Evaluation Of Trace Elements In Water Of An Environmental Protection Area Located In The Lagoa Farm, Monte Belo District, Minas Gerais State, Brazil

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ABSTRACT

Trace elements are present in aquatic environment due to natural geological processes, spilling of industrial and agricultural residues. Aluminum, iron and manganese are important in aquatic oxidation processes, besides being essential micronutrients. The aims of this study was to determine metals (Al, Fe and Mn) in water samples of an environmental protection area, located in the Lagoa Farm, Monte Belo District, Minas Gerais State, Brazil, and to make inferences about its contribution in the ecosystem. Samples of different points were collected from April to September 2004. Physico chemical parameters were analyzed, such as pH, redox potential, temperature and conductivity. The metals were determined by flow injection analysis (FIA) with spectrophotometric detection. The highest concentrations were found in April (Al: 0.621 mg L^{-1}; Fe: 1.667 mg L^{-1}; and Mn: 0.553 mg L^{-1}) and the lowest in June(Al: 0.199 mg L^{-1}; Fe: 0.638 mg L^{-1}; and Mn: 0.059 mg L^{-1}). Thus, a seasonal variation of these elements was verified. Relationships between metals concentrations and redox potential, were also noted.   © 2006 Trade Science Inc. - INDIA

KEYWORDS

INTRODUCTION

Trace elements are chemical elements found in nature at low concentrations, from parts per billion to parts per million. For metallic elements, other terms, as "toxic metal" and "heavy metals", are also found in literature[1].

In this work, aluminum, iron and manganese are focused. These elements occur in natural environment due to geochemicals processes[2] and in the aquatic system are affected by ox reduction conditions, besides being essential micronutrients, i.e., are necessary in physiological processes.

In the aquatic system, trace elements can be absorbed in different proportions by the microorganisms[3]. A meticulous approach allows inferring that the bacteria *Leptothrix sp* uses iron and manganese to get energy through the oxidation of these elements, metabolizing the organic substances and precipitating metals[4,5].

Another form to introduce metals in the environment is through the production of domestic, agricultural and industrial residues, which contribute for water, air and ground pollution[4,6]. In this context, lakes and dams can be affected strongly by diverse environment polluting agents due to its depositary and accumulating characteristics.

The aims of this work were to evaluate trace metals concentration in an environment protection area, in which the insertion of these elements should be essentially defined by natural processes, and to verify its influence on ecosystem.

Study area description

The environment protection area studied is named: "Instituto Sul Mineiro de Proteção Ambiental" and is localized in the Lagoa Farm, Monte Belo District, Minas Gerais State, Brazil. The region chosen is constituted of one spring, a brook, a coffee plantation, a forest, several waterfalls and an artificial dam.

The distance between the extreme points of collection (from the spring to the dam) is about 10 km. The brook crosses a forest and, after, is dammed artificially. The dam was constructed about twenty years ago and has low depth (ca. 2.50 m). The lake formed has about 3 Km^2.

MATERIAL AND METHOD

Samples and collection places

Only dissolved metals were determined. The water samples were collected monthly, submitted to filtration with 0.45 μm membrane and acidified, with one drop (about 0.1 mL) of concentrate nitric acid (12 mol L^{-1}) to each 100 mL of sample, and kept in polyethylene bottles at 4°C in ice bath. The determinations were always made in less than one week.

The samplings were made in six points situated from the spring to the end of the dam. The first collection point was in the spring (21° 25704'S and 46° 16034'W).

After leaving the spring, the brook crosses an area bordered by coffee plantations where the second collection point was chosen (21° 25238'S and 46° 15899'W). The brook goes by a small vegetation area and reaches a decline area with several small waterfalls until disemboguing at the dam. The thirty collection point was selected in a natural pool formed after one waterfall (21° 24890'S and 46° 15697'W). The other collection points were located in the dam (21° 24671'S and 46° 15758'W).

