Anais da Academia Brasileira de Ciências (2018) 90(3): 2711-2719
(Annals of the Brazilian Academy of Sciences)
Printed version ISSN 0001-3765 / Online version ISSN 1678-2690
http://dx.doi.org/10.1590/0001-3765201820170808
www.scielo.br/aabc | www.fb.com/aabcjournal

Environmental diagnosis of metals in streams near sugarcane cultivation areas: current and historical analysis in the central region of the State of São Paulo

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Manuscript received on October 11, 2017; accepted for publication on January 22, 2018

ABSTRACT

In Brazil, innumerable regions of native landcover have been removed and replaced by agricultural cultivation, especially of sugarcane. In this culture, the application of fertilizers containing metals has caused impacts on the water resources causing contamination of stream sediments and occasioning bioaccumulation of metals in aquatic invertebrates. In the year of 2006, an environmental diagnosis of metals in sediments of streams located near sugarcane cultivation areas and in streams located in preserved areas, was published. That study pointed to high concentrations of metals in stream sediments in agricultural areas. These streams have been monitored over the last 10 years conducting analyses of metals and monitoring possible changes in land use. In the present paper, a historical comparison of metals contamination in the sediments of the same streams is conducted, aiming to present a status of 10 years later, analyzing 5 metals (Zn, Cd, Mn, Cr and Fe) found in the sediments of 8 streams, five located in areas of sugarcane cultivation and three located in preserved areas. This study also shows that there is higher concentration of metals in the sediments of streams near sugarcane cultivation than in preserved areas. The temporal historical evaluation showed high concentrations of Cd in 2016 when compared to the year 2006 for streams near sugarcane cultivation.

Key words: Aquatic biota, aquatic invertebrates, fertilizers, riparian vegetation.

INTRODUCTION

Brazil is the world's largest producer of sugarcane which, among Brazilian crops, from the products it generates, is considered to be one of the most important agricultural activities in the country (Instituto de Desenvolvimento Agroindustrial 1998). In Brazil, data obtained by Macedo (2007) indicate a growth of sugarcane activity in the country, with a high expansion for the State of Mato Grosso, with Brazil already contributing 34% of world production, a growth of 7% since 2002. Data from 2015 (Bastos et al. 2016) point that sugarcane farming has expanded significantly, reaching over 634.8 million tons. Currently, Brazil produces about 684 million tons of sugarcane, representing a growth of 2.9% in relation to the

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previous year, in an area of 9 million hectares, manufacture approximately 29 billion liters of alcohol and about 39 million tons of sugar (UNICA 2015, CONAB 2016). Sugarcane is the main source of sugar (sucrose) and alcohol (obtained by the fermentation process of sugarcane).

The State of São Paulo is the largest national producer, reaching 54% of the total cultivated area, with a production of 180 million tons and an area of 2.5×10^6 hectares, and its production is destined to the sugar and ethanol supply, reaching a prominent position in agroindustry (M.S. Nery, unpublished data). Presently, the State of São Paulo produces 381 million tons from an area of 4.8 million hectares (UNICA 2015). At the same time, in the State of São Paulo, sugarcane accounts for about 15% of rural land use, and in 2002 this crop was responsible for about 12% of agrochemical and fertilizer sales in Brazil (Armas et al. 2005).

The application of fertilizers during the distinct periods of sugarcane cultivation, together with the problem of the devastation of riparian forests, has led to different impacts on the water resources of the adjacent areas to these plantations, mainly through the process of soil leaching from cultivated areas. Fertilizers provide nutrients for crops (N, P, K) but also contain other elements that are potentially harmful to human health and the environment such as heavy metals (Pb, Cd) or first transition metals (Cu, Zn, Cr, Ni) (Peris et al. 2008). Previous studies (Angelotti-Netto et al. 2004, Bizarro et al. 2008) found that different concentrations of Cd, Pb, Cr and Ni are found in fertilizers widely used in sugarcane cultivation.

