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Monitoring metals in surface water of a small watershed in Amazon region

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ABSTRACT: In this study authors aimed to monitor the quality of surface water in the Caiabi watershed regarding the concentration of metals. In the watershed area, the land use and occupation occurs mainly for agricultural activities, with the adoption of various managements in the production system and agrochemical applications throughout each season. Water samples were collected in two stages, the first from July 2012 to June 2013, and the second in two campaigns, one in September 2014 and another in February 2015. The methodologies used followed the procedures described in Standard Methods for the Examination of Water and Wastewater. The results of monitoring in the first stage showed that Cu concentrations were not detected; Fe and Mn were below the maximum levels permitted by CONAMA Resolution No. 357/2005, whereas Zn, Cd, Pb and Ni concentrations were higher than the recommended. In the second stage there was the same situation only for Fe and Mn. Thus, it was found that the sampling frequency of the second stage was not sufficient to represent the water quality towards metal concentration.

Keywords: water quality, agrochemicals, agricultural activities, toxic metals.

Monitoramento de metais em água superficial de microbacia hidrográfica na região Amazônica

RESUMO: Neste trabalho teve-se por objetivo monitorar a qualidade da água superficial da microbacia hidrográfica do rio Caiabi em relação a concentração de metais. Na área da microbacia, o uso e ocupação do solo ocorre basicamente por atividades agropecuárias, com a adoção de diversos manejos do sistema de produção e com aplicações de agroquímicos ao longo de cada safra. As coletas de água ocorreram em duas etapas, sendo a primeira de julho de 2012 a junho de 2013, e a segunda, em duas campanhas, uma em setembro de 2014 e outra em fevereiro de 2015. As metodologias utilizadas seguiram os procedimentos descritos no 'Standard Methods for the Examination of Water and Wastewater'. Os resultados do monitoramento na primeira etapa mostraram que concentrações do elemento Cu não foram detectadas, Fe e Mn ficaram abaixo dos valores máximos permitidos pela Resolução CONAMA n° 357/2005, enquanto as concentrações de Zn, Cd, Pb e Ni ficaram acima. Na segunda etapa constatou-se o mesmo comportamento observado na primeira etapa, apenas para o Fe e Mn. Sendo assim, verificou-se que a frequência das amostragens da segunda etapa não foram suficientes para representar o comportamento da qualidade da água em relação à concentração de metais.

Palavras-chave: qualidade da água, agroquímicos, atividades agropecuárias, metais tóxicos.

1. INTRODUCTION

Surface water is rarely free from contamination, even in water basins with little or no human presence (AZEVEDO, 2006). The different processes that take place in a basin depend on the characteristics of the site where it is located (ALVARENGA et al., 2012). Rivers are complex systems characterized as natural sinks of adjacent drainage areas, which in principle form the watersheds. The complexity of these river systems is due to the size and shape of drainage basins, the local climate (TOLEDO and NICOLELLA, 2002), the manner of use, soil types and topography, existing local vegetation, the deforestation and the presence of cities exerting great pressure on natural resources that make up a river basin, reflecting on river water quality from its source to its mouth (PARANÁ, 2013).

According to Tundisi and Tundisi (2010), vegetation plays a crucial role in regulating biological cycles and biogeochemical watersheds, because its structure reduces erosion and alters the chemistry of surface water and groundwater.

This ground cover has the function of dissipating the kinetic energy of the direct impact of rain drops on the surface, decreasing the initial disaggregation of soil particles and thus the concentration of sediment in runoff, as it represents a mechanical obstacle to the free flow of surface water (SILVA et al., 2005), reducing the risk of diffuse pollution.

Pereira (2004) describes that there are two forms of pollution of water resources. These can be classified into specific, when released in the water body at a specific point, or diffuse, when pollutants reach the water body at random, thus being difficult to control.

Agriculture is classified as an activity that generates diffuse pollution, mainly due to the large areas used for the activity.

The main pollutants arising from these activities are agrochemicals (synthetic fertilizers and pesticides), which when used in excessive amounts in crops can pollute soil and water from rivers and poison and kill many living components of ecosystems (PEREIRA, 2004). Some studies show that pesticides can be found in groundwater (GOMES et al., 2001) and superficial water (FREIRE et al., 2012).

In addition to the key elements, many pesticides and fertilizers have metals as impurities in their formulations, which, in contact with soil, can contribute to environmental contamination. Gimeno-Garcia et al. (1996) reported the presence of iron (Fe), manganese (Mn), zinc (Zn), lead (Pb) and nickel (Ni) in herbicides applied to the soil and concentrations of cadmium (Cd), copper (Cu) and zinc (Zn) in inorganic fertilizers. Goncalves Junior et al. (2000) also mention the presence of chromium (Cr) in fertilizers.

However, natural conditions can also supply metals to aquatic ecosystems, such as the weathering of rocks, which provides metal to the soil-water system.

The movement of metals in the soil-water system will depend on their mobility. Their degree of mobility will be determined by soil properties, such as levels and types of clay, pH, capacity of cation exchange, organic matter content and others, which influence the reactions of adsorption/desorption, precipitation/dissolution, complexation and oxi-reduction (OLIVEIRA and MATTIAZZO, 2001).

