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Water and sediment quality assessment - Ribeirão do Laranjal watershed

Avaliação da qualidade da água e sedimento - Ribeirão do Laranjal

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ABSTRACT

The sediment and water of a river can be impacted by the development of modern society. The sediment is responsible for the transport, release and accumulation of toxic compounds and nutrients and can alter the quality of the water. Thus, the objective of this study was to analyze the water and sediment quality of Laranjal stream, located in Laranjal Paulista (São Paulo, Brazil). Water and sediment samples were collected in the rainy and dry seasons of the year 2012. The analysis indicated that the sediment presented high content of Cd, Ni, Pb, Cu and Cr. The toxicity test indicated that the river mouth was distinct from the spring and the middle course and the electrical conductivity of the water was high at the sampling point within the urban mesh of Laranjal Paulista. Considering the use and occupation of the Laranjal stream watershed, the rural mesh (dominated by pasture and plantation) influences predominantly the quality of water and sediments.
Keywords: limnological variables, land use and land occupation, toxicity, metals, lotic environment.

RESUMO

O sedimento e a água de um rio podem ser impactados pelo desenvolvimento da sociedade moderna. O sedimento é responsável pelo transporte, liberação e acumulação de compostos e nutrientes tóxicos, podendo alterar a qualidade da água. Dessa forma, o objetivo deste estudo foi analisar a qualidade da água e dos sedimentos do Ribeirão do Laranjal, localizado no município de Laranjal Paulista (São Paulo, Brasil). As amostras de água e sedimento foram coletadas nas estações chuvosa e seca do ano de 2012. As análises indicaram que o sedimento apresentou altos teores de Cd, Ni, Pb, Cu e Cr. O teste de toxicidade indicou que a foz do rio foi distinta da nascente e do curso médio e a condutividade elétrica da água foi elevada no ponto amostral dentro da malha urbana de Laranjal Paulista. Considerando o uso e a ocupação da bacia hidrográfica do Ribeirão do Laranjal, a malha rural, dominada por pastagens e plantações, influencia predominantemente a qualidade da água e dos sedimentos.
Palavras-chave: variáveis limnológicas, uso e ocupação da terra, toxicidade, metais, ambiente lótico.

INTRODUCTION

During urbanization, an increase of sediment load due to landscape transformation is currently observed in urban areas; therefore, the anthropic activities intensify the natural erosion processes from the drainage basin (Issaka and Ashraf, 2017), causing negative effects on the quality of water and sediments limnological characteristics. The high rate of urbanization also impacts the water (Ternus et al., 2011) and sediment quality, changing its physical and chemical characteristics and causing aesthetic, physiological and ecological impacts. From the analysis of sediment and water, it is possible to determine the main sources of pollution within a given aquatic system. By the combination of water and sediment analysis with the land use and land occupation, it is possible to diagnose the environmental quality of a stream. The aim of this study was to analyze the water and sediment quality of the Ribeirão do Laranjal watershed at three different points and in two different hydrological periods (i.e. dry and rainy season). We hypothesized that there are significant differences in the water quality of the Laranjal Paulista watershed as a function of the hydrologic period.

MATERIAL AND METHODS

The municipality of Laranjal Paulista is located in the São Paulo state and is bordered by the Tietê, Jumirim, Cesário Lange, Pereiras, Conchas, and Piracicaba municipalities. According to the 2010 census conducted by the Brazilian Institute of Geography and Statistics (Instituto Brasileiro de Geografia e Estatística, 2011), the municipality has an area of 384.27 km^2 and a population of 25,251 inhabitants, with a population density of 65.71 inhabitants per km^2. The hydrographic network of the municipality consists of the Tietê and Sorocaba rivers. The Ribeirão do Laranjal is a 2nd order river with a length of 11.3 km that flows into the Sorocaba river.

