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Monitoring of toxic chemical in the basin of Maringá stream

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ABSTRACT. This study aimed to track the spatial and temporal variations of toxic chemical compounds, such as the metals Al, Cd, Pb, Cu, Cr, Mn, Zn and the pesticide glyphosate, in Maringá stream and in a stretch of Pirapó river. The results pointed out that, in the case of metals, one of the possible sources of these elements is associated to agricultural activities. For glyphosate, were not found concentrations above those established by the Brazilian Water Quality Legislation (CONAMA 357/2005). Concerning this, we emphasized that the impact caused by the agrochemical on water quality should be evaluated considering the adverse effects to the environment caused by its degradation, that produces recalcitrant and surfactant compounds that may be even more toxic for humans and aquatic environment.

Keywords: water pollution, environmental impact, metals, glyphosate.

Monitoramento de compostos químicos tóxicos na bacia do ribeirão Maringá

RESUMO. Esse estudo teve por objetivo monitorar a variação espaço-temporal de compostos químicos tóxicos, como os metais Al, Cd, Pb, Cu, Cr, Mn, Zn e o defensivo agrícola glifosato, nas águas do ribeirão Maringá e de um trecho do rio Pirapó. Os resultados obtidos mostraram que no caso dos metais uma das possíveis fontes destes elementos na bacia está vinculada às atividades agrícolas. Para o defensivo glifosato, neste trabalho não foram encontradas concentrações acima do permitido pela legislação (CONAMA 357/2005). Sobre esse aspecto, ressalta-se que o impacto dos produtos agrícolas sobre a qualidade da água deve ser avaliado do ponto de vista dos efeitos adversos ao ambiente causados por sua degradação, gerando, por sua vez, compostos recalcitrantes e surfactantes e que podem ser muito mais tóxicos à vida aquática e ao homem.

Palavras-chave: poluição da água, impacto ambiental, metais, glifosato.

Introduction

The impacts created by the release of different substances into the water can produce several changes in aquatic systems. The presence of these elements in the water may stem from urban and industrial discharges or even from agriculture that makes use of supplements and pesticides, recalcitrant and surfactant organic compounds (BRAGA et al., 2005; ESTEVES, 1998; VON SPERLING, 2007).

Garcia et al. (1996) studied the incidence of trace elements in lotic environments as impurities coming from fertilizer and pesticide applied to agricultural soils. The authors concluded that the most significant addition consisted of Mn, Zn, Co and Pb. According to Carmo et al. (2005), studies in fluvial systems pointed out the processes of land use through urbanization and cultivation areas as the possible source of the elements Ni, Cr, Cu, Fe, Al, Mn, Ca, Mg, Ba, Na and Zn.

In accordance with Sanches et al. (2003), Coutinho et al. (2005) and Pinheiro and Rosa (2008), the agriculture requires the application of external energy into its ecosystem, whether to increase the yield or to replace the losses by the leaching of nutrients and by harvests. Furthermore, the aggregation of individuals, along with the biodiversity changes, gave rise to undesirable forms of life, such as fungi, insects and weeds.

For the economic maintenance of agricultural systems it is necessary to use fertilizers and pesticides of numerous chemical classes, such as organochlorines, organophosphates, carbamates, chlorophenoxy acids, among others. However the pesticides are considered as the second largest source of contamination of water bodies. In agreement with Vasconcelos et al. (2006) and Piveli and Kato (2006), the runoff water is the main means of transport of pesticides to the aquatic environments.

Among marketed products, the glyphosate is the most used herbicide for weed control, due to its broad-spectrum properties (AMARANTE JÚNIOR et al., 2002; GALLI; MONTEZUMA, 2005).

The glyphosate is one of the most studied herbicide molecule worldwide in terms of environmental safety and human health. According to the World Health Organization, the toxicity of this herbicide is relatively low. Nevertheless, some elements of its formulated products, such as surfactants and some metals, present higher toxicity than the active ingredient.