The topography of the area and its agricultural use have a marked effect on the accumulation of metals in the soil. The lower the slope and the more frequent the use of chemicals, the greater the metal concentration in the surface layers of the soil (RAMALHO et al., 2000).

It is noteworthy that agrochemicals are not the only sources of metals in river basins. Industrial effluents and sewage can be important sources of metals (SANTOS and BONFIM DE JESUS, 2014; PINTO et al., 2009). In addition, trace of metals are also present in the chemical composition of most soils in the form of carbonates, oxides, sulfides, or salts, but in quantities that may vary between different types of soils (HE et al., 2005; FADIGAS et al.,2002). These traces, arising from the weathering of rocks and soil, can be carted to the watercourse by surface runoff.

It is essential to identify locations where water contamination may occur with greater ease, indicating where priority measures of protection and control should be applied, assisting in the management of water resources, to effect disciplinary actions in the use and occupation of land (BARBOSA et al., 2011).

According to the above, this work aimed to evaluate the quality of surface water of Caiabi watershed with respect to cadmium (Cd), lead (Pb), copper (Cu), iron (Fe) , manganese (Mn), nickel (Ni) and zinc (Zn), comparing them to the maximum amounts permitted by Resolution No. 357/2005 of the National Environment Council - CONAMA, for class 1 freshwaters, relating them as to seasonal variations and the use and soil occupation.

2. MATERIAL AND METHODS

2.1. Study location

The study location was the Caiabi watershed, located in the north of Mato Grosso state, in the coverage area of the Legal Amazon, with drainage area belonging to the municipalities of Vera and Sinop (Figure 1). Its main water course is the Caiabi river, with approximately 51 km long, with its confluence happening in the Teles Pires river, in the border region between the cities of Sinop-MT and Sorriso-MT. The Teles Pires river is an important water course for that region and contributes for the Amazon basin.

The state's northern region has a tropical climate, according to the Köppen-Geiger climate classification, with two well-defined seasons. The rainy season extends from October to April and the rest of the period is characterized as dry, with low levels of rainfall; in a few months, there is no rainfall at all. The annual rainfall is about 2,000 mm (SOUZA et al., 2013).

Soil use and occupation is basically held by agricultural activities, with the production of grain and livestock. The form of planting is performed by various managements in production systems, but with of applications of significant amounts of pesticides and fertilizers during each harvest. Rural roads and carriers are present throughout the basin. Part of the urban area of the municipality of Vera is located in the catchment area of the Caiabi watershed; however, there is a certain distance from this channel, not contributing directly to waste dumps or sewage.

The Caiabi river has marginal native forest along its entire course, except to its source. This forest serves as a barrier to sediment input originating from the basin soils and also reduces the erosion of margins, as the vegetation roots act as a means of support (ANDRIETTI et al., 2016).

2.2. Sampling, transport, preservation and analytical methods

The collection of surface water was conducted in two stages. In the first stage, samples were taken during 12 consecutive months between July 2012 and June 2013, at five points along the river and in the morning. In the second stage, sampling was conducted in two campaigns, one in September 2014 (dry season) and another in February 2015 (rainy season), at two points and in the morning. Water sampling sites were defined in terms of logistics and accessibility during the rainy and dry seasons. The points were named P1, P2, P3, P4 and P5. P1 was at the river spring, P5 was near the mouth and the other points were distributed along the Caiabi river (Figure 1). The collection, transportation, preservation and determining the concentration of elements in the water samples were performed in accordance with Standard Methods for the Examination of Water and Wastewater (APHA, 2012). The samples were stored in glass bottles, previously prepared, acidified with nitric acid, placed in insulated containers and held to 8° C until arrival at the laboratory. Analyses of metals were carried out in the Waste Treatment Laboratory and in the Integrated Laboratory for Research in Chemistry - Lipeq, at the Federal University of Mato Grosso, at Sinop campus.

The preparation of surface water samples to determine the concentration of total metals, Mn, Ni, Zn, Cd and Pb, was