The first collection point in the dam (Dam Pt1) was situated in the entrance of the brook in the dam and had 1.25 m depth approximately. Thus this point had high movement of water. The second point (Dam Pt2) had 2.50 m depth approximately and it was located in the center of the dam, being the depthest place. The third point (Dam Pt3), which had 2.25 m depth approximately, was located in the dam exit. In the three last points, superficial and at 1 m depth samples were collected.

Apparatus

In this work the following equipments were used: analytical balance (SARTORIUS®); peristaltic pump with eight canals (ISMATEC®); polyethylene tubes (d.i. 0.8 mm) for the fluids transport; Tygon® tubes for the fluids propulsion; condutivimeter model Q-405C (QUIMIS®); calomel electrode (ANALYSER®); GPS (GARMIN®); platinum electrode (ANALYSER®); spectrophotometer UV-Vis (FEMTO®) model 482

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equipped with 1.0 cm² flow cells; proportional-commutator 2:3:2 (CENA-USP); interface PCL-711 (ADAVANTECH®); water purification system model Milli-Q Academic (MILLIPORE®); pH-meter (HANDYLAB®).

Reagents and solutions

All the polyethylene and glass flasks were cleaned in 10% v/v nitric acid solution, during at least 24 h, followed by washing with distilled-deionized water.

All the solutions were prepared using analytical reagents, and Milli-Q water (Millipore®, MA) was used throughout, unless otherwise mentioned.

The Al determination is based on chromogenic reaction of the Al with eriochrome cyanine R(Merck®) in micellar medium (cetyltrimethyammonium bromide) (Merck®). Ethylenediamine (Merck®) was used as buffer; the readings were done at 577nm[7].

Al stock solution was prepared by diluting Al nitrate (Merck®) in water. Analytical reference solutions (20–550 μg L⁻¹) were prepared by appropriate dilutions from the stock solution.

The Fe determination is based on 1,10-phenanthroline (Merck®) with ferrous ions reaction. Ascorbic acid (Merck®) as reductor, and acetic acid (Vetec®) plus ammonium acetate (Vetec®) as buffer solution were used. The spectrophotometric signals were measured at 512nm[8].

Fe stock solution was prepared with ferrous ammonium sulfate (Sigma®) and reference solutions (1.0 to 10.0 mg L⁻¹) were prepared by appropriate dilutions from the stock solution.

For Mn determination the following reagents were used: formaldehyde hydroxylamine hydrochloride (Biotec®), nitric acid (Merck®), potassium cyanide (Merck®), sodium hydroxide (Vetec®) sulfuric acid (Merck®). The measurements were done at 455nm[9].

The manganese stock solution was prepared with manganese sulfate in nitric acid (0.25 mol L⁻¹); the reference solutions (0.05 to 1.00 mg L⁻¹) were prepared through appropriate dilutions from the stock solutions.

Flow injection analyses for Al, Fe and Mn

The FIA system, for Al determination, is shown in figure 1. Through the proportional-commutator, the sample was introduced on the carrier stream. In the first confluence, the sample was mixed with a solution composed of the chromogenic reagent and the cationic surfactant (R1), beginning the Al complexation. In the second confluence, the ethylenediamine buffer solution (R2) was introduced, and the signal was recorded at 577 nm.

