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The Fertilizer-Effect on Al, Ba, Fe, Mn and Ni Released in a Watershed with Influence of Sugar Cane Crops in the São Paulo State, Brazil

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Abstract

São Paulo State is the main sugar cane producer and these agricultural activities are carried out in predominantly sandy soils, which require large amounts of phosphate fertilizers and amendments. This work evaluated the fertilizer-effect on the Al, Ba, Fe, Mn and Ni released in a watershed with influence of sugar cane crops in the São Paulo State, Brazil, namely the Monjolo Grande Stream basin. Five surface water sampling campaigns were carried out at the mouth of Monjolo Grande Stream in February, April, June, September and November 2010, characterizing the following parameters: discharge, pH, temperature, electric conductivity, dissolved oxygen and total and dissolved concentrations of Al, Ba, Fe, Mn and Ni. Approximately 99% of Al and Fe are transported annually in association with suspended sediments carried to the Monjolo Grande Stream by sheet erosion. The results also demonstrated that the increasing Al, Ba, Fe and Mn concentrations dissolved in the waters of the Monjolo Grande Stream basin in the wet season are associated to phosphate fertilizers and amendments that are used extensively in agrichemical activities. However, with the current application rates, there has been no increase in the dissolved concentrations of these metals at levels that could pose risks to human health.

Keywords

Sugar Cane Crops, Phosphate Fertilizers and Amendments, Total and Dissolved Metal, Environmental Management

1. Introduction

Over the past centuries, Brazil's Southeast and Midwest regions have undergone various environmental impacts associated with land use changes, mainly due to the removal of natural vegetation of the Cerrado region for agropastoral activities and coffee cultivation in the nineteenth century. In the twentieth century these activities were replaced by sugar cane crops which are widely used for ethanol production, a biofuel that is being used to replace gasoline in several Brazilian States. In the 1980s, after the Federal Government implemented the National Alcohol Program (PROALCÓOL), the sugar cane production areas expanded by more than 3 million hectares in the Central Southern regions of Brazil, while still requiring an additional 7 million hectares of sugar cane plantations for the ethanol supply in Brazil by 2021 [1]. The São Paulo State accounts for 52% of Brazil's sugar cane production [2]; most of this production occurs in sandy soil areas derived from sedimentary rocks of the Paraná Sedimentary Basin, specifically in the São Bento and Bauru groups.

The soils derived from these groups are composed mainly of quartz and hence have low agricultural productivity. Consequently, the sugar cane crops require large amounts of phosphate fertilizer applications (NPK-5:25:25) and amendments, such as KCl, limestone and phosphogypsum. These materials are water soluble and, consequently, can result in several metal leaching processes (*i.e.* Al, Ba, Fe, Mn and Ni) [3], including radioactive elements [4], in the surface waters from a watershed. Another adverse effect of sugar cane crops is the increased of the sediment transport to watercourses, causing their sedimentation. Thus, the changes in aquatic systems linked to sugar cane crops have an anthropogenic impact on these environmental systems, promoting different effects at different biological, economic, social and public health levels.

Since metals can be leached into river waters, it is important studying their behaviour given the environmental concern related to the impact they cause, since they are non-biodegradable inorganic and often toxic substances, even at low concentrations [5]. Equally important as the analysis of the total amount of metals, is studying the metal species found in the environment, known as chemical speciation. There are many parameters which can influence the reactivity of available metals, such as pH, particles in suspension, colloidal materials and the concentration of organic substances, which play an important role in the behaviour of metals in aquatic environments [6]. Evaluating the total and dissolved metal concentrations requires understanding the general characteristics of a water body and the drainage basin under study [7], since the river metal load depends on the geological, ecological and seasonal characteristics of the drainage basin and the type of human activity that takes place in its area of influence.

In Brazil there are still no studies addressing levels of total and dissolved metal in river water in areas of sandy soils with intense agricultural activity related to sugar cane crops. The Monjolo Grande Stream basin has a predominantly agricultural land use associated with sugar cane crops, with no adjacent urban and industrial activities, implying the absence of domestic and industrial effluents discharged into its surface waters. Moreover, the Monjolo Grande Stream is one of the main tributaries of the Corumbataí River, which supplies water to a population of approximately 800,000 people. Therefore, this watershed is an excellent study area to understand the river flow rates of total and dissolved Al, Ba, Fe, Mn and Ni over a complete hydrological cycle, in order to verify whether the sugar cane crops are affecting the natural dynamics of these metals in the water resources, modifying its natural quality and, consequently, with potential risks to human health.