The importance of the analyses of these chemical compounds is that they have high persistence in the environment and, the water as the main means of transport, raising concern about the ability of chemicals to be incorporated by the organisms, including by human that, direct or indirectly are in contact with or make use of water resources (FÖRSTNER; WITTMANN, 1981).

In this respect, a very big concern is focused on the basin of Maringá stream, located in the northern region of Maringá municipality (Paraná State), belonging to the management unit of the Pirapó river basin. According to Borsato and Martoni (2004), the basin of Maringá stream is an important watershed in the northern area of Maringá city, since among the preponderant uses stand out the water supply for animals, irrigation, fishing and recreation.

Nevertheless, this water body undergoes pressure from human activities both in the urban environment, when receives materials from the runoff of urban water of the Maringá municipality, the illegal dumping of sewage, and the effluent from a sewage treatment plant (STP) of the city; and in rural environment, through the runoff and thus taking all the load of sediment and some chemical substances used in the crops, to the water body.

Santos et al. (2008) examined the occurrence of metals in the Ivaí river basin (Paraná State) as a result of land use. The results presented the concentrations (μg L^{-1}) in the following ranges: Pb – 13.0 to 67.0; Co - > 2.0; Cu – 1.0 to 100; Cr - > 4.0; Fe – 90.0 to 4,400.0; Mn - >130.0; Ni - > 6.0; Zn – 4.0 to 400.0. The authors concluded that the heavy metals Pb, Zn, Cu and Fe have potential to impact the river as consequence of agricultural activity in the watershed.

Farias et al. (2007) monitored the presence of the metals B, Cu, Pb, Cd, Fe, Mn, Ni and Zn in the water of the Cabelo river basin (Paraíba State), as the influence of the industrial district Mangabeira. Considering the results, the authors observed an overcoming of the levels established by the Brazilian law for B, with concentrations that varied between 23.0 and 53.0 mg L^{-1}; for Cd, with concentrations up to 0.005 mg L^{-1}; the Pb, with concentrations up to 0.05 mg L^{-1}; and for Fe, with concentrations ranging from 0.30 to 0.60 mg L^{-1}. These results, according to the authors, indicate that the concentration levels may harm aquatic life, wildlife and humans, through primary contact or along the food chain.

Mattos et al. (2002) monitored the presence of glyphosate in water samples collected in an area of rice in the State of Rio Grande do Sul, subjected to direct plantation. It was found in that research, average levels of this herbicide at concentrations of 0.0144 mg L^{-1} in the master channel of water input to Mirim Lagoon, and of 0.0130 mg L^{-1}, in the output of Bretanhas stream. These results present concentrations of this herbicide above the maximum allowed by the US. EPA – 0.007 mg L^{-1}.

Regarding this and the problems relative to the impacts suffered by the Maringá stream, mainly those originated from urban and rural environments, and the interference of them on water quality, this study aimed to monitor the spatial and temporal variation of toxic chemicals, such as the metals Al, Cd, Pb, Cu, Cr, Mn, Zn and the pesticide glyphosate, in the water of this stream and in a stretch of Pirapó river, upstream and and downstream of the confluence with the Maringá stream. With this, we intend to help with proposals of measures for proper management of water quality in this watershed.

Material and methods

Study area

The physical characterization presented in Borsato and Martoni (2004) shows that the basin of Maringá stream has altitudes that vary between 600 m and 375 m, and drains an area of 90.37 km^2, which characterizes it as a medium-sized stream.

The climate of this region is classified as mesothermic humid subtropical - Cfa. The average annual rainfall ranges from 1,250 to 1,500 mm, with hot and rainy summers, winter with uncommon frosts, without a well defined dry season.

In the study area, three soil types predominate: Ferric Red Latosols, derived from basalt and occurring with lower proportion only in the flat top areas in the basin; Distroferric Red Nitosols, with latosolic characteristics, which develop in areas with average slopes; and the Fluvic Neosols with alluvial features (hydromorphic), which are found near some drainage channels. Mineralogically, these soils are rich in iron, aluminum and magnesium.