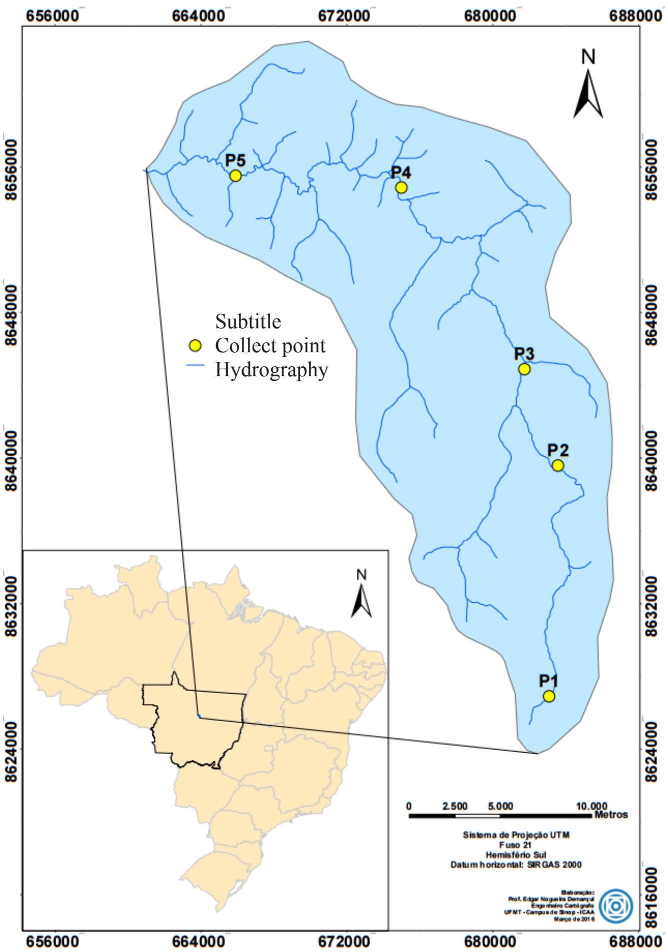


Figure 1. Location of the Caiabi watershed and collection points.
Figura 1. Localização da microbacia hidrográfica do rio Caiabi e dos pontos de coleta.

made by hot acid digestion, and samples to determine the concentration of dissolved metals, Fe and Cu, were vacuum filtered on cellulose acetat membrane with 0.45 µm pore diameter, and acidified to pH less than 2.0. After the preparation of the samples for total metals and dissolved metals, all samples were kept frozen at 4 °C. The determination of the concentration of metals was carried out by atomic absorption spectrometry with atomization in flame air and acetylene gas.

2.3. Statistical analysis and legislation

The concentration values of the metals found in the water samples were represented by descriptive statistics with box-plot graphics used to evaluate the distribution of the data, using the R 3.2.2 program (2015). For the evaluation of differences between the averages between seasons, points and in the interaction between points and seasons, analysis of variance was performed. In cases where difference was identified, researchers used the Tukey test at 5% significance for the comparison of averages.

The results of environmental monitoring were discussed in the light of Resolution No. 357/05, of the National Environment Council - CONAMA. As the Caiabi river has no specific classification, legislation indicates the adoption of Class 2. However, it was framed in class 1 of freshwaters for the watershed region has recent use and occupancy, with less than 50 years. Also, this understanding arises from the justification that, when there will be a framework of water bodies by the competent bodies, there are basic conditions that they will be classified in Class 1.

This class indicates that waters may be intended for supply for human consumption after simplified treatment; for protection of aquatic communities; for primary contact recreation; for irrigation of vegetables and fruits, and for protection of aquatic communities in Indigenous Lands.

3. RESULTS AND DISCUSSION

3.1. First step - Monthly monitoring

The analyzes showed that the Cu was not detected in Caiabi river in the water samples collected between the years 2012 and 2013. The non-detection of Cu in surface waters was not expected, since Cu is found in inorganic fertilizers, and these are applied in agricultural areas on a regular basis. The non-detection of this element may be due to the low mobility of Cu in the soil, accumulating on the surface thereof (OLIVEIRA et al., 2002). Gonçalves et al. (2015) also reported non-detection of Cu in the waters of Cuiaba and Sao Lourenco rivers (Class 2), whose basins have agricultural activities similar to those of the present study.

The elements Zn, Pb, Cd, Fe, Ni, and Mn were detected in the surface water of Caiabi river. For the Mn, the results obtained in the 12 months of monitoring showed that its concentration ranged from non-detected (42% of the collected samples) to a maximum of 0.028 mg L^{-1} found in the source of the river. Figure 2 shows the behavior of Mn concentration in the five monitored points. It is also observed that all the values obtained in monitoring present concentration of that element below the maximum levels permitted by CONAMA Resolution No. 357 of 2005, which is 0.10 mg L^{-1}.

The analysis of variance for Mn showed a significant difference in the concentrations found between points and seasons. Through the average test, as for the points, there was significant difference in the point P1 in relation to other points (Table 1), featuring higher concentration at the source of Caiabi river, but still below the maximum allowed by law, which is 0.10 mg L^{-1}. Surrounding the Caiabi river's source, there was cultivation of soybean and corn, and its spring was unprotected and degraded, but in recovery process.

In relation to the seasons, it was found that in the dry season, from July 2012 to September 2012 and from May 2013 to June 2013, Mn showed a mean concentration of 0.010 mg L^{-1}, whereas in the rainy season the concentration was 0.007 mg L^{-1},

Table 1. Average concentration of manganese (Mn) in the first stage of monitoring (2012/2013) in monitored points in surface water of Caiabi watershed (mg L^{-1}).
Tabela 1. Concentração média de manganês (Mn), na primeira etapa de monitoramento (2012/2013), nos pontos monitorados na água superficial da microbacia hidrográfica do rio Caiabi, mg L^{-1}.