Similarly, studies conducted in streams pointed to higher concentrations of metals, mainly Zn, Cu, Al, Cd and Fe in the sediments of streams adjacent to sugarcane cultivation, when compared to areas with riparian forests preserved (Corbi et al. 2006, 2013). At the same time, some studies indicated higher concentrations of Cd, Cu, Pb, Mn, Ni, and Zn in insect larvae found in streams located in impacted areas with sugar cane activity (Corbi et al. 2008, 2010). It is known that high concentrations of metals, such as cadmium, a non-essential metal to animals, can cause changes in the life cycle, decrease in body size and cephalic capsule besides deformities in the mouth parts in some species of aquatic insects (Postma et al. 1995, Massabni et al. 2002, Corbi and Trivinho-Strixino 2017). In the same way, the exposure of insect larvae to the sediment of streams located in agricultural areas has led to genetic modifications in these larvae, causing loss of genetic diversity (Seeland et al. 2013, Colombo-Corbi et al. 2017).

The present study aims to gather current information regarding the contamination of metals in sediments of streams located in areas of sugarcane cultivation, without riparian vegetation, and in preserved areas, to conduct a historical comparison on the status of contamination by metals in sediments compared to the study conducted in 2006 (Corbi et al. 2006). These streams have been monitored over the past 10 years in different environmental assessments (Corbi et al. 2006, 2010, Corbi and Trivinho-Strixino 2017). This work presents the following hypothesis: sugarcane agricultural practices contaminate with metals the sediment of adjacent streams, causing accumulation over time. In the present study 5 metals (Zn, Fe, Cd, Mn and Cr) were analyzed in the sediments of 8 streams.

MATERIALS AND METHODS

STUDY SITES

The eight streams are located in the Jacaré-Guaçu and Moji-Guaçu Rivers Basins, in the State of São Paulo, Brazil (Table I and Figure 1). The streams are of low order (1st and 2nd order), have low water velocity (<1 m.s^{-1}), small depth (<1.5 m), small width (<2 m) and are located at low altitude, 500 m to 700 m. The values of dissolved oxygen varied from 5.63 mg L^{-1} to 8.3 mg L^{-1} and the pH ranged from 5.3 to 6.97.

TABLE I
General characteristics of the eight sampling sites, showing the land use types and city.

Legend	Stream	City	Land use
C1	São João	Guarapiranga	Sugarcane
C2	São Vicente	Guarapiranga	Sugarcane*
C3	Água Preta	Ribeirão Bonito	Sugarcane
C4	Chibarro	Araraquara/Ibaté	Sugarcane
C5	Andes	Araraquara	Sugarcane
C6	Monjolinho	São Carlos	Riparian vegetation
C7	Espraiado	São Carlos	Riparian vegetation
C8	Anhumas	Araraquara	Riparian vegetation

* - Stream with impacted riparian vegetation.

These measurements were analyzed using a Yellow Springs multiparameter model 556 MPS. The analyzed streams are in Cerrado areas and have sand (fine sand) substrates (70% of the total) and low organic matter in the aquatic sediment (<25%) (Corbi and Trivinho-Strixino 2008). The normal annual precipitation in the river basins is about 1400 mm (Ometo et al. 2000). The rainy season occurs between October and March and the dry season occurs from April to September.

SAMPLING AND STORAGE

Sediments for metals analysis (Zn, Cd, Cr, Fe and Mn) were collected in duplicate from the ten sites using a standard Ekman-Birge grab (sampling area of 255 cm^2). Samples were taken twice at each site, from July and August 2016. Sediments were stored at 4°C before testing (Pourang 1996).

Due to the importance of the organic matter content of the sediment in the absorption of metals in the aquatic system (Rocha and Rosa 2003), three sub-samples of sediments from each point of the streams were collected between July and August 2016 for the determination of organic matter in the sediment. The organic matter of the sediment was determined by the loss of mass after ignition (550°C, 4 h) in dry sediment fractions (in an oven at 60°C for 12 h), according to the techniques described in the literature (Maitland 1979).

ANALYTICAL PROCEDURES

For analysis, deionized double distilled water (DDDW) was used. All acids were purchased from Merck® (analytical grade). The cleaning of the material was performed with concentrated nitric acid as described (Tschöpel et al. 1980).