Important sources of contaminants in this basin are the diffuse sources, such as agriculture, present in virtually the entire basin, with the intense use of pesticides and fertilizers (ALVES et al., 2008). In the springs with the presence of urbanization, there are

sewage spills into the river channel without proper treatment. The release of sewage after being treated in the STP, and the ponds for fish farming in the basin also represent strong interferences to the environment and are punctual sources of contamination (SCHNEIDER et al., 2011).

In order to monitor the concentration the toxic chemicals in the water of the Maringá stream, nine sampling sites (S) were distributed throughout the basin covering since its main springs until its mouth in the Pirapó river, with monitoring sites up- and downstream of this confluence, as shown in Figure 1.

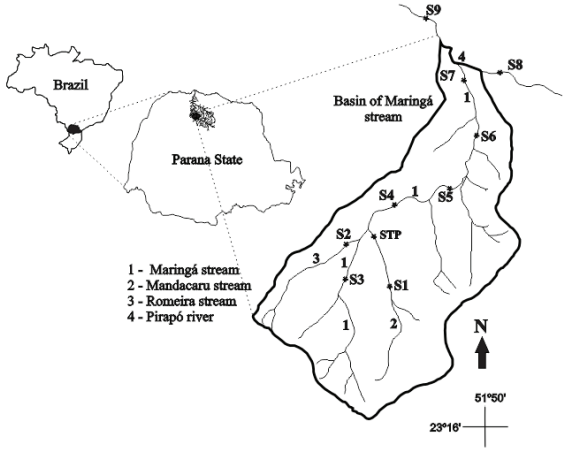

Figure 1. Maringá stream basin with the location of the sampling sites.

Water samplings were conducted in the morning, in the stream and at a stretch of Pirapó river, punctually with simple sampling at the central point of the water course, totaling nine samples

For metals, monthly samplings were performed from September 2008 to August 2009. Samples were placed in polyethylene bottles (2 L), preserved by adding nitric acid until pH < 2, and kept in cooling.

Two methodologies of sample preparation were undertaken, one for the dissolved metals (Al) and the other for total metals (Mn, Cd, Pb, Zn, Cu and Cr). For the dissolved metals, we filtered 45 mL of the sample without prior acidification, through a 0.45 µm membrane, and then the sample was acidified. The preparation of the samples for the total metals (250 mL) was performed in hot acidic conditions (APHA, 1998). This process is known as digestion or opening and were used the nitric acid and hydrochloric acid for this purpose. Once digested, the samples were filtered through quantitative paper to remove remaining particles of inorganic material.

All the samples were stored under cooling until determination of metal concentration, which was carried out using atomic absorption spectroscopy (Spectr AA. B50), taking into consideration the detection limits of each metal and the respective care in preparation of the blank solution and the work curve.

For glyphosate, samplings were performed monthly from July to December 2009. Samples were gathered in polypropylene vials (500 mL) and immediately sent for analysis. For the analysis, initially, 10 mL was filtered through a 0.45 µm membrane.

The concentration was determined by ion chromatography with suppressed conductivity detection, in Metrohm compact chromatograph of anion, model 850 Professional IC. For this, we determined the calibration curve with standard solution, following the conditions: eluent flow: 168 mL $min.^{-1}$; system pressure: 5.3 MPa; conductivity: 21.31 $\mu S\ cm^{-1}$; loop: 25 μL (APHA, 1998).

Analyses of metals were carried out at the Laboratory of Management, Preservation and Environmental Control of the Department of Chemical Engineering, and of glyphosate, at the Central Complex of Research Support, both in the State University of Maringá (UEM). To ensure reliability of the obtained results, tests were performed in duplicate.

Additional field work was accomplished with an investigative purpose. The climatological data relative to the study period were furnished by the Main Weather Station of the State University of Maringá (Figure 2).