Point	Mean concentration of Mn (mg L^{-1})
1	0.014 a
2	0.008 b
3	0.006 b
4	0.006 b
5	0.007 b

Averages followed by the same letters indicate no significant difference at 5% significance.

that is, there was a reduction of the Mn concentration from the dry season to the rainy season, probably as a result of increased river flow and consequent dilution of its concentration.

Manganese occurs naturally in soil and can also be found in pesticides used on crops. It has considerable mobility in soil, and in surface water bodies, its concentration rarely exceeds 1.0mg.L^{-1}. It is often found associated to the Fe, but its oxidation is more difficult and, unlike Fe, simple aeration is not enough for its removal. The Fe oxidation forms precipitate of iron hydroxide, which is of easy sedimentation. On the other hand, forms of manganese dioxide resulting from oxidation of this metal appear as very small flakes, of hard sedimentation. These can be involved by Fe hydroxide flakes, a fact that favors its sedimentation. (LIBANIO, 2010). In this sense, there was no impairment of water quality by this metal in Caiabi river water. Similar results for Mn were also reported by Azevedo (2006) who, in a study on the quality of the surface water of the Amazon River in a lowland rural area in the Amazon region, found that the Mn concentrations were below the maximum levels allowed by applicable law.

For the Ni element, there was oscillation in its concentrations, ranging from non-detected (27% of samples) to the maximum amount of .089 mg L^{-1}, which occurred in a single event, during the end of the dry season, in September 2012, the month in which the measurement of the minimum flow in the river (4.68 m^3 s^{-1}) was detected, at point P3, and it was above the maximum allowed by Resolution No. 357/2005 of CONAMA (0.025 mg L^{-1}). This fact may have its origin in the agricultural activities surrounding that particular point, as it is located after the confluence of two rivers, and this value may be related to the other course of the river, which was not monitored. It was found that the remaining detected amounts were below the maximum allowed by the same resolution, as shown in Figure 2.

The result of analysis of variance showed that there was no difference between the concentrations between points, between seasons or interaction between points and seasons, i.e., the concentration was seasonal and spatially constant. Ni can be found naturally in the soil, but in very low concentrations. It can also be found in phosphate fertilizers, according to Santos and Jesus Bonfim (2014). It has low mobility in the soil (OLIVEIRA et al., 2002), accumulating on its surface. However, this river has native marginal forest throughout its course, which serves as a barrier to sediment input arising from the basin soils, reducing erosion of margins, with exception to its source (ANDRIETTI et al., 2016). Thus, despite the Caiabi watershed region has its use and occupation basically linked to agriculture, with fertilizer applications over the crops, there was no impairment of water quality by this metal, except for P3 in a single event, which should be further investigated.

Oliveira Filho et al. (2012), in monitoring the quality of surface water of Southwestern Parana basin, compared results upstream (area of agricultural use) and downstream (area of intense urban occupation) of Santa Rosa river and also reported Ni concentrations below the maximum value allowed by the CONAMA resolution No. 357/2005 for class 2 rivers.

For Zn element, it was observed that the concentrations found ranged from non-detected (in 63% of samples) to a maximum value of 4.5 mg L^{-1}, in point P4 (near the mouth of the Caiabi river) (Figure 3). Point P1 (source of the Caiabi river) had only one value slightly above the maximum allowed by Resolution No. 357/2005 of CONAMA, which is 0.18 mg L^{-1}. For all other points the concentration values were above the