The sampling occurred during the rainy season (C1: November to March) and dry season (C2: April to October). The samples of water and sediment were collected at three points: (i) river mouth next to its source on the Sorocaba river (P1: 47° 53’ 58” W, 23° 04’ 09” S), in the middle course, located in the urban mesh (P2: 47° 50’ 32” W, 23° 02’ 32” S) and in the spring, located in the rural mesh (P3: 47° 49’ 51” W, 23° 01’ 32” S). The collection of the sediment was performed manually with a shovel and the water sampling was performed with the sterile polyethylene bottle. Analysis of sediment and water was performed by methods listed in Table 1. A portion of the sediment samples were dried in an oven (Artlab, model 315 SE) and another fraction was maintained fresh for the development of other analysis (i.e. moisture and toxicity).

Principal component analysis (PCA) was used to order the six sample units and 21 limnological variables

Table 1. Limnological variables and methods/equipment used for analysis.

Limnological variables	Method	Reference or Equipment
Water sample		
Temperature (°C)	Mercury thermometer	-
Electrical conductivity (EC: mS/cm)	Potentiometric	Horiba multiparameter probe: model U10
Dissolved oxygen (DO: mg/L)	Polarographic	ODmeter: YSI, model 58
pH	Potentiometric	pHmeter: Qualxtron, model 8010
Turbidity (NTU)	Nephelometric	Turbidimeter: Hach, model 2100P
Sediment sample		
Moisture	Gravimetric	Empresa Brasileira de Pesquisa Agropecuária (1997)
Toxicity	Root stretching method	Bagur-González et al. (2011)
Density	Gravimetric	Empresa Brasileira de Pesquisa Agropecuária (1997)
Granulometry	Sieving Gravimetric	Sampaio and Silva (2007)
Organic matter	Calcination	Faithfull (2002)
pH	Potentiometric	Queiroz and Boeira (2006)
Metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn: mg/kg)	Atomic absorption spectroscopy	American Public Health Association (1998)

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in order to reduce the dimensionality of the data and to describe the relationships between these variables. The analysis was performed in software R (R Core Team, 2015) using the vegan package (Oksanen, 2015). The land use and land occupation analysis of the Ribeirão do Laranjal watershed was performed using ARCGis Desktop 10.1 program and Landsat TM5 satellite image, with a pixel size of 30x30 m, orbit 220, point 76 and date of passage on August 12, 2012. The gapfill method was performed between a previous Landsat SLC on image (date of passage on April 24, 2001), to guide the spectral interpolation across the gaps in SLC off images (data of passage on August 12, 2012). The spectral bands 3, 4, and 5 were processed using the ENVI 4.7 software resulting in a R5G4B3 color composition.

RESULTS AND DISCUSSION

The following figures show the results obtained from laboratory analyzes. The EC (Figure 1A) reflects the amount of salts in the water and concentrations above 0.100 mS/cm indicate sewage release into a water body (Companhia Ambiental do Estado de São Paulo, 2009). The P1 (mean: 0.16 mS/cm) and P2 (mean 0.18 mS/cm) exceeded that value in both rainy and dry station. The lowest EC was registered in the P3.

The DO (Figure 1B) is influenced by the water partial pressure and temperature and the rate of aeration depends on the hydraulic characteristics of the river channel and to the water velocity (Allan and Castillo, 2007). In both sampling period, the highest concentration