2. Study Area

The Monjolo Grande Stream is part of the drainage network of the Corumbataí River basin, which has an important regional role in the supply of industrial and domestic water to the municipalities in its basin and neighbouring basins, such as the cities of Rio Claro and Piracicaba (**Figure 1(a)**). The Monjolo Grande Stream basin drains an area of 28.87 km^2 in the Ipeúna, central-east region of São Paulo, and located between latitudes 22˚18'S and 22˚23'S and longitudes 47˚48'W and 47˚42'W (**Figure 1(b)**).

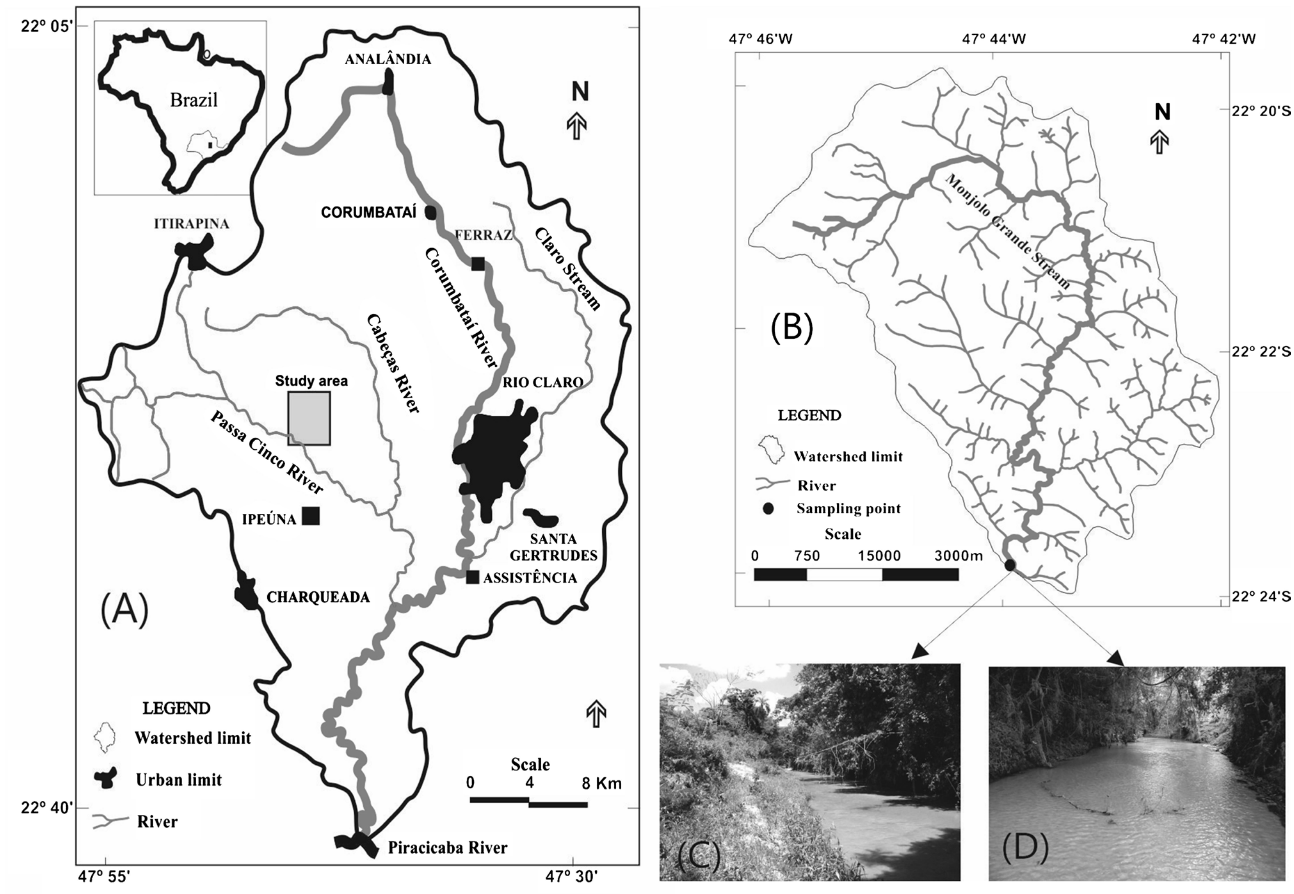

Figure 1. Location of Corumbataí River basin (a) and Monjolo Grande Stream basin (b), with its sampling point in dry (c) and wet (d) periods.