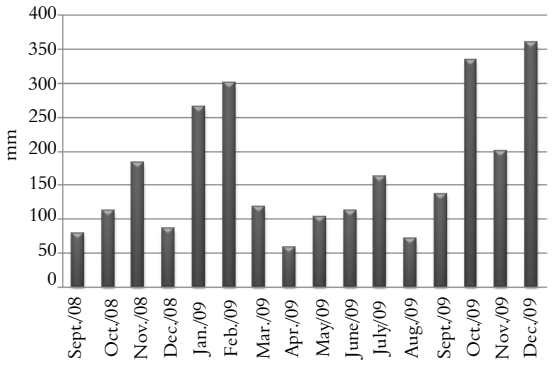

Figure 2. Monthly rainfall in the watershed during the study period.

Results and discussion

The results presented will be discussed based on the standards of classification for the water courses

established in the Conama Resolution no. 357, from March 17th, 2005 (BRASIL, 2005). The Surehma Ordinance no. 004, from March 21st, 1991, stated that all the water courses in the planning unit of Pirapó river, including Maringá stream, belong to class 2, except for Mandacaru stream that belongs to class 3 (PARANÁ, 1991). In the Figures 3 to 7, the line represented by Res. 357 refers to the Conama Resolution no. 357/2005, and indicates the maximum allowable concentration for each metal.

In relation to the aluminum (Al), it was observed a similar trend between monitored sites. Nevertheless, reservations must be made for the sites 1 (0.1334 mg L^{-1}) and 2 (0.1354 mg L^{-1}) in September 2008, and for the site 5 (0.1100 mg L^{-1}), in December 2008. At these sites in Maringá stream, the Al concentration was above that established in law (0.1 mg L^{-1}).

In the Figure 3, it can be noted that in the period from May to July 2009, there was an increase in Al concentration in almost all monitored sites. In the stretch represented by the site 4, located at Maringá stream, downstream of the release of the sewage treatment plant (STP), the concentration reached 0.1920 mg L^{-1}.

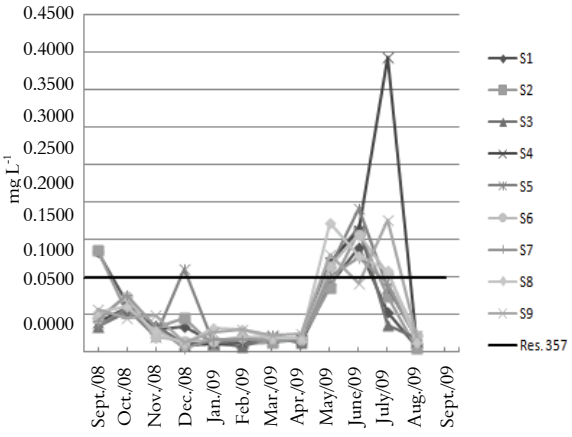

Figure 3. Variation of aluminum concentration.

The high concentrations of Al may be related to the soil erosion in the basin. However, comparing the Figure 2 with the Figure 3, Al presented higher concentrations in the periods with lower rainfall. This suggests that the sources of Al are constant regardless water availability and in this way when there is increase in the river flow, the dilution of this metal takes place.

For cadmium (Cd), the values have been low in almost all sites during most samplings, but the Figure 4 shows three periods with concentrations above the limit established by the law (0.0010 mg L^{-1}).

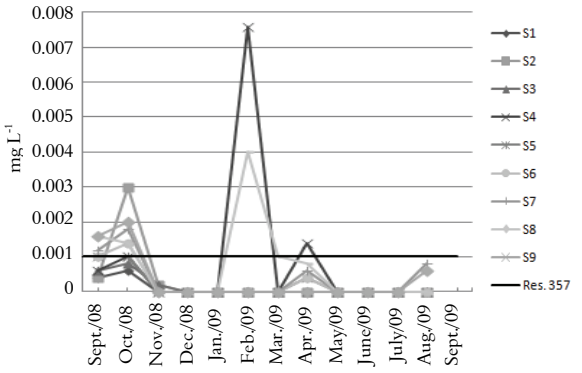

Figure 4. Variation of cadmium concentration.