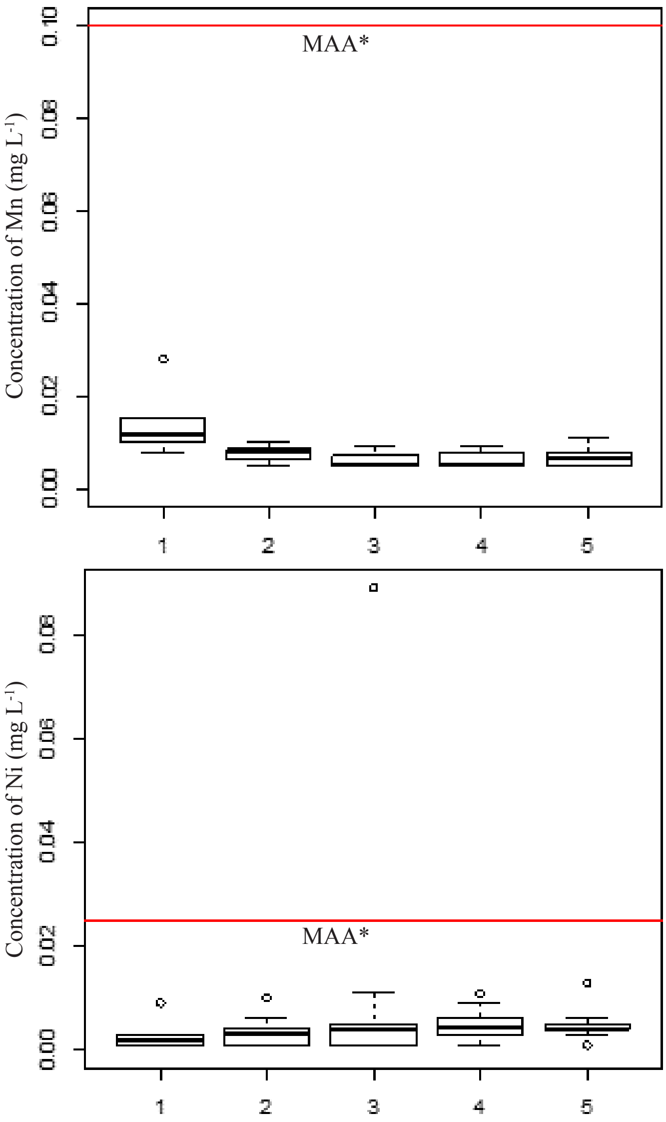


Figure 2. Variation of the concentration of Mn and Ni in the first stage of monitoring, along the watershed of the Caiabi river (MAA* Maximum Amount Allowed by CONAMA Resolution No. 357/2005, which is 0.1 and 0.025 mg L^{-1} respectively, for Class 1 rivers.)

Figura 2. Variação da concentração de Mn e Ni, na primeira etapa de monitoramento, ao longo da microbacia hidrográfica do rio Caiabi (VMP* Valor Máximo Permitido pela Resolução CONAMA n° 357/2005, que é de 0,1 e de 0,025 mg L^{-1} respectivamente, para rios de Classe 1).

maximum allowed by the resolution.

Although it appears that there was an increasing trend in Zn concentration values as for the points, the analysis of variance showed no difference in concentration between points, between seasons and even in interaction between points and seasons. Zn concentrations above the maximum permitted by Resolution No. 357/2005 of CONAMA (Class 2) in surface water were also found by other authors such as Santos and Jesus Bonfim (2014), who attributed the value found to the use of fertilizers and pesticides in crops, in the same way of Ramalho et al. (2000). This same situation may be occurring in the Caiabi watershed, where pesticides and fertilizers used in agriculture may be coming to the river bed by the processes of superficial runoff and river recharge by groundwater.

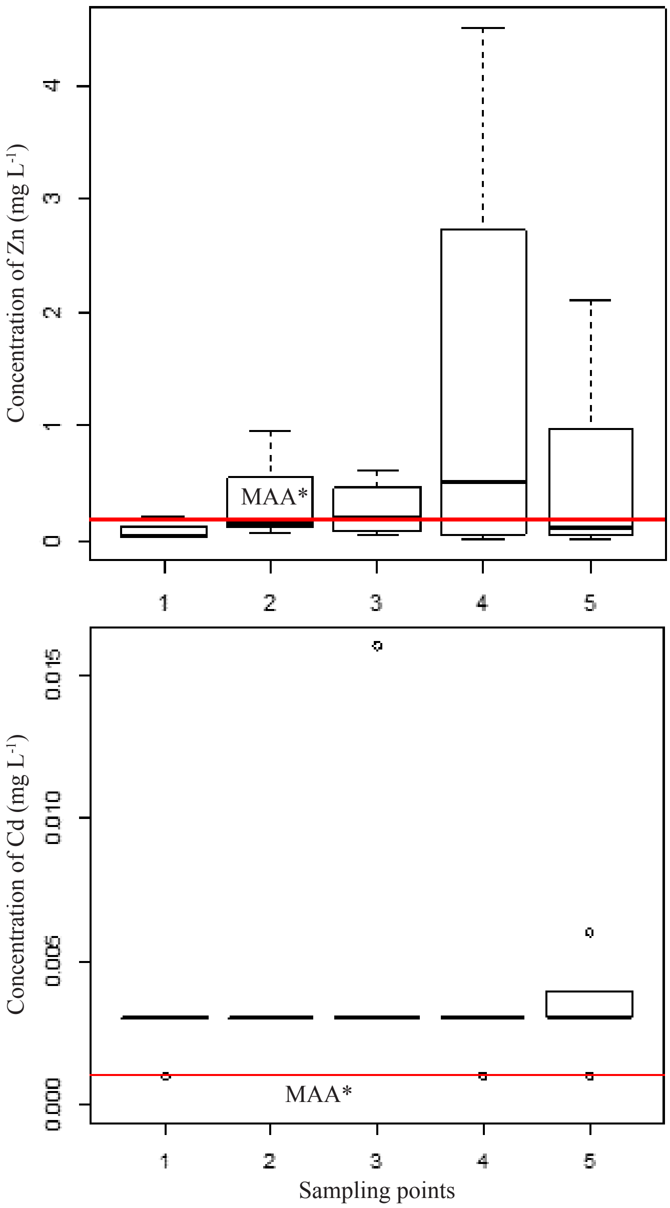


Figure 3. Variation of Zn and Cd concentration in the first stage of monitoring, along the Caiabi watershed (MAA* Maximum Amount Allowed by CONAMA Resolution No. 357/2005, which is 0.18 and 0.001 mg L^{-1} respectively, for Class 1 rivers).
Figura 3. Variação da concentração de Zn e Cd, na primeira etapa de monitoramento, ao longo da microbacia hidrográfica do rio Caiabi (VMP* Valor Máximo Permitido pela Resolução CONAMA n° 357/2005, que é de 0,18 e de 0,001 mg L^{-1} respectivamente, para rios de Classe 1.)