Sediment samples for metals determination were oven dried at 65°C on glass dishes, homogenized by using a pestle and mortar and each of the weighed samples (about, 5.0 g) was placed in a 100 mL beaker, to which 5.0 mL of HNO_3 was added and digested close to dryness at 90°C on a hot plate. The digested samples were cooled at room temperature and filtered by using filter papers and collected in a 100 mL beaker. The filter papers were washed with ca 20 mL of water and the contents of the beaker were transferred to 100 mL volumetric flasks. The solutions were analyzed for metals in a Pye Unicam flame atomic absorption spectrophotometer. Analyses were undertaken in triplicate (De Paula and Mozeto 2001). The limits of detection are: Cd - 0.0002 mg L^{-1}; Cr - 0.001 mg L^{-1}; Fe - 0.001 mg L^{-1}; Mn - 0.0005 mg L^{-1}; Zn - 0.0004 mg L^{-1}.

STATISTICAL ANALYSIS

In order to verify the significance of the data, a Cluster Analysis, using UPGMA and Cosine as a similarity measure was applied on the concentrations of metals (Zn, Cd, Cr and Mn) obtained in the sediments of 8 streams. To analyze the significance of the differences observed in the Cluster analysis, a similarity analysis was performed (ANOSIM). This analysis was applied to investigate differences in current concentrations between land uses (sugarcane and forest) and to analyze historical changes after 10 years. Statistical

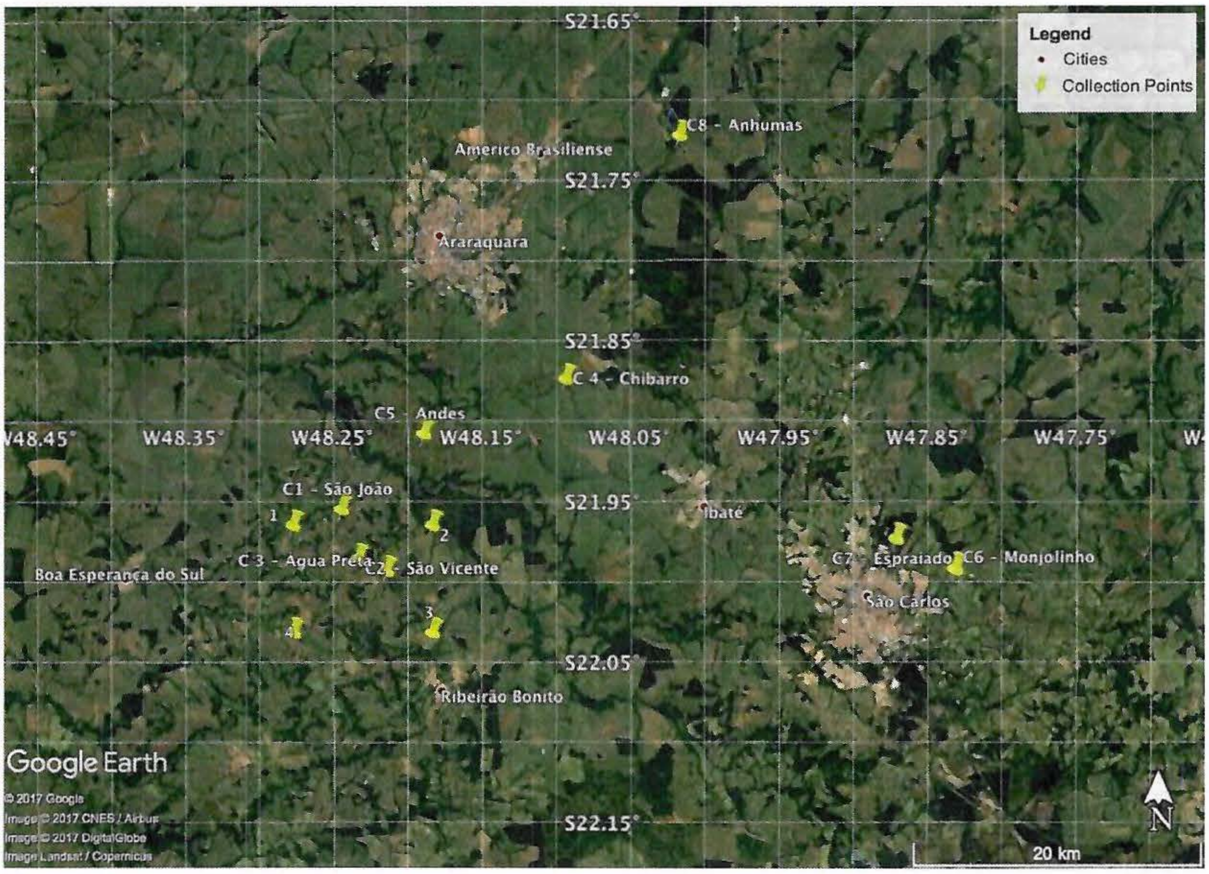

Figure 1 - Location of the eight sampling sites, State of São Paulo, Brazil. Streams C1 to C5 are located in sugarcane cultivation areas. Strems C6 to C8 are located in preserved areas. Streams detailed information in Table I.