In September 2008, Cd concentrations (mg L^{-1}) above the limit were determined in the stretches represented by the sites 5 (0.001), 6 (0.001), 7 (0.0012), 8 (0.0016) and 9 (0.0016). in October 2008, these conditions were found for the sites 2 (0.0030), 4 (0.0010), 5 (0.0010), 6 (0.0014), 7 (0.0018), 8 (0.0014) and 9 (0.0020).

As the Cd concentration in the stretch represented by the site 4, located downstream the STP, was lower than those obtained in the stretch represented by the site 2, with strong influence of rural area, we can infer that the cadmium in the water of Maringá stream possibly arises from the composition of any agricultural product. Usually the pesticides, whose manufacture includes the use of natural phosphate without treatment, can accumulate Cd. Furthermore in field trips we observed that in this year period is common the use of pesticides in the soil, once there is planting of soybean in the area of the basin. The survey of pesticides in the watershed area was performed by Peruço et al. (2006).

Two other peaks of Cd concentration are verified in the Figure 3, referring to the sites 4 and 8. It is assumed that the rains promoted a leaching of this chemical from the agricultural soil to the river bed. But no sediment analysis was made to confirm this hypothesis. Still due the magnitude of the values found, these were probably generated by the contamination during the procedures of sample preparation.

In the monitored period, lead (Pb) concentrations above the established limit (0.01 mg L^{-1}) were detected in the stretches represented by the sites 2; 3; 8 and 9, as presented in Figure 5.

In the site 2, Romeira stream, in October 2008 and January 2009, it was found 0.018 and 0.014, in mg L^{-1}, of total Pb in the water. In the stretch

relative to the site 3, a concentration above that allowed in law was found in January 2009, with 0.016 mg L^{-1}. In Pirapó river in the stretch of the site 8, high concentrations were found in May 2009 (0.040 mg L^{-1}) and, in the stretch of the site 9, soon after the inflow of water from the stream, in December 2008 and March 209, both with 0.010 mg L^{-1}.

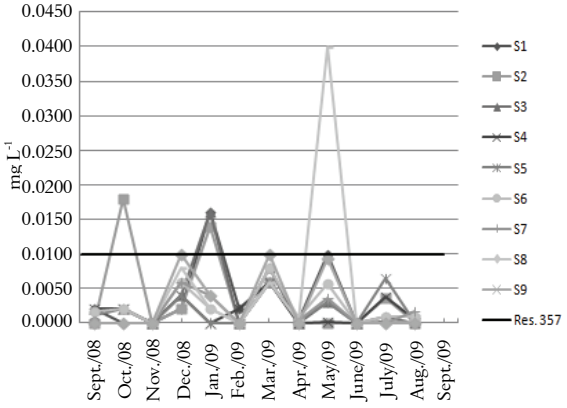

Figure 5. Variation of lead concentration.

From the analysis of the obtained results and considering the rainfall before the sampling, it is likely that the Pb in the water had arisen from the runoff soil. Several polluting sources still can have contributed to the identified change, since according to Santos et al. (2008) and Ramalho et al. (2000), the Pb takes part of the composition of several products, such as welds, inks, plumbing, fuel, pesticides containing lead arsenate etc.

By analyzing the results for the copper (Cu) concentration in the Figure 6, it was observed in the sites 4; 6; 7; 8 and 9, very high concentrations, above the limits established in the Resolution 357/2005 (0.009 mg L^{-1}).