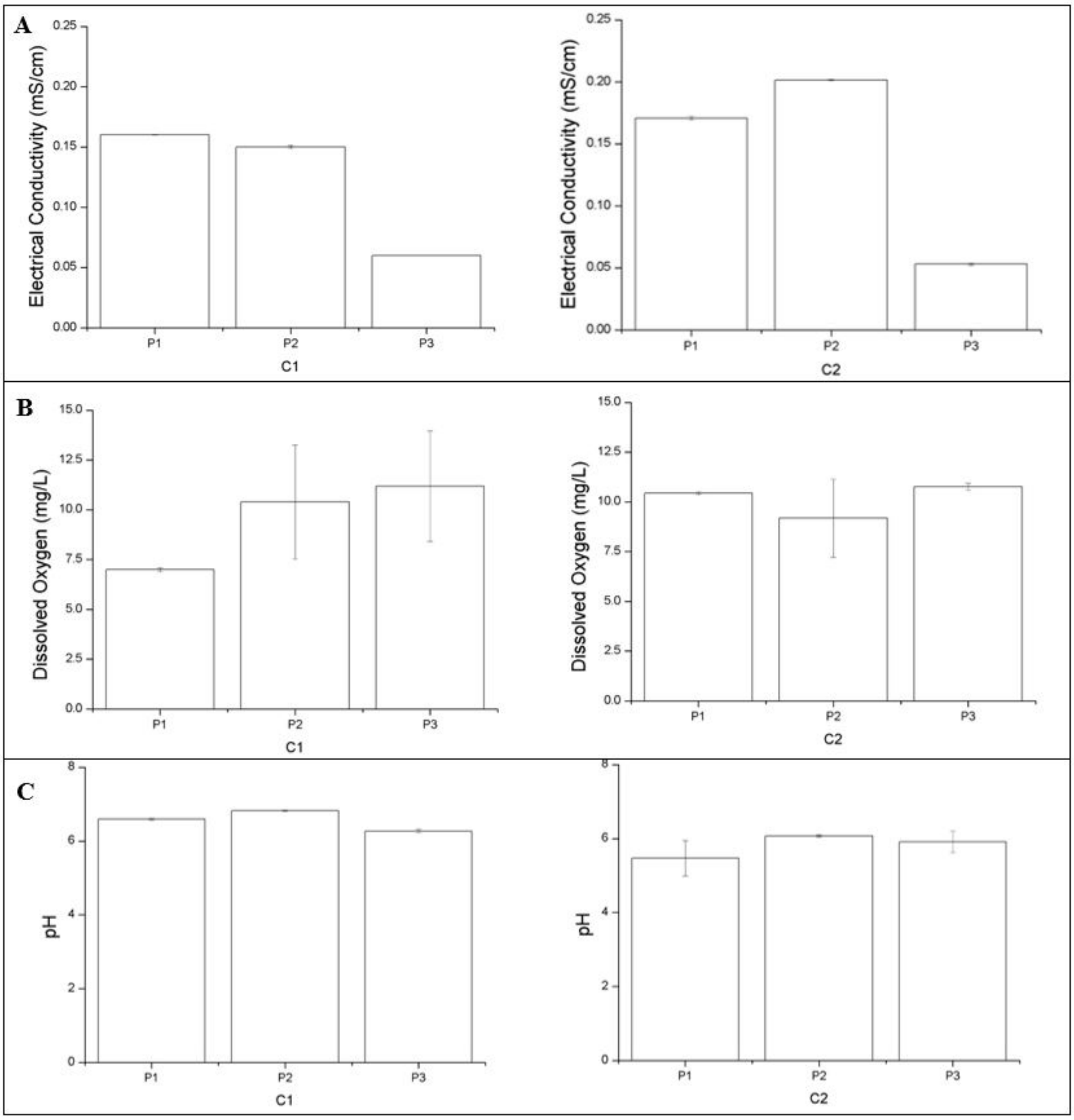

Figure 1. Electrical conductivity (A), dissolved oxygen (B) and pH of water (C) rainy (C1) and dry (C2) seasons in the three sampling points: river mouth (P1), middle course (P2) and spring (P3).

of DO was observed in P3 (spring): 11.18 mg/L in C1 (rainy season) and 10.76 mg/L in the C2 (dry season); the lowest concentration (6.99 mg/L) was registered in the P1 in the C1 (rainy season). All sampling points and hydrological periods presented concentrations within the limits established in CONAMA 357/05 for Class 1 (Brasil, 2005). The water pH influences the metabolism of the aquatic ecosystems, acting directly on the physiology of biota and contributing to the precipitation of toxic chemicals (higher pH values) such as metals. In both seasons (mean pH: C1 = 6.56 and C2 = 5.82; Figure 1C) the pH was acid. As stated in CONAMA Resolution 357/2005, for Class 1 to 4, the water pH should vary between 6 and 9; thus, all sampling points showed values within the limit established by legislation.

