-fraction concentrations of samples collected at the other points (approximately 80% of the residual).

The evaluation of the results obtained from the sediment samples collected in December 2005, September 2006, November 2006 and April 2007 reveals that Fe exhibited a higher concentration in the soluble fraction than in the residual fraction at sampling points P1, P2 and P6, all of which are located in rural areas, compared to the points located in urban areas (P3 and P5), as shown in Figure 3.

On the other hand, the highest concentrations in the soluble fraction recorded for Zn was at collection points P1 and P2 in September 2006 (dry season). This phenomenon may be attributed to contributions from agricultural activities because of an irrigated agricultural area in the vicinity of the two sampling points. The irrigation process is intensified during the dry season.

Conclusions

The results of this study showed that the concentrations of some metals in the soluble fractions of sediments are directly associated with rainfall indices in the region. Thus, the evaluation of Zn, Cd, Ni, Cu, Mn and Fe in the soluble fractions of the sediments may be a valuable tool to identify the trend of the availability of these elements in the aquatic ecosystems of rivers that run through urban and semi-urban areas.

The study also indicated that high rainfall indices at the end of the rainy season (April 2007) may have contributed to the intensification of the existing drainage of soluble metals in the urban and semi-urban areas.

The evaluated elements Zn, Cu, Cd and Ni exhibit higher concentrations in the residual fraction of the sediments within the city at sampling points P3, P4 and P5. The elements Mn and Fe showed higher concentrations in sediments collected outside the urban area at sampling point P2, and this result may be attributed to contributions from agricultural activities.

Other important indication of this study is the contributions of the irrigation process in the drainage of soluble zinc in the agricultural areas during the dry season.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br as PDF file.

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