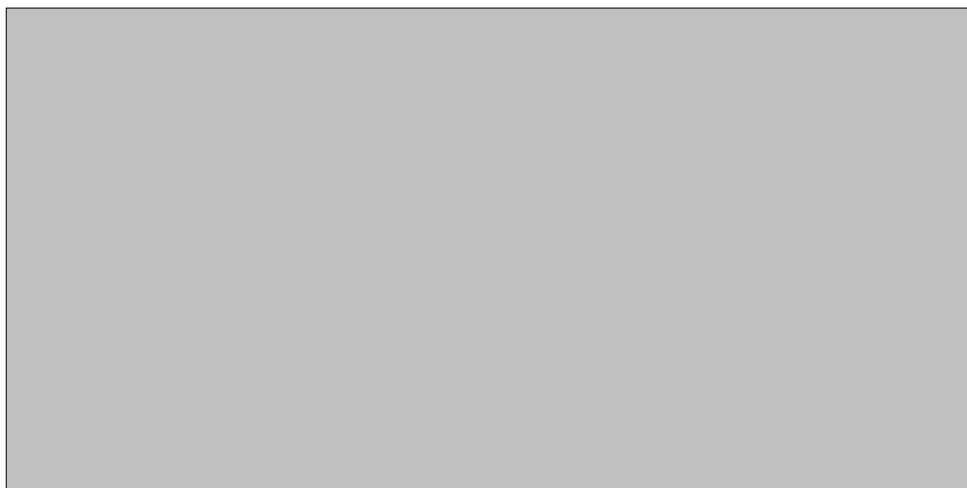The FIA system, for iron determination, is shown

Figure 1: FIA System Module: A = sample; C = carrier flow (water; flow = 3.96 mL min⁻¹); R1 = 0.0050 mol L⁻¹ eriochrome cyanine and 0.025 mol L⁻¹ cetyltrimethylammonium bromide (flow = 0.57 mL min⁻¹); R2 = 0.30 mol L⁻¹ ethylenediamine buffer (flow = 2.96 mL min⁻¹); D = detector (spectrophotometer λ = 577 nm); W = waste; L = 30 cm sample loop (volume = 0.150 mL).
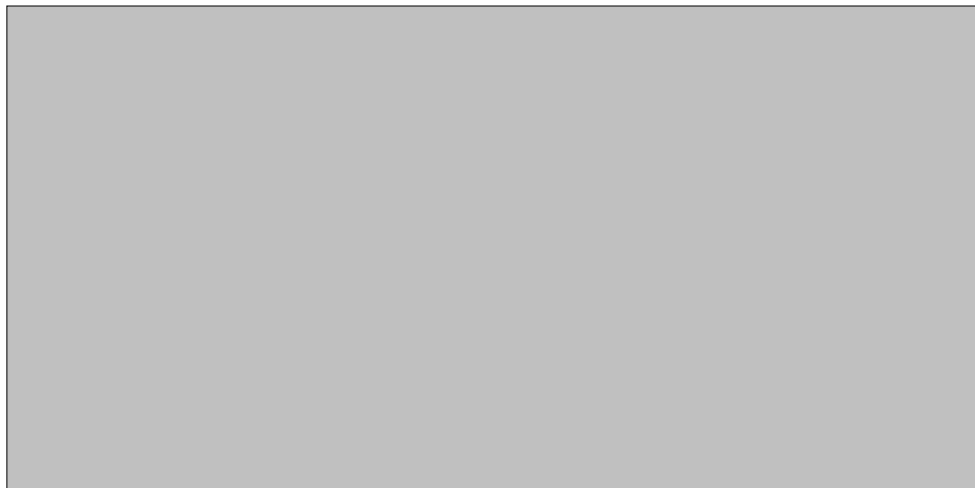
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Figure 2: FIA System Module: A = sample; C = carrier flow (water, flow = 3.96 mL min^{-1}); R1 = 1 % (m/v) ascorbic acid (flow = 1.0 mL min^{-1}); R2 = 0.25 % (m/v) 1,10 phenanthroline (flow = 1.0 mL min^{-1}); R3 = 1.5 mol L^{-1} ammonium acetate (flow = 1.0 mL min^{-1}); D = detector (spectrophotometer λ = 512 nm); W = waste; L = 100 cm sample loop (volume = 0.5 mL).

in figure 2. Through the proportional-commutator, the sample was introduced on the carrier stream. In the first confluence the sample was mixed with ascorbic acid solution. The acetate buffer and phenantroline solutions were mixed in the confluence two and reached the carrier stream into confluence three beginning the chromogenic reaction that was measured with spectrophotometer at 512 nm.