At the site 4, the changes in mg L^{-1} were found in November 2008 (0.0092) and in January (0.0114), February (0.0126) and June (0.0116) of 2009. For the site 6, it was found values above the allowed, mg L^{-1}, in January (0.0154) and in February 2009 (0.0096). At site 7, stand out the months of November 2008 (0.0118), and of January (0.0294), February (0.0182), March (0.0096) and June 2009 (0.0240). The site 8 had concentration, mg L^{-1}, in disagreement with the law in the months of November 2008 (0.0132), January (0.0602), February (0.0844) and June 2009 (0.0402). At the site 9, these changes were observed in November 2008 (0.0136) and in January (0.0648), February (0.0800), March (0.0148), April (0.0146) and June 2009 (0.0378).

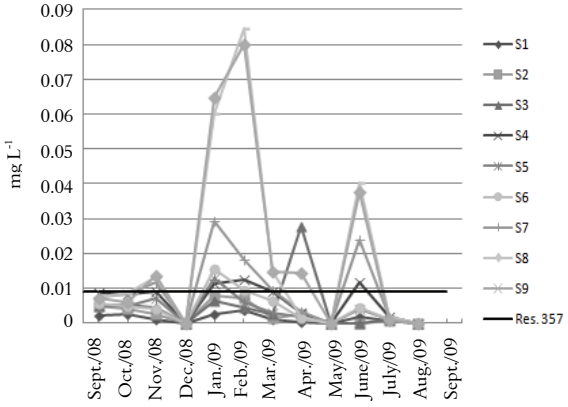

Figure 6. Variation of copper concentration.

Once all these sites are downstream of the release of the STP of the city, it is inferred that these releases have had influence on these values of concentration.

The values obtained in the stretches referring to the sites 6 and 7 may be linked to the water inflow from a tributary, with the spring located under the influence of the urban area. Still since the Cu is used as algicidal in ponds of fish farming, probably these values can be associated to the discharges of waste water of these ponds, located near the sampling sites.

Besides that, this area is under rural influence, as well as the sites 8 and 9, and then it is likely that, in accordance with Ramalho et al. (2000), the concentrations of Cu are related to the use of agricultural compounds containing copper arsenate or copper sulphate.

For the chromium (Cr) the concentration remained within the range established by the legislation (0.05 mg L^{-1}) in the Maringá stream and Pirapó river. Exceptions took place at site 7, in June 2009, and site 9, in May 2009, where it was verified concentrations of 0.0640 mg L^{-1} and 0.0900 mg L^{-1}, respectively.

In this case, it is difficult to define a source for the chromium both in Maringá stream and Pirapó river, since it was found at concentrations above the allowed only at the last site of monitoring in these water bodies, and only once.

The variation in manganese (Mn) concentration is presented in Figure 7. There were concentrations above the limit allowed by the law for the rivers class 2 (0.1 mg L^{-1}), highlighting the stretches represented by the sites 2, 7, 8 and 9.

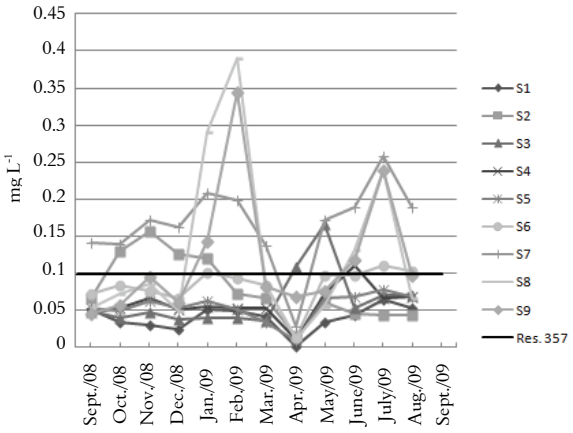

Figure 7. Variation of manganese concentration.

In the site 2, Romeira stream, it was verified that the concentrations of Mn decreased over the study, even reaching after February 2009, concentrations close to those found in the other sites in the basin. Examining this trend, it is possible to state that the Mn concentrations herein obtained can be related to the soil surface runoff in the rainy season.