The values of Cd concentrations over the monitoring year were from non-detected, in 60% of samples, to a maximum of 0.016 mg L^{-1}, found at point P3, in September, at the end of the dry season. The values found were all above the maximum permitted by Resolution No. 357/2005 of CONAMA, which is 0,001 mg L^{-1} (Figure 3). As Cd can be originating from the application of agrochemicals, its presence in surface water may be due to the rainy season, which may have dragged the element to the river directly, or due to the possibility of this element is present in groundwater (EIDT, 2015, unpublished data) being carried to the river through the water recharge process. If Cd concentrations continue to rise due to human additions, there may be future toxicity risks of this metal in intensive cultivation soils (RAMALHO et al., 1999), and consequently water contamination, due to carriage and leaching caused by rainwater, introducing this element in the food chain.

The analysis of variance for Cd showed no difference between the values regarding the monitored points, nor regarding the seasons and nor in the interaction between these two factors.

Ramalho et al. (2000), in assessing the water contamination of Caetes watershed, also found Cd concentrations above the maximum allowed by law and attributed the results to the flow of soil by the action of rain to water sources and it may be derived from pesticides and fertilizers for agricultural use.

Pb concentrations ranged from non-detected (in 72% of analyzed samples) to the maximum amount of 0.023 mg L^{-1} found at point P4 (Figure 4). Metal concentrations showed

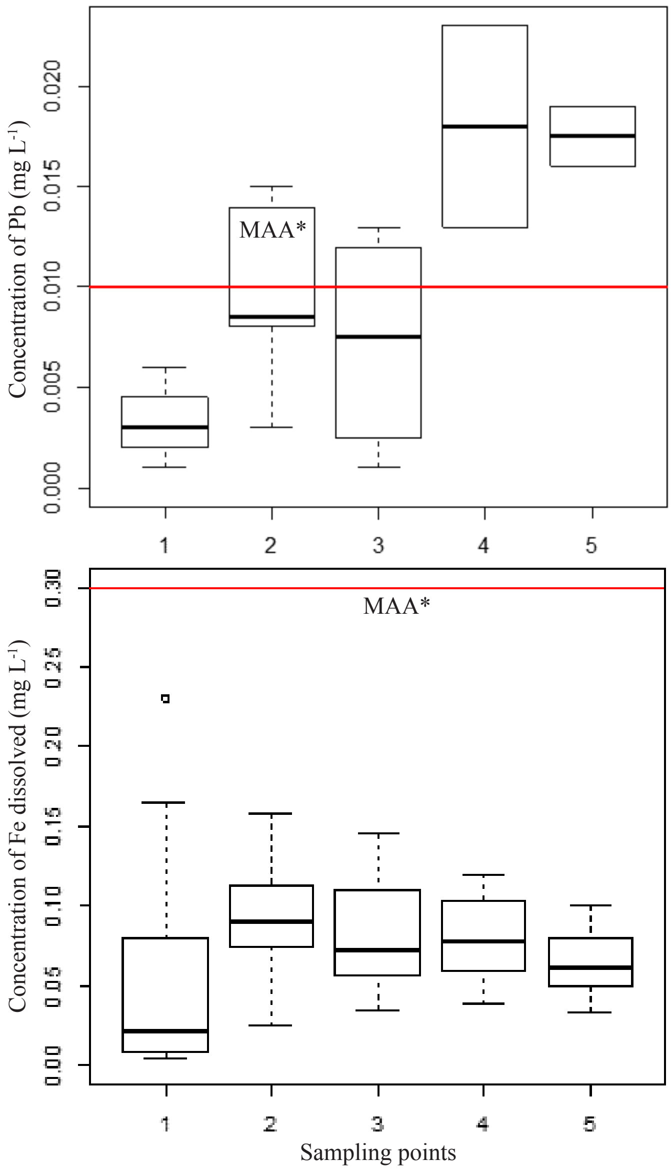


Figure 4. Variation of dissolved Fe and Pb concentration in the first stage of monitoring, along the Caiabi watershed (MAA* Maximum Amount Allowed by CONAMA Resolution No. 357/2005, which is 0.01 mg.L^{-1} and 0.3 mg.L^{-1} respectively, for class 1 rivers).
Figura 4. Variação da concentração de Pb e Fe dissolvido, na primeira etapa de monitoramento, ao longo da microbacia hidrográfica do rio Caiabi (VMP * Valor Máximo Permitido pela Resolução CONAMA n° 357/2005, que é de 0,01 e de 0,3 mg L^{-1} respectivamente, para rios de Classe 1).

that the monitored points showed concentrations above the maximum allowed by law, which is 0.010 mg L^{-1}, except for the P1, the source of the river. It seems that there is a tendency of higher metal concentrations in points P4 and P5, next to the river mouth; however, according to the analysis of variance, this was not confirmed, demonstrating the equality between all values in points, in seasons and in the interaction between these.