The Monjolo Grande Stream basin has a predominantly agricultural land use associated with sugar cane crops, with no adjacent urban and industrial activities. Much of its natural vegetation, which consists of tropical broadleaf forest and gallery forest along the streams, was removed to plant coffee and install sawmills in the nineteenth and twentieth century [8].

Situated in the geomorphologic province of the Paulista Peripheral Depression at the eastern border of the Paraná Basin [9], the watershed under study is characterized by a topography consisting of hills, with elevations ranging between 550 and 600 m a.s.l. The average slope of the drainage basin is 0.04 $m \cdot m^{-1}$, and 0.3 $m \cdot m^{-1}$ in the headwaters region. The major soil types in the Monjolo Grande Stream basin are ultisols and oxisols, which cover about 75% of the basin area. Other minor soil types at this watershed include alfisols, orthents, entisols and quartzipsamment.

The geology of the area comprises sedimentary rocks from Passa Dois and São Bento groups [10]. The Passa Dois Group has the Corumbataí Formation, with the presence of claystone, sand and siltstone, which are emerging lithologies only at the mouth of the Monjolo Grande Stream. Regarding the São Bento Group, the units described in the Monjolo Grande Stream basin are: the Serra Geral Formation, fractured basalt in the region of its headwaters; Pirambóia Formation, medium to fine grained sandstone beds; and Botucatu Formation, fine and very fine grained sand deposited in a desert cycle, which covers over 90% of the area of this watershed.

Considering the rainfall distribution and temperature variations over the year, according to the Köppen classification, the Monjolo Grande Stream basin is classified as humid subtropical (Cwa), with dry winter and rainy summer. The average annual rainfall between 1964 and 2004 was 1475 mm, with January the rainiest month, with an average monthly rainfall of 267 mm, and July the driest month, with average monthly rainfall of 32 mm. Therefore, between the wettest and driest month the ratio was approximately 8:1 times, indicating a large rainfall range between the dry winter and rainy summer. The study area is under the predominance of tropical and equatorial masses in more than 50% of the year, with prevailing S and SE quadrants winds.

3. Materials and Methods

To assess the riverine flow of total and dissolved metals in the Monjolo Grande Stream basin, five surface water sampling campaigns were performed at the mouth of this watershed in 2010 (22˚23'44"S, 47˚43'56"O), in February, April, June (**Figure 1(c)**), September and November (**Figure 1(d)**). This sampling allowed comparing the wettest and driest months, which covers all possible discharge variations of this stream over a complete hydrological cycle. The sample collection and preservation followed the procedures described in the Technical Guide for Collection and Preservation of Water Samples [11]. The discharge at the sampling point was determined by Equation (1).

$$Q = A \cdot V \tag{1}$$

where:

Q = discharge ($m^3 \cdot s^{-1}$);

A = cross-sectional area of the river (m^2);

V = river flow velocity (m l$\cdot s^{-1}$), quantified using the Global Water flow meter model 201.

The hydrogenionic potential (pH), temperature (Temp.-˚C), electrical conductivity (Cond.-$\mu S \cdot cm^{-1}$) and dissolved oxygen (DO-$mg \cdot L^{-1}$) were characterized using a multiparametric probe YSI 556 (Xylem, Inc.), with direct reading at the sampling site [12]. The pH electrode was calibrated using a standard solution with pH 4.00 (4.01˚C ± 0.01˚C to 25˚C ± 0.2˚C) and 7.00 (7.01˚C ± 0.01˚C to 25˚C ± 0.2˚C). The conductivity meter was calibrated using a standard solution of KCl (1.0 $mmol \cdot L^{-1}$), with known electrical conductivity of 147 $\mu S \cdot cm^{-1}$ at 25˚C.