analyzes were performed using the PAST Program (Version 1.68) (Hammer et al. 2000).

RESULTS AND DISCUSSION

In the present study, the metals analyzed were detected in higher concentrations in the streams located in adjacent areas to sugarcane cultivation than in the preserved streams (Figure 2), confirming the results obtained in 2006 (Figure 3). Zinc presented high concentrations for the Andes stream (C5), located in agricultural areas with a value of 90.7 mg kg^{-1} and low concentrations for Monjolinho (C6) and Espraiado (C7) streams with 1.0 mg kg^{-1} and 3.72 mg kg^{-1} respectively, both located in preserved areas. Zinc is mobilized in the environment due to natural processes of erosion, forest fires, volcanic eruptions, biological activity, and has also been widely found in fertilizers. Thus, zinc is naturally present throughout the environment, but can also be found in fertilizers and thus be carried to aquatic environments by the process of surface runoff in adjacent areas (Angelotti-Neto et al. 2004). Cd was detected in low concentrations in all streams, but with high concentrations in streams without riparian forest, located in sugarcane areas. In the Anhumas (C8) and Monjolinho (C6) streams, both located in preserved areas, Cd was not detected in the sediments. The highest concentration of this metal was detected for the Andes stream (C5), in an agricultural area, with concentration of 1.99 mg kg^{-1}. Cd is a toxic metal that usually occurs in nature associated with other metals like zinc and lead. As pointed out by Bizarro et al. (2008), Cd