According to Gonçalves Junior et al. (2000), if Pb is not absorbed by plants, it can leach out easily in the soil profile. Other authors, in evaluating water quality in watersheds found Pb concentrations above the maximum allowed by Resolution No. 357/2005 of CONAMA, as Gonçalves et al. (2015), and Santos Bonfim Jesus (2014), Ramalho et al. (2000), Freire et al. (2012). All attributed the results to the flow of soil by the action of rain to rivers and it may be from various sources, including pesticides and fertilizers for agricultural use. Santos and Jesus Bonfim (2014) also raise the possibility that Pb can be found in the atmosphere in the form of particles, disposed relatively quickly by dry and wet deposition; but small particles can be transported over long distances and may contribute to contamination of rivers.

Thus, since there were no observed differences of Pb concentration in the water of the Caiabi river, both the supply of groundwater to the river as the superficial runoff and even some atmospheric contribution may have provided certain amount of Pb to surface waters.

The values found for Fe on the monitored period ranged from non-detected (in 15% of samples) to a maximum of 0.23 mg L^{-1}, found in the river mouth (Figure 4). All Fe concentration values were below the maximum permitted by Resolution No. 357/2005 of CONAMA, which is 0.30 mg L^{-1}. That is, it was found that despite the soil of the region is rich in iron oxide, this metal is not in excess in dissolved form in surface water of Caiabi watershed. According to Libanius (2010), surface aeration of the river due to wind action oxidizes Fe and causes it to precipitate and sediment on the bottom of its bed, which may explain the absence of this metal in the Caiabi river.

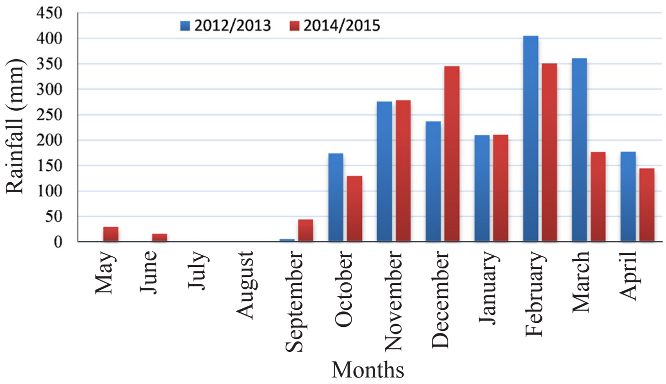
The analysis of variance showed, as well as to some other elements, that there was variability in Fe concentration values, but on average, the values did not show differences between points, seasons and interaction between points and seasons.

Based on the results of the annual monitoring, due to the absence of significant differences of the elements monitored between points, seasons and in the interaction between points and seasons, and according to results of analysis of variance, except for Mn, which had a significant difference only between seasons, researchers concluded that monitoring in only two points, at the source and at the mouth of Caiabi river, and only two samples throughout the year, one in the dry season and another in the rainy season, could be enough to show the behavior of the concentration of metals in the watershed as a whole. From this result, the second stage of monitoring of metals in the Caiabi river was carried out between 2014 and 2015.

3.2. Second stage - Monitoring at two points in two seasons

Figure 5 shows the rainfall data for the months of 2012/2013 and 2014/2015. Variations in rainfall can lead to changes in the amount of sediment and in the water volume of the channel.

Comparing the rainfall data between the first stage of monitoring (2012/2013) and the second stage of monitoring (2014/2015), it was observed that the rainy season is made up



Source: UFMT Weather station - Campus Sinop, 2015.

Figure 5. Rainfall data of the two stages of monitoring in the watershed of the Caiabi river.

Figura 5. Dados de precipitação das duas etapas de monitoramento na microbacia hidrográfica do rio Caiabi.

of seven months, from October to April, and the dry season is made up of five months, from May to September, which confirms data found by Souza et al. (2013). It was also observed that in the second stage there was always less or equal rainfall during the rainy season, compared to the same month of the first stage, except for the month of December/2014, whose difference was 108 mm extra in the second stage. However, there was no sample collection for monitoring water quality in that month. In the dry period, there was greater rainfall in the second stage of monitoring, totaling 89 mm compared to 5 mm from the first period of monitoring. However, this precipitation occurred sparsely, not interfering significantly in increasing concentrations of the monitored elements. In the first stage of monitoring there was a total precipitation of 1845 mm and in the second stage of monitoring the total precipitation was 1724, with a difference of 121 mm extra in the first stage.

Flow measurement was performed only in point P5, near the mouth of Caiabi river. In the first stage, river flow measurements were not conducted in February, May and June. In the other months, the measurement was performed, reaching minimum, average and maximum values of 4.68, 7.97 and 14.06 $m^3 s^{-1}$ respectively. In the dry season, the average flow rate was 5.63 $m^3 s^{-1}$, and in the rainy season, the average flow rate was 9.14 $m^3 s^{-1}$. In the second stage, the flow rate was measured only in the months of collection. In September 2014, during the dry season, the monthly average flow was 6.06 $m^3 s^{-1}$ and in February 2015, during the rainy season, the monthly average flow was 10.05 $m^3 s^{-1}$. The average flow rate in the second stage of monitoring was higher than in the first stage of monitoring, indicating that the higher rainfall of 2012/2013 increased water box in the soil, producing the highest flow in the period 2014/2015. This can further justify the results for metals, due to the dilution of the water course, diluting impurities such as metals.