To quantify the total concentration of Al, Ba, Fe, Mn and Ni, the surface water samples were acidified with HNO_3 distilled to 2% (pH < 2), and subjected to a digestion procedure following the EPA 3010A procedures [13]. The dissolved concentration was determined by *in situ* filtration of the surface water samples using a 45 μm Millipore filter (Merck Millipore Corp) attached to a 20 mL disposable syringe, followed by acidification with HNO_3. The total and dissolved fractions of Al, Ba, Fe, Mn and Ni were quantified by inductively coupled plasma atomic emission spectrometry (ICP-OES), after sample pre-preparation, with the following detection limits: 2.2, 0.5, 0.5, 0.1 and 0.4 $\mu g \cdot L^{-1}$ of Al, Ba, Fe, Mn and Ni, respectively. The weighted average concentration (C_{MNQ}) of the analyzed chemical species was obtained by Equation (2).

$$C_{MNQ} = \frac{\sum_{i=1}^{n} C_i \cdot Q_i}{\sum_{i=1}^{n} Q_i} \tag{2}$$

where:

C_i = concentration of the chemical species in the i-th sample ($mg \cdot L^{-1}$);

Q_i = river flow observed on the collection date of the i-th sample ($m^3 \cdot s^{-1}$).

4. Results and Discussion

4.1. Physical and Chemical Parameters

Table 1 shows the results of physical and chemical parameters for the Monjolo Grande Stream during the study period.

The Monjolo Grande Stream discharge was seasonally influenced, with the highest discharge values in the rainy summer when compared with the dry winter, ranging from 0.1 (in September) and 1.7 $m^3 \cdot s^{-1}$ (in February). The variation (6.4 to 7.2) and weighted average pH (6.8) showed that the waters of the Monjolo Grande Stream are close to neutrality. Electrical conductivity was higher in the dry season compared to the rainy season, which is related to a dilution effect of the Monjolo Grande Stream by rainwater during the rainy season. The electrical conductivity values were below the limit expected for natural waters, which is of 100 μS·cm^{-1} [14]. The water temperature followed the seasonal trend, with lower values in winter (13.0˚C in June) and higher values in summer (23.5˚C in February). The dissolved oxygen concentration followed a similar trend, ranging from 6.4 (June) to 8.0 (November) mg·L^{-1}, indicating the occurrence of good oxygenation due to small waterfalls along its course.

Table 2 shows the concentrations of total and dissolved fractions of Al, Ba, Fe, Mn and Ni. The concentration of Ni in total and dissolved fractions was below the detection limit (<0.4 μg·L^{-1}) in all samples collected throughout the year. The weighted average concentrations of Al, Ba, Fe and Mn in total and dissolved fractions were 8593, 114, 3247 and 47 and 48, 102, 44 and 38 μg·L^{-1}, respectively. The concentrations of these metals change in the total and dissolved fractions,

Table 1. Physical and chemical parameters in the surface water from Monjolo Grande Stream.

Sampling date	Discharge (m^3·s^{-1})	pH	EC (μS·cm^{-1})	Temp ˚C	DO (mg·L^{-1})
February	1.7	6.4	32.5	23.5	7.6
April	0.3	7.2	51.4	19.3	6.8
June	0.2	6.5	54.2	13.0	6.4
September	0.1	6.5	52.0	17.8	6.8
November	0.3	6.6	44.0	22.5	8.0
C_{MNQ}	0.5	6.8	40.0	22.7	7.6

Table 2. Total and dissolved concentration of Al, Ba, Fe, Mn and Ni (μg·L^{-1}) in the surface waters from Monjolo Grande Stream.

Sampling date	Al	Ba	Fe	Mn	Ni
Total					
February	12390	112	4260	57	<0.36
April	523	104	977	20	<0.36
June	131	102	590	14	<0.36
September	677	106	1236	21	<0.36
November	566	107	1135	33	<0.36
C_{MNQ}	8593	114	3247	47	<0.36
Dissolved					
February	58	108	51	48	<0.36
April	23	80	25	10	<0.36
June	18	72	20	7	<0.36
September	22	79	26	10	<0.36
November	32	85	32	24	<0.36
C_{MNQ}	48	102	44	38	<0.36

with higher values quantified in the total fraction when compared to dissolved fractions. The lowest total and dissolved concentrations of Al, Ba, Fe and Mn were obtained in the driest months, especially in June 2010, with the highest levels quantified in February, indicating seasonality for these fractions. This is a remarkable fact, when the total and dissolved fractions of Al and Fe are taken into account.