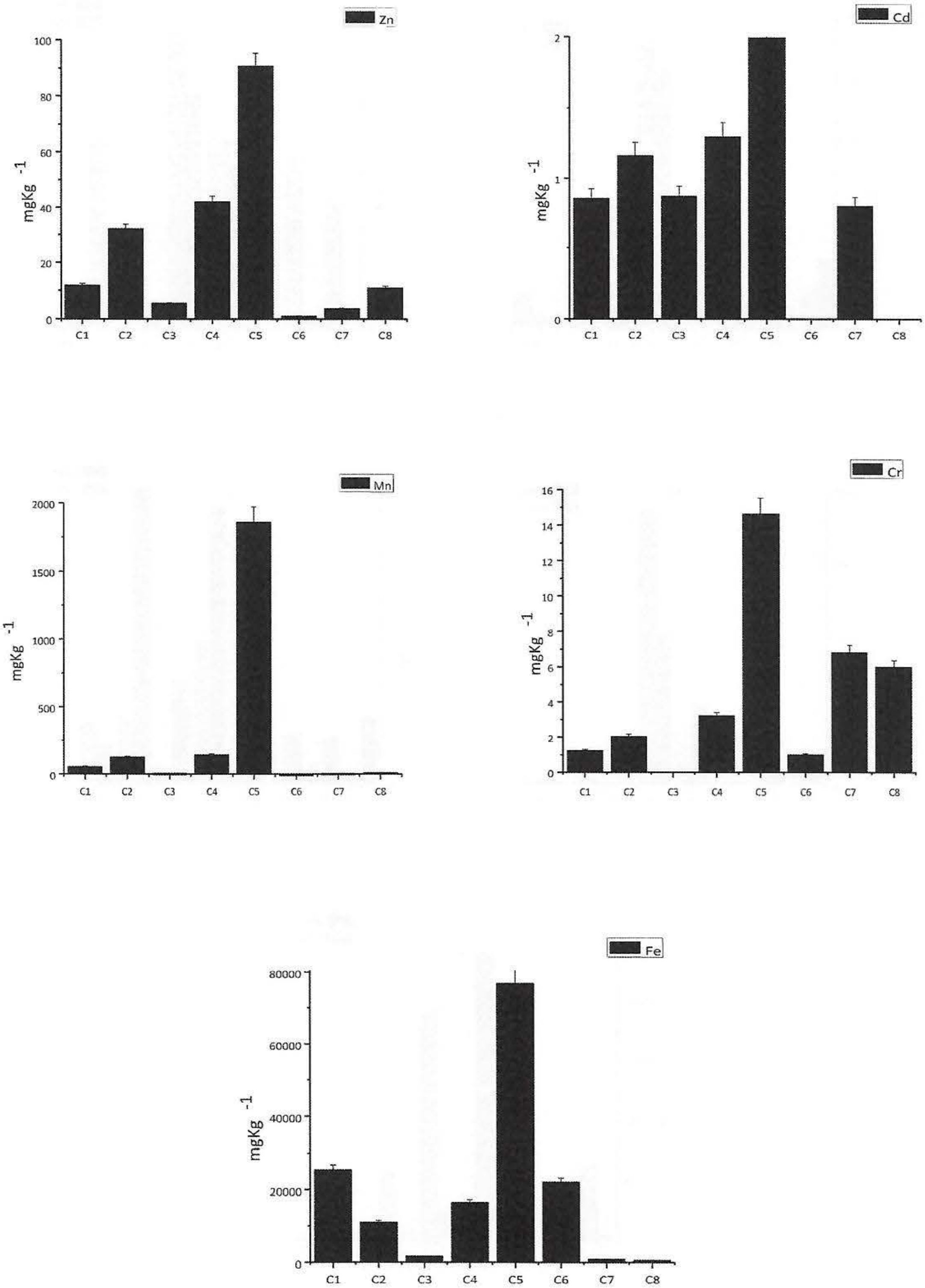

Figure 2 - Mean values and standard deviation of actual metal concentrations (2016) determined in sediments from the eight sampling sites. Streams C1 to C5 are located in sugarcane cultivation areas. Strems C6 to C8 are located in preserved areas. Streams detailed information in Table I.