In the stretch represented by the site 7 and in the stretches referring to the sites 8 and 9, the high concentrations recorded can be consequence of agricultural management, once they are located in areas with intense cultivation, and Mn is a typical mineral of soils in the watershed. Meanwhile, urban sources can have contributed to the identified change, since according to Santos et al. (2008), the Mn takes part of the composition of batteries, catalyzers, disinfectants, cosmetics and medicines.

The zinc (Zn) concentration exceeded the limit allowed by the law for the water bodies class 2 (0.18 mg L^{-1}) in January 2009, in the site 8 (0.2790 mg L^{-1}) and in May 2009, for the stretches corresponding to the site 2 (0.1970 mg L^{-1}), site 6 (0.1900 mg L^{-1}), site 7 (0.3030 mg L^{-1}), site 8 (0.2610 mg L^{-1}) and site 9 (0.2410 mg L^{-1}).

Since in the stretch relative to the site 4, downstream of STP release, it was not detected high concentrations of Zn certainly this release does not contribute to change the stream quality, regarding this metal, during this study.

The glyphosate was registered at low concentrations in the waters of Maringá stream and in the stretch of Pirapó river. The Table 1 lists the results obtained during the study. The result in bold had exceeded the limit established by the Resolution no. 357/2005 (0.065 mg L^{-1}).

Although the glyphosate presents strong trend to link to soil particles and present a high degradation rate, its solubility makes it liable to reach the water sources, but at low levels. The low values obtained may be associated to its rapid hydrolysis in aqueous solution.

In general, the results showed that the glyphosate concentration in the water is related to the soybean crops, since that during the sampling period, it was observed the application of the product in the plantations of the basin. Other factor is associated to the occurrence of rainfall in the days before the samplings. Indeed, the surface runoff carries the components present in the soil to the water bodies.

Armas et al. (2007) registered similar results in the basin of the Corumbataí river (São Paulo State) in an area of sugarcane cultivation. The occurrence of greater number of glyphosate molecules at higher levels in water samples gathered in November, had coincided with the initial period of rains, but not necessarily with the period of greatest application.

In a single moment, the glyphosate concentration in the waters of the Maringá stream basin exceeded the concentration limit allowed. In August 2009, it was detected in the stretch of the site 2, a much higher concentration than that established for this product, including for the water bodies class 3. Considering that this result is unique and is extremely high compared with the other records, it is difficult to establish a reason to explain this concentration. However, probably an error occurred during the analysis procedure, and that may have undermined the results obtained in this month.

Table 1. Variation of glyphosate concentration (mg L^{-1}).

Date	S 1	S 2	S 3	S 4	S 5	S 6	S 7	S 8	S 9
07-28-2009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
08-26-2009	0.000	2.024	0.000	0.000	0.000	0.000	0.000	0.000	0.000
09-24-2009	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10-13-2009	0.000	0.014	0.000	0.029	0.000	0.000	0.000	0.023	0.021
11-11-2009	0.000	0.009	0.000	0.006	0.029	0.027	0.028	0.000	0.000
12-07-2009	0.000	0.002	0.000	0.031	0.035	0.041	0.041	0.000	0.000

Conclusion

An issue to be highlighted in the evaluation of the toxic chemicals is the significant presence of metals in the water of Maringá stream and in the stretch monitored of Pirapó river.

In part, it is possible to state that the composition of the soils of the basin and the rain that occurred before the samplings had influenced the concentration of some metal compounds in the surface waters. Meantime, the analyzed metals frequently presented concentrations above the established in law or above that one could expect by the soil type of the region. This indicates that the human sources are the main responsible for the changes recorded.

Like most sites that had changes are located under rural influence, it can be said that in the study area, one of the human sources of these elements is strongly linked to agricultural activities. However, in this study, there was no concentration of glyphosate above the allowed by the legislation.

In conclusion, the aquatic ecosystem of the Maringá stream basin is undermined by the presence of metals in its waters, and the great concern generated by our results is related to the users of this water resource.

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