Monjolo Grande Stream is classified as Class 2, according CONAMA Resolution No. 357 of 17 March 2005 [15], wish is defined as freshwater, which after conventional treatment can be used for human consumption; the protection of aquatic communities; the protection of primary contact recreation such as swimming, water skiing and scuba diving. Comparing the concentrations obtained in this study with the maximum reference values for dissolved Al (0.1 mg·L^{-1}), total Ba (0.7 mg·L^{-1}), dissolved Fe (0.3 mg·L^{-1}), total Mn (0.1 mg·L^{-1}) and total Ni (0.025 mg·L^{-1}) recommended for Class 2 [15], all values are below the maximum values determined. In Brazil, the Ordinance No. 2914 of the Ministry of Health [16], of December 12, 2011, sets forth the control and surveillance procedures of water quality and drinking water standards for human consumption. The concentrations of dissolved Al, Ba, Fe, Mn and Ni quantified in the surface waters of the Monjolo Grande Stream basin are below the tolerable limits allowed for human consumption of these metals, *i.e.* 0.2 mg·L^{-1} of Al and Fe, 0.7 mg·L^{-1} of Ba, 0.1 mg·L^{-1} of Mn and 0.07 mg·L^{-1} of Ni.

4.2. Daily and Annual Fluxes of Al, Fe, Ba, Mn and Ni

The chemical dynamics of a river in areas with no major environmental impacts related to water pollution using Equation (3) [17].

$$W = C_{MNQ} \cdot Q_m \tag{3}$$

where:

W = daily flow (kg·day^{-1});

C_{MNQ} = total or dissolved concentration for each metal (μg·L^{-1});

Q_m = discharge (L·day^{-1}).

At the Monjolo Grande Stream, most of the total or dissolved Al, Ba, Fe and Mn transport occurs in the higher temperature months (**Table 3**). February was the month with the highest transport rates of these metals in their total and dissolved fractions due to the significant discharge increase. The results in **Table 3** show that 90% Ba and 81% Mn were transported annually in the dissolved fraction. However, approximately 99% of Al and Fe were transported annually associated with undissolved materials, *i.e.* the suspended sediments were carried to the Monjolo Grande Stream through sheet erosion, which is composed of minerals that have Al and Fe in their composition, such as kaolinite, goethite and magnetite. A study by Spatti Junior *et al.* [18], reported an annual transport of suspended material of 887 t·year^{-1} in the Monjolo Grande Stream basin, where approximately 90% of this total is transported in the rainy season.

Finally, multiplying the total weighted average flow rate concentration of each metal by the average annual discharge of 0.5 m^3·s^{-1}, can be obtained a total annual

Table 3. Instantaneous daily flux (kg·day^{-1}) of Al, Ba, Fe and Mn in the Monjolo Grande Stream basin.

Sampling date	Al	Ba	Fe	Mn
Total				
February	1819.8	16.5	625.7	8.4
April	13.6	2.7	25.3	0.5
June	1.1	0.9	5.1	0.1
September	11.7	1.8	21.4	0.4
November	14.7	2.8	29.4	0.9
Dissolved				
February	8.5	15.9	7.5	7.1
April	0.6	2.1	0.6	0.3
June	0.2	0.6	0.2	0.1
September	0.4	1.4	0.4	0.2
November	0.8	2.2	0.8	0.6

transported of 135.5, 1.8, 51.2 and 0.7 t·year^{-1} of Al, Ba, Fe and Mn, respectively. The transport flux for dissolved metal were 0.8 t·year^{-1} of Al, 1.6 t·year^{-1} of Ba, 0.7 t·year^{-1} of Fe and 0.6 t·year^{-1} of Mn.

4.3. Natural Water/Rock-Soil Interactions

The chemical weathering reactions are responsible for the presence of dissolved chemical elements in the river water, in addition to rainwater in the watersheds, which have significant human activities. These reactions are strongly influenced by the type of primary minerals, climate, biosphere and time [19]. Regarding the weathering processes, the Monjolo Grande Stream basin is inserted in a region where the climate (rainfall of 1465 mm and temperature of 22˚C) causes a chemical weathering, with a predominant monosensitization process [18]. This process occurs through partial hydrolysis of the bedrock, with part of the SiO_2 remaining in the weathering profile for the formation of secondary minerals such as kaolinite ($Al_2Si_2O_5(OH)_4$), goethite (FeOOH), among others, and Na, Ca, K and Mg are eliminated.