The results of metal concentration in the second stage of monitoring of surface water of Caiabi watershed, collected at the river spring (P1) and close to the mouth (P5) in the dry season (September/2014) and in the rainy season (Feb/2015) are shown in Table 2. There was an increase in the concentrations of Mn, Cu, Zn and Fe comparing the dry to the rainy season. This behavior may be attributed to a higher carriage of these elements to the watercourse.

The Mn and Fe concentrations, both natural constituents of red-yellow dystrophic latosols, the predominant soil in the

Table 2. Concentrations of Mn, Cu, Ni, Zn, Cd, Pb and Fe in the second stage of monitoring, as for the dry season (September/2014) and the rainy season (February/2015), near the river spring (Point 1) and the river mouth (Point 5) of the watershed of Caiabi river.
Tabela 2. Concentrações encontradas dos metais Mn, Cu, Ni, Zn, Cd, Pb e Fe na segunda etapa de monitoramento, em função das estações seca (setembro/2014) e chuvosa (fevereiro/2015), próximos à nascente (Ponto 1) e à foz (Ponto 5) da microbacia hidrográfica do rio Caiabi

	Point	Mn	Cu	Ni	Zn	Cd	Pb	Fe
September/2014	1	0.002	0.015	0.001	ND	ND	ND	0.025
February/2015	1	0.002	0.020	ND	0.001	ND	ND	0.035
September/2014	5	0.002	0.010	0.002	ND	ND	ND	0.095
February/2015	5	0.004	0.020	ND	0.001	ND	ND	0.115
VMP *	mg L^{-1}	0.1	0.009	0.025	0.18	0.001	0.01	0.3

*: Maximum Amount Allowed by CONAMA resolution n ° 357/05.

watershed of Caiabi river, were below the maximum levels allowed by Brazilian law, confirming the results found in the first stage of monitoring, as aeration favors the precipitation of these metals, which sediment on the river bottom, according to Moruzzi and Reali (2012 (2012).

It was found concentrations of Cu above the maximum amount set by Resolution No. 357/2005 of CONAMA, which is 0.009mg.L^{-1} (Table 2), for both points located on the spring and near the mouth of Caiabi river, noting that in the first stage of monitoring, Cu was not detected.

As the concentration of Cu was identified at the spring, it is believed that there is some factor contributing to this element in the water body. The spring is a wet area and water pH is low (<5.0) (ANDRIETTI et al., 2016). This factor may contribute to the presence of Cu, since according to Bartolomeo et al. (2004), in this pH value, metals, in general, have greater mobility in the aquatic ecosystem.

The Cu was also detected in surface water of surveys conducted by Freire et al. (2012), who related its presence to the use of agricultural compounds containing copper arsenate or copper sulfate, used in the fields surrounding the Maringa stream.

Ni and Zn concentrations ranged from non-detected to 0.002mg.L^{-1} and 0.001 mg.L^{-1}, respectively. These values were well below the maximum allowed by the Brazilian legislation.

Cd and Pb were not detected in any of the samples (dry and rainy seasons), at no point. Considering the size of the studied watershed, the rainfall associated with water sampling may have not occurred in the same time intervals after rainfalls.

Given the results obtained in the second stage of monitoring, in part contradicting the values found in the first stage of monitoring in relation to Pb, Cd, Ni, Zn and Cu, researchers found that the monitoring in only two points, the spring and the mouth of Caiabi river, and only two samples throughout the year, one in the dry season and another in the rainy season, were not enough to show the behavior of the watershed as a whole. On the other hand, with the exception of Cu, all other metals showed concentrations below what is expected in the Brazilian legislation, as in the first stage concentrations of Pb, Cd, Ni and Zn were above the maximum allowable limits, whereas in second stage there was no detection of metal concentrations, only of Cu.

4. CONCLUSION

The absence of specific sources of pollution, such as the dumping of industrial and domestic effluents, indicates that the results of metal concentrations ranged sometimes due to the climatic period and sometimes depending on the location along the watershed or it showed no change.

The form of land use and occupation affected the quality of surface water in the of watershed Caiabi river, with contamination in some places and at certain times of year, even though authors could not determine a pattern of water pollution behavior in terms of metals.

Despite the analysis of variance indicates no difference in concentrations between the monitored points in most analyzed metals, it is important to point out that over the years and the intensive use of the watershed there may be possible to observe the differentiation of concentrations between the spring and the mouth of the basin.

By verifying the absence of pattern of behavior of the results of the evaluated metals at different times and stages in the form of land use and occupation and due to the frequent use of agrochemicals, there must be a frequent monitoring of water quality of this watershed, as a management tool of water resources by government agencies.

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