The FIA system, for manganese determination, is showed in figure 3. The sample was introduced in the carrier stream and through the first confluence received the ascorbic acid. The chromogenic reagent formaldoxim 0.5 mol L^{-1} reacted with potassium cyanide 5 % (m/v) in sodium hydroxide 1.0 mol L^{-1} solution in the second confluence and was inserted in the carrier stream through the third confluence for
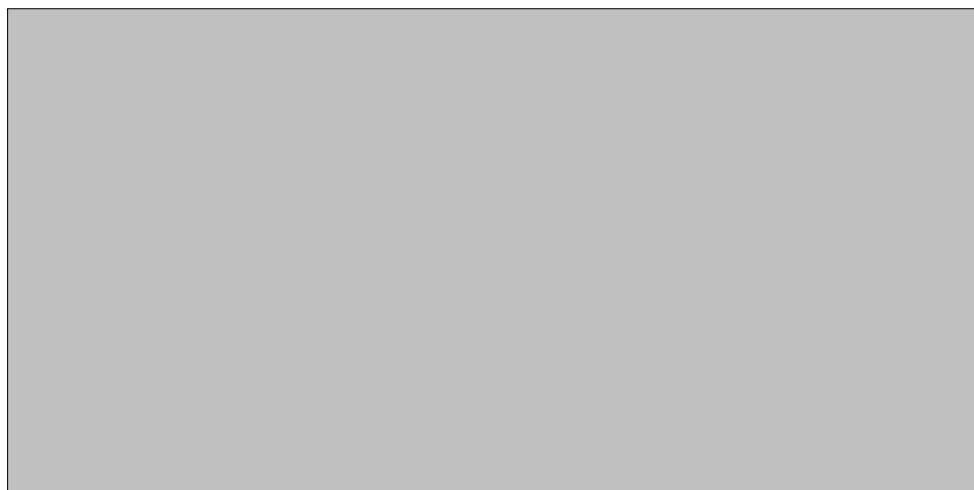

Figure 3: FIA System Module: A = sample; C = carrier flow (water; flow = 5.0 mL min^{-1}); R1 = 3 % (m/v) ascorbic acid (flow = 0.4 mL min^{-1}); R2 = 0.5 mol L^{-1} formaldoxim (flow = 0.4 mL min^{-1}); R3 = 1 mol L^{-1} sodium hydroxide and 5 % (m/v) potassium cyanide (flow = 0.4 mL min^{-1}); D = detector (spectrophotometer λ = 455 nm); W = waste; L = 200 cm sample loop (volume = 1 mL).

spectrofophometric detection at 455 nm.

Measures of the physico chemical parameters

The physico chemical parameters: pH, redox potential (Eh), electric conductivity, temperature, were measured in the instant of the collection with portable equipments.

For the pH measurements, glass electrode combined with saturated calomel reference electrode were used. The calibration was made with two buffer solutions: pH 4.00 and 7.00.

The Eh was measured with platinum electrode and saturated calomel reference electrode combined. The calibration was made with Zobell solution, 184 mV[10].

The conductivity was measured with platinum conductometric cell of 1 cm², the calibration was made with NaCl 30 mg L^{-1} solution (74.0 μS/cm).

RESULTS AND DISCUSSION

Analytical parameters

The figures of merit for the metals determination are shown in TABLE 1. The three methods,

TABLE 1: Figures of merit.

Figure of merit	Al	Fe	Mn
Sensitivity (L mg^{-1})	0.365	0.066	0.117
Correlation coefficient	0.998	0.997	0.999
LOQ (mg L^{-1})	0.017	0.074	0.059
LOD (mg L^{-1})	0.005	0.022	0.018

used in this work, had satisfactory results. Only in two samples it was not possible to determinate the aluminum and manganese concentrations.