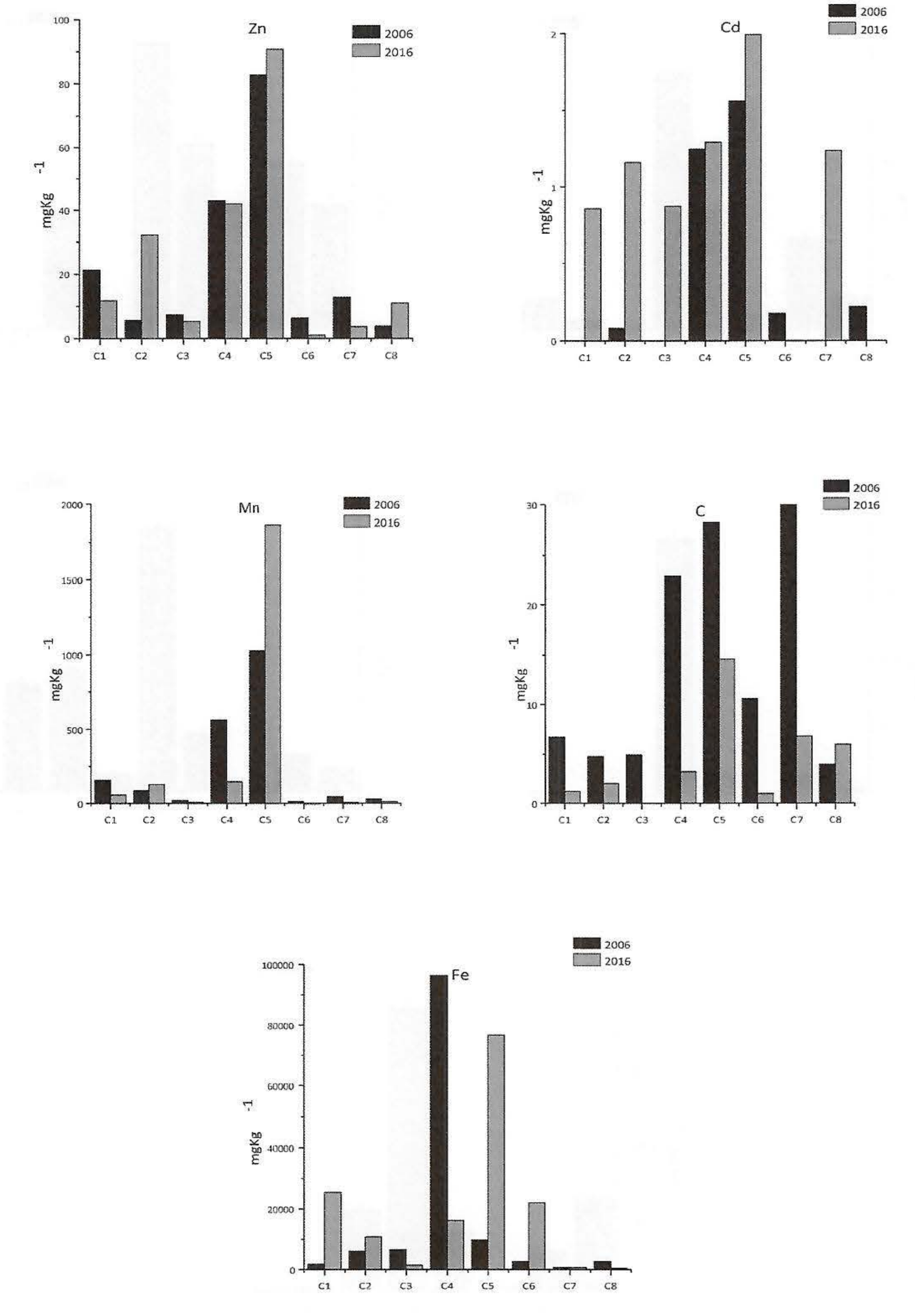

Figure 3 - Mean values of metal concentrations in 2006 and 2016 determined in sediments from the eight sampling sites. Streams C1 to C5 are located in sugarcane cultivation areas. Strems C6 to C8 are located in preserved areas. Streams detailed information in Table I.

is toxic to organisms. Phosphate fertilizers may contain Cd at varying concentrations depending on the phosphate rock from which they were obtained. Continuous phosphatic fertilization can cause soil Cd accumulation and environmental impacts due to its high toxicity. Environmental pollution by this metal is worrisome since less than 5% is recycled (Batalha and Parlatore 1993, Massabini et al. 2002, Bizarro et al. 2008). Fe was detected at high concentrations in all streams analyzed. This fact may be related to the type of soil existing in the region that is rich in this metal (Batalha and Parlatore 1993). On the other hand, iron is not considered toxic to organisms, and is present in the hemoglobin of some animals, including some species of aquatic insects such as the *Chironomus sancticaroli* species. Cr and Mn were also detected in high concentrations in streams located in impacted areas. The highest concentrations of these metals were detected in the Andes stream (C5), located in areas with sugarcane activity and the lowest concentrations were detected in the Monjolinho stream (C6) in a preserved area (Figure 2).

In general, metals are essential to the biota. Organisms require small amounts of some metals, including, for example, cobalt, copper, manganese, molybdenum, zinc and iron to perform vital functions in the body (Mertz 1986, Melo et al. 2012). On the other hand, despite being essential, metals have reference values, which at levels above these can be toxic to organisms. Other metals such as mercury, lead and cadmium are considered toxic, have no function in organisms and their presence and bioaccumulation can cause serious diseases, especially in mammals, species at the highest level of the food chain. Metals in organisms can participate in a range of responses, for example, to act directly with deoxyribonucleic acids (DNA), as is the case of Cr, which when bound with genetic material, forms Cr-DNA damaging the genetic material. Cadmium (Cd) can damage DNA by inactivating repair enzymes. Cadmium is considered to be non-essential to biota, and the characterization of cadmium inputs in aquatic systems is considered incomplete (Mertz 1986, Melo et al. 2012). The availability of metals in the aquatic environment can be related to chemical and physical properties of the systems such as temperature, pH and redox potential. For the aquatic sediment, the organic matter contents and the granulometry compound are fundamental factors for its dynamics (Maitland 1979, Kostial 1986, Rocha and Rosa 2003). Sediments rich in organic matter tend to contain more metals when compared to sediments with low organic matter. In the studied region, the streams are located in areas of the Cerrado biome, and for that reason, they present generally sandy soils with low organic matter and predominance of fine sand (Corbi et al. 2008).