The water turbidity and temperature are presented in Figure 2. According to CONAMA Resolution 357/2005, water turbidity can present a maximum value of 40 NTU for Class 1 due to its interference in underwater radiation. The highest values registered in C1 and C2 was, respectively, 46.97 UNT in P1 and 13.83 UNT in P2 (Figure 2A). Thus, only the P1 in C1 exceed the limit settled by the resolution cited.

The water temperature displays a very important role in the aquatic environment, since it is responsible for conditioning the influences of various physic-chemical variables (Hauer and Hill, 1996). The mean water temperature (Figure 2B) in the C1 was 26.5 °C (P3), 21.5 ºC (P2) and 30 °C (P1) and in the C2, the temperature ranged from 18.5 °C (P1 and P2) to 20 °C (P3). In the period of higher precipitations, the temperature was 1.37 times higher than in the dry season.

The density, pH and organic and inorganic materials are show in Figure 3.

The highest value of density (Figure 3A) was obtained in P2 (1.4 g/cm^3) in both hydrologic period (C1 and C2; Figure 3A). The lowest density (0.8 g/cm^3) was observed in P1 and P3. The pH of sediments (Figure 3B) in C1 was below 7 (P1 = 5.19, P2 = 6.56 and P3 = 5.11), demonstrating an acidic character, especially in P1 and P3 (Figure 3C). In C2, P2 presented a pH of 7.25, indicating the neutrality of the interstitial water; P1 (6.17) and P3 (4.95) showed pH lower than 7. The interstitial pH is a key variable that control the bioavailability of metals (Simpson et al., 2005).

In sediments, the OM fraction tends to form stable complexes with metal, altering their distribution between