Physico chemicals parameters

Some physico chemicals parameters, such as pH, redox potential, conductivity and temperature, can influence the metals concentration in aquatic environments, as follow:

In this work, the pH values varied between 6.24 and 6.65 that are adequate for solubilization of the studied elements because in acid medium, the metals tend to remain dissolved[5].

The measured Eh values, which varied between 116.3 and 165.0 mV, are characteristic of oxidants environments that lead the ions to a more oxidant state and it explains the higher concentration of iron and manganese[4].

The temperature variation was a typical seasonal characteristic of the tropical region climate of the south hemisphere, where the temperatures are raised in the spring and summer, and low in the fall and winter. It is also known that the temperature increase lead to a higher quantity of metals dissolved in solution. The concomitant increase of temperature and metals concentration can be seen comparing figures 4 and 6.

Regarding conductivity, it is proportional to ionic concentration[4] and this can be verified from April to August, to compare the figures 4 and 6, only in September this relation can not be verified.
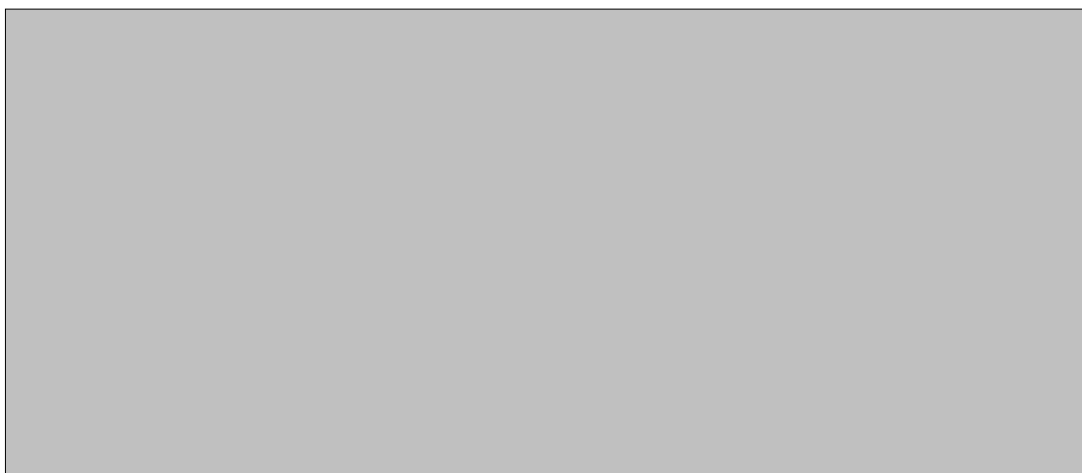