According to Conceição and Bonotto [20] (2004), it is possible to describe the main mineral phases associated to sedimentary and magmatic rocks found at Monjolo Grande basin as:

- the base of the Corumbataí Formation consists of quartz (SiO_2), hematite (Fe_2O_3), illite ($KAl_2Si_4O_{10}(OH)_2$), kaolinite ($Al_2Si_2O_5(OH)_4$), calcite ($CaCO_3$), microcline ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$), and the top layer of this formation has the presence of quartz, illite, kaolinite and hematite;
- the sandstones of the Pirambóia Formation are composed of quartz and kaolinite. The Pirambóia Formation differs from Botucatu by the presence of illite in the latter;

- quartz, magnetite (Fe_3O_4), augite ($(Ca(Mg)Si_2)_6$ and labradorite ($(Ca, Mg)(AlSi)_2SiO_8$) are the mineral constituents of the diabases of the Serra Geral Formation and of the basic intrusive rocks.

The chemical reactions involving the mineral phases during the water-rock/ interactions indicated that Na is leached by the hydrolysis of albite and labradorite, Ca by the hydrolysis of labradorite and augite, Mg by the hydrolysis of augite and K by the hydrolysis of microcline and kaolinite. The carbonates are dissolved and magnetite, quartz and kaolinite are the primary minerals of the rocks that constitute the Monjolo Grande Stream basin that is not weathered. Thus, the metals (Al, Fe, Ba, Mn and Ni) studied are not leached during the water-rock/interactions process in the current pH conditions characterized in the waters of the Monjolo Grande Stream. Thus, the suspended material to be transported by Monjolo Grande Stream will likely be composed of quartz, magnetite, kaolinite, goethites and other secondary minerals.

4.4. Fertilizer-Effect on Al, Ba, Fe, Mn and Ni Released

Considering the natural water-rock/interactions processes occurring in the Monjolo Grande basin, it is expected that in this watershed the surface waters will have a low concentration of these dissolved elements, confirmed by results of the annual transport fluxes of dissolved Al, Ba, Fe and Mn. If there was only the natural distribution of Al, Ba, Fe and Mn to the waters of Monjolo Grande Stream, a dilution effect of its dissolved concentrations could be expected in the rainy season, meaning that the highest rates would correspond to the dry months, as described earlier for the dissolved transport of Na, K, Ca and Mg by the Monjolo Grande Stream [19]. However, in this study the results demonstrated an inverse dilution effect that should have occurred naturally (**Table 2**). The relationship between the concentration these dissolved metals and the flow at each sampling site suggests another source of contribution, besides the natural one associated with the water/rock-soil interaction processes, for the presence of these metals in the Monjolo Grande Stream waters.

The higher concentrations of dissolved uranium and phosphate in Corumbataí River are also more pronounced during the wet periods when natural and fertilizer-derived U are more easily released from the soil cover [5]. In addition, the ^{226}Ra, ^{232}Th and ^{40}K activity concentrations in phosphate fertilizers and amendments used on sugar cane crops at the Corumbataí river basin increased the natural concentrations of these radionuclides in soils, indicating that the uptake of these radionuclides by sugar cane occurred in the following order: $^{40}K > {}^{226}Ra > {}^{232}Th$ [21]. Another study conducted at the Corumbataí River basin showed that the Cd, Cr, Cu, Ni, Pb and Zn incorporated in phosphate fertilizers and amendments are annually added in the sugar cane crops, but if used in accordance with the recommended rates, they do not raise the concentration levels in soils to hazardous values [3]. However, these metal concentrations in a sediment core increased progressively from 1974 to 2000 due to anthropogenic activities, mainly sugar cane crops, indicating adverse biological effects on the aquatic environment and on organisms living in or having direct contact with sediments.