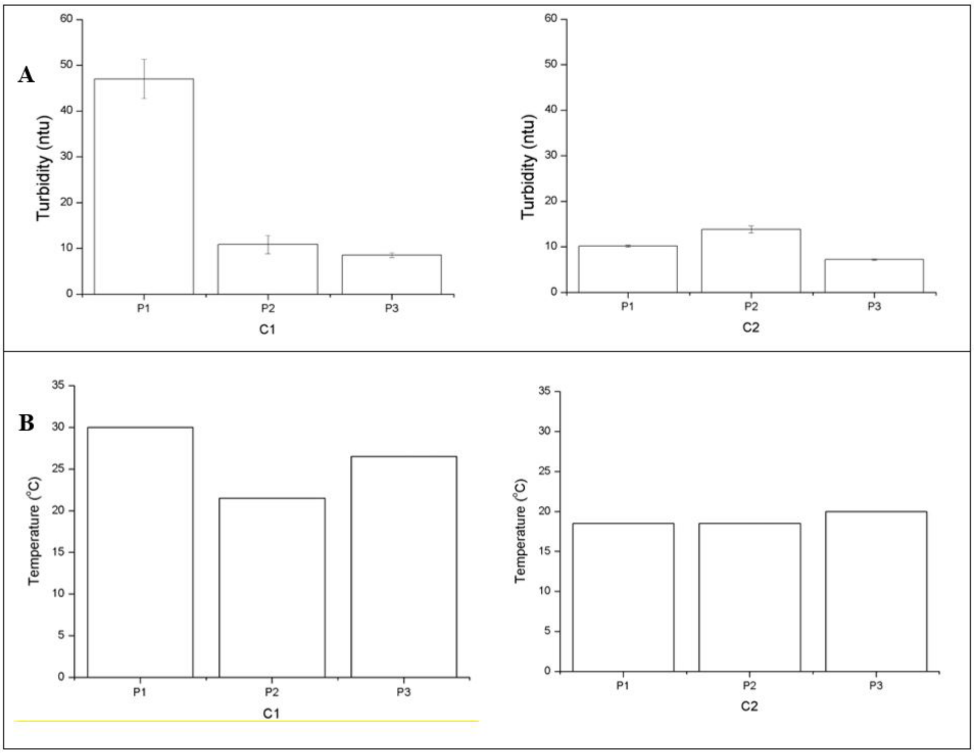

Figure 2. Water turbidity (A) and temperature (B) of the Laranjal stream in rainy (C1) and dry (C2) seasons in the three sampling points: river mouth (P1), middle course (P2) and spring (P3).

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the reduced and oxidized forms, bioavailability and toxicity to aquatic life (Baird, 2002). Sediments are classified into organic and inorganic (Hillel, 2007); content of ca. 10% of organic matter in dry mass classify sediments as an organic substrate. The aquatic sediment may have autochthonous and/or allochthonous origin with a huge variety of organic and inorganic materials. The sediments composition and distribution depend on the rock types, topography, meteorological factors and characteristics of terrestrial vegetation (Ward, 1992). The average content of OM (Figure 3C) corresponded to 9.96% (P1), 3.23% (P2) and 15.59% (P3) in C1 and 4.77% (P1), 2.53% (P2) and 5.97% (P3) in C2. P1 and P3 presented organic sediments in C1; however, in C2 sediments were classified as inorganic.

Figure 4 shows the results obtained from granulometry (Boggs, 2006; Sampaio and Silva, 2007) and toxicity analysis. P2 is mainly composed of gravel with a diameter particle varying between 2 mm and 60 mm, in both seasons (C1 = 36.96% and C2 = 64.42%; Figure 4A). Sand is not a cohesive substrate formed by minerals or rock particles with a diameter between 0.6 mm and 2.0 mm (Associação Brasileira de Normas Técnicas, 1997) and is also registered in P2 in both seasons (C1 = 31.19% and C2 = 22.48%). The low resistance particle with a diameter between 0.002 mm and 0.06 mm is known as silt and this fraction was registered in P1 in both