Figure 4: Potential redox (mV), conductivity (μS cm^{-1}), temperature (^{o}C) and pH monthly averages.
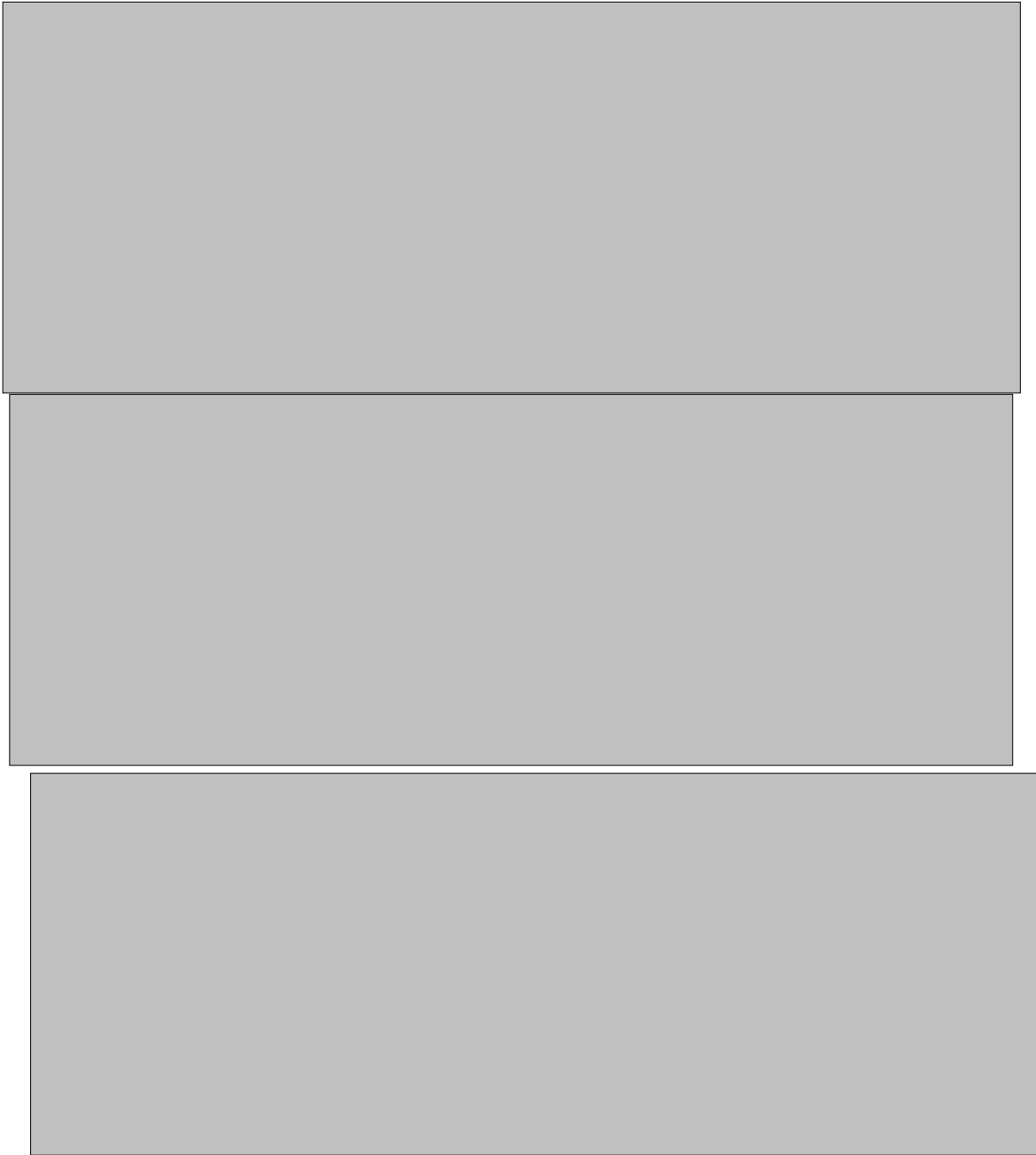
Figure 5: Aluminum, iron and manganese concentrations (mg L⁻¹) for each sampling point.

Concentration of trace elements

The metal concentrations found in this work (TABLE 2) are in agreement with that are obtained in the not polluted environment regions[6].

Correlations among the metals in study were verified. The highest correlation was between aluminum and iron (r=0.976), while between iron and manganese (r=0.864) was higher than that one between aluminum and manganese (r=0.835). The similarity between aluminum and iron had been observed in other articles[11,12]. They suggest that those metals, associated to the fine-grained material of mineral origin, are distributed evenly at the place studied by them.

Usually, in waters with pH between 5 and 8, the iron amount was between 0.05 and 0.20 mg L⁻¹, while that ones of manganese were between 0.01 and 0.85

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TABLE 2: Metal concentrations values expressed as average ± standard deviation in each point of collection from April to September 2004.