Sugar cane is extensively cultivated at the Monjolo Grande Stream basin by the alcohol and sugar industry. Phosphate fertilizers and amendments are widely used in this type of agriculture, particularly in tropical regions where weathering of soil nutrients is more intense. The cultivation of sugar cane at the Monjolo Grande Stream basin generally starts in September/October, with application of phosphate fertilizers NPK 5:25:25, *i.e.* 5% of nitrogen, 25% of phosphate and 25% of potassium [22]. The amendments used are limestones, phosphogypsum and KCl. The sugar cane crops require annual applications of phosphate fertilizers and agricultural correctives, with about 600 kg·ha^{-1} of NPK phosphate fertilizers, 2 ton·ha^{-1} limestone, 200 kg·ha^{-1} of KCl and 1.5 ton·ha^{-1} of phosphogypsum [3] [21]. **Table 4** shows the concentration of Al, Ba, Fe e Mn in phosphate fertilizers and amendments used in sugar cane crops at Corumbataí River basin, which is the same used by the farmers in the study area. Using the application rates of phosphate fertilizers and amendments and their Al, Ba, Fe and Mn concentrations (**Table 4**), the estimated annual amount of these metal elements deposited in the soils that cover the Monjolo Grande Stream basin is of 225 kg·ha^{-1} of Al_2O_3, 30 kg·ha^{-1} of BaO, 348 kg·ha^{-1} of Fe_2O_3 and 5 kg·ha^{-1} of MnO.

As presented above, large amounts of N (as fertilizer NPK, being N=NH_4Cl), SO_4^{2-} (as phosphogypsum-$CaSO_4 \cdot 2H_2O$) and K and Cl^- (as KCl and fertilizer NPK, being K=KCl) are applied in the studied area. The comprehension regarding the mobility of all metals must also be associated with these products. The higher K, N and SO_4^{2-} inputs increase the mobility of metals [23] [24] [25] [26] [27]. This increase in heavy metals mobility is attributed to fractionation of these metals to water soluble and/or exchangeable fractions [23] [27] [28]. Thus, the change in the speciation and mobility of metals may be associated not only with the use of fertilizers NPK, but mainly the amendments application in sugar cane crops at Monjolo Grande Stream basin, allowing their lixiviation during the wet period or uptake by sugar cane crops.

The results of this work indicated that the Monjolo Grande Stream could be receiving large quantities of Al, Ba, Fe and Mn from sheet erosion (of the acid

Table 4. Concentration of Al, Ba, Fe and Mn in phosphate fertilizers and amendments used in sugar cane crops at Corumbataí River basin [22].

Description	Al_2O_3	Fe_2O_3	BaO	MnO
	%			
NPK	0.15	1.44	<0.10	<0.10
KCl	0.05	0.14	<0.10	<0.10
Limestone	0.89	0.75	<0.10	<0.10
Phosphogypsum	0.25	0.73	2.00	0.25

soils in the basin, composed mainly of quartz, with low organic matter), associated with phosphate fertilizers and amendments which are extensively used in agricultural activities. Furthermore, a study of the bioavailability of Al, Ba, Fe and Mn using diffusive gradients in thin films (DGT) and a toxicity test have provided additional information on how the increase of these metals affect surface water with benthic and epibenthic organisms.

5. Conclusion

The physical and chemical parameters and the concentrations of Al, Ba, Fe and Mn, in the total and dissolved fractions, showed they were influenced by the seasonal changes in the Monjolo Grande Stream basin. However, over the year this variation remained within the ranges recommended for Class 2 Rivers, according to Brazilian Laws. The dissolved form was the dominant transport for Ba and Mn, while Al and Fe are associated with the suspended particulate fraction. Increasing concentrations of Al, Ba, Fe and Mn due to increased discharge indicated the participation of another source of contribution, besides the natural one associated with the water-rock/soil interaction processes, *i.e.* the application of phosphate fertilizers and amendments in the sugar cane crops in the Monjolo Grande Stream basin. Despite the introduction of dissolved Al, Ba, Fe and Mn derived from agricultural activities, the values quantified in this work indicate that the water of this watershed can be used for public supply. However, the production of sugar cane will increase, given the fuel supply for Brazilian commercial vehicles changing from gasoline to ethanol. Thus, in the Monjolo Grande Stream basin, the currently land used for pasture will likely start producing sugar cane soon, generating a greater demand for phosphate fertilizers and amendments and, consequently, an increase of dissolved Al, Ba, Fe and Mn in the surface waters of the Monjolo Grande Stream. Therefore, a monitoring program of total and dissolved concentrations of these metals in the water of the Monjolo Grande Stream basin should be put into action in order to implement preventive measures to avoid future environmental problems arising from these agricultural activities.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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