The cluster analysis applied to the metal concentrations of the 8 streams delimited two distinct groups. A group of streams located in preserved areas and another group of streams located in areas with sugarcane activity, without riparian vegetation. The similarity analysis (ANOSIM) applied to these two groups showed significant differences ($p = 0.01$) among the studied environments (Figure 4). In this way, this analysis confirmed the results obtained in 2006 (Corbi et al. 2006), which also pointed out significant differences between streams preserved and impacted by sugarcane activity and seems to confirm the studies conducted (Angelotti-Netto et al. 2004) regarding the presence of Cu, Zn and Cd in fertilizers, which has resulted in impacts to the water resources of the central region of São Paulo (M. Peláez-Rodríguez, unpublished data).

When analyzing the results of the historical analysis of the contamination of the streams, comparing the concentrations obtained in 2006 and the current concentrations, we can observe that Zn, Cd, Mn, Fe and Cr presented, in general, smaller concentrations in the present, for the streams localized in preserved areas (Figure 3). Cadmium was higher in the present than the concentrations obtained in 2006. Zn varied, currently presenting high concentrations for streams C2 and C5, with a concentration six times high for stream C2 (São Vicente) and with an increase of 8 mg kg^{-1} for stream C5 (Andes). Cr showed an opposite result, presenting low concentrations in the present when compared to 2006. Mn presented high concentrations in 2016 for streams C2 (São Vicente) and C5 (Andes) and iron presented high concentrations for the streams C1, C2 and C5 (Figure 3). The Cluster analysis applied to the metal concentrations obtained in 2006 and 2016 did not show significant differences between the environments (preserved and impacted areas). However, although there are no significant differences in the historical analysis of metals, the highest concentrations of Cd for all sugarcane streams when compared to 2006 is worrying because it is known that phosphate fertilizers from phosphate rock, contains cadmium in its composition and has been intensively used in agricultural activities in general (Bizarro et al. 2008). This fact makes evident the need for an adequate management of the region's water resources, which includes the preservation of riparian forests and the restoration of the forests devastated in the past. We also emphasize the need for greater control in the application of fertilizers, adopting more secure practices in agricultural areas and the improvement in the process of production of these products, with the aim of ensuring good water and food quality for future generations.

The present study reiterates the need for the reforestation of riparian vegetation, since in agricultural areas, without riparian forest, concentrations of metals in the sediments have been high and have generally increased over recent years when compared to the preserved areas. Likewise, the need to design a system that uses sediment as an important part in environmental assessment studies is emphasized, since numerous aquatic organisms, such as aquatic invertebrates, use this aquatic compartment as a place of survival and feeding. This fact may cause, consequently, the bioaccumulation of metals in the food chain, including fish, birds and mammals.

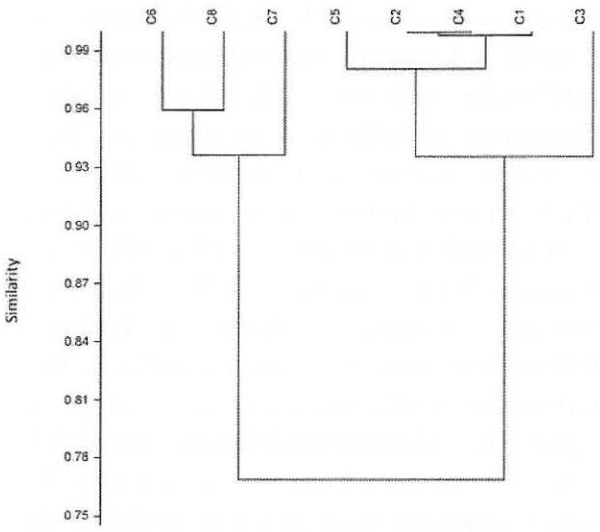

Figure 4 - Cluster analysis (using UPGMA with Cosine similarity measure) applied for the actual metal concentrations of the eight streams. Cophenetic correlation: 0.87. Streams C1 to C5 are located in sugarcane cultivation areas. Strems C6 to C8 are located in preserved areas. Streams detailed information in Table I.

ACKNOWLEDGMENTS

We thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) for the financial support, process number 2013/24268-2.

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