Collection points	Al	Fe	Mn
Spring	0.135 ± 0.139	0.353 ± 0.462	0.084 ± 0.092
Stream	0.197 ± 0.069	0.441 ± 0.070	0.089 ± 0.018
Waterfall	0.192 ± 0.110	0.429 ± 0.269	0.094 ± 0.081
Dam Pt1 (surface)	0.444 ± 0.131	0.997 ± 0.360	0.189 ± 0.179
Dam Pt1 (1m of depth)	0.544 ± 0.184	1.250 ± 0.370	0.196 ± 0.104
Dam Pt2 (surface)	0.484 ± 0.177	1.074 ± 0.400	0.213 ± 0.181
Dam Pt2 (1m of depth)	0.630 ± 0.271	1.546 ± 0.844	0.259 ± 0.184
Dam Pt3 (surface)	0.472 ± 0.154	1.181 ± 0.555	0.252 ± 0.260
Dam Pt3 (1m of depth)	0.595 ± 0.230	1.418 ± 0.745	0.263 ± 0.242

mg L^{-1}[5]. However, higher levels in some lakes were found due to the presence of organic material or dissolved humic compounds, becoming with a yellow-brownish color. In this work, in July, were found concentrations that varying from 0.10 to 0.79 mg L^{-1}, 0.15 to 1.86 mg L^{-1}, and 0.06 to 0.82 mg L^{-1}, for aluminum, iron and manganese, respectively. The coloration yellow-brownish was observed in those samples.

A space distribution of metals concentration can be observed (Figure 5). The concentration of the three metals in the brook increases from the spring to the dam. Moreover, the highest metal concentrations were found in the dam because of the lentic environment, i.e., an environment where trace elements were deposited due to the low mobility of water.

Other contributing factors for the metals concentrations are the relief and the hydrographic characteristics. The relief is marked by an accented declivity, where waterfalls are formed. The forest, which surrounds the dam, and some brook stretches may be considered as contributors in the metals addition to the lacustrine ecosystem. It is known that metals as Fe and Mn have the capacity to complex with organic composites or the forests debris[5].

A season behavior of the metals concentrations could be observed (Figure 6). The highest metal tenors are found in April, while June presents the minors. In the same way the highest and lowest pluviometric rate are obtained in April (651.9 mm) and June (55.8 mm), respectively[13]. Thus there is evident correlation between metals concentrations and rain intensity. The metals entries in the rivers are resultant of rain that leaches the ground[14].
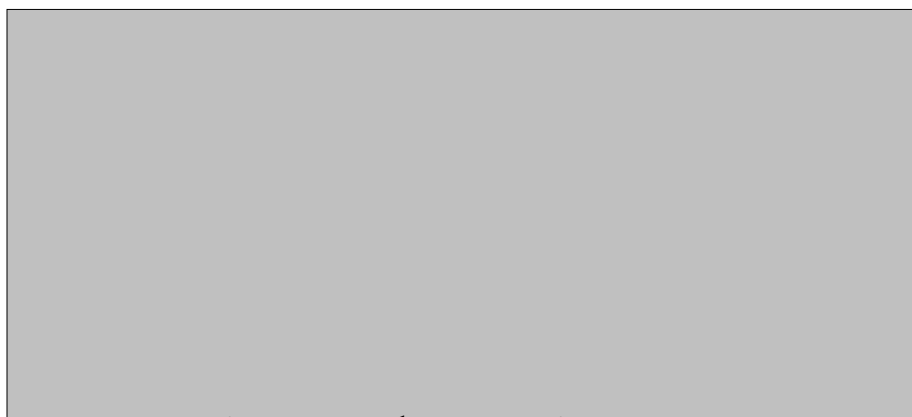

Figure 6: Month concentrations average.

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CONCLUSION

The metal concentration had increased from the spring to the dam of the brook because of geological processes such as leaching of the soil.

Seasonal variations of metals concentrations occur due mainly to pluviometric rate: were observed higher concentrations during the rain period and lowest during the dry period.

The conductivity, redox potential, temperature and pH were characteristics of natural environment and had presented correlation with metal tenors.

The environment researched can be considered one reference area for comparative studies because the sources for metals concentrations are natural and, therefore, there are no anthropic influences.

ACKNOWLEDGES

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