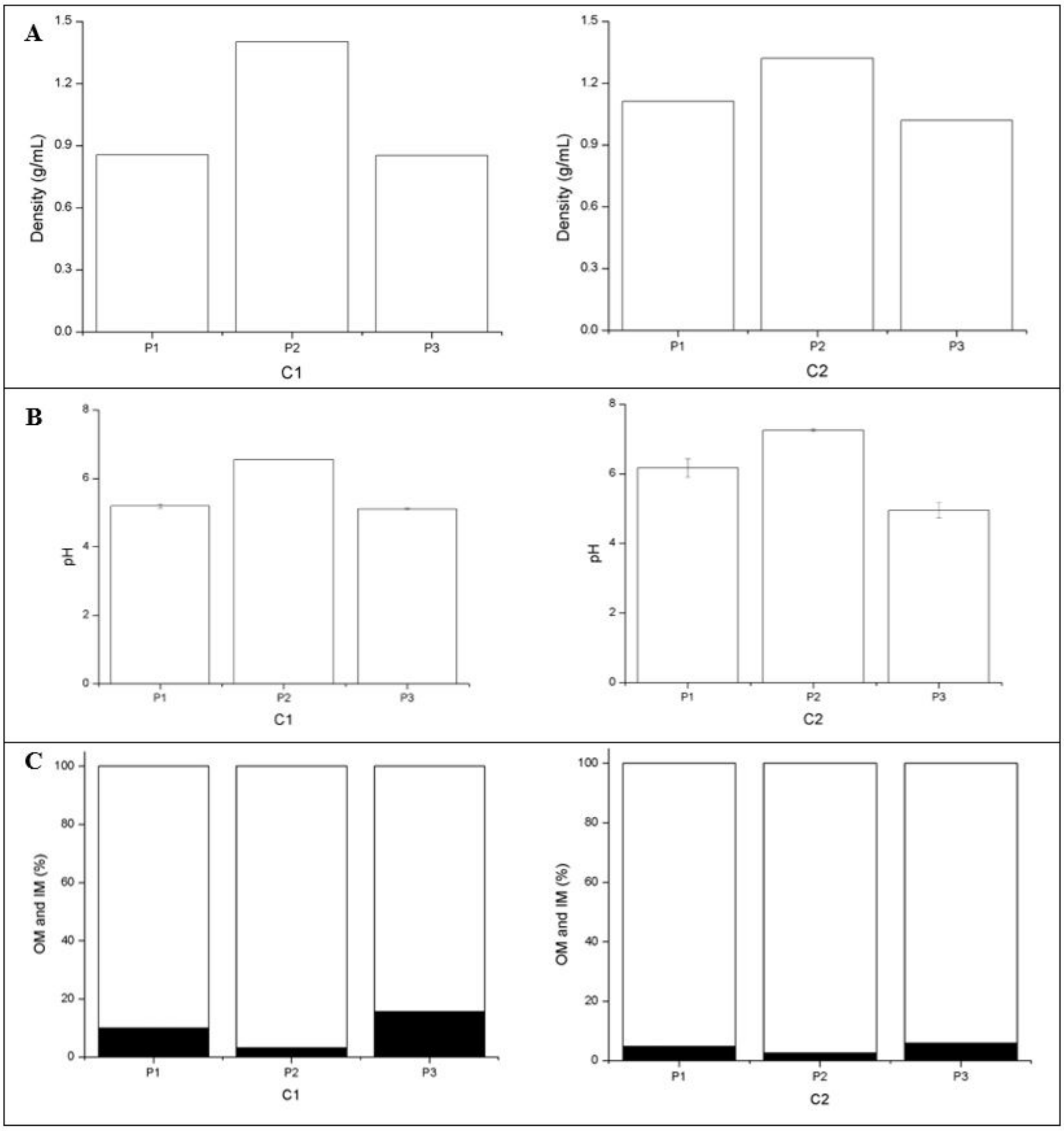

Figure 3. Density (A), pH (B) and organic (OM in black) and inorganic material (IM in white; C) of sediment of the Ribeirão do Laranjal in rainy (C1) and dry (C2) seasons in the three sampling points: river mouth (P1), middle course (P2) and spring (P3).

seasons (C1 = 76.59% and C2 = 56.57%). This fraction is considered as fine-grained and it is responsible for the transportation of expressive amount of metals, phosphorus and chlorinates pesticides and industrial compounds (Ongley, 1996).

The toxicity analysis (Figure 4B) provides precise information about the substances effects in living biota (Koivisto, 1995). Toxicity bioassay using *Lactuca sativa* is considered a simple, quick and sensitive test in order to evaluate a potential environmental contamination. Bagur-González et al. (2011) tested phytotoxicity associated with As, Cu, Mn, Pb and Zn in soils from an abandoned mining area concluding that this test is sensitive. Regardless the hydrological period, the P1 showed the lowest root growth of lettuce in relation to the P2 and P3.

Pesticides and heavy metals are the main substances responsible for the toxicity of an ecological compartment. Considering the surrounding areas of P1, it was observed that there is an occurrence of anthropic alterations, such as the main activity that occurred on the riverbank (i.e. livestock) associated with the absence of riparian vegetation. The metals found in the Ribeirão do Laranjal watershed are listed in Table 2.

Metals are not degradable and can undergo chemical transformation being even more harmful to the biota. They are rapidly adsorbed on particulate matter or can be released as a result of chemical changes in the environment (Baird, 2002; Nasr et al., 2006). The contents of metals (Table 2) found in the sediments of the Ribeirão do Laranjal were compared with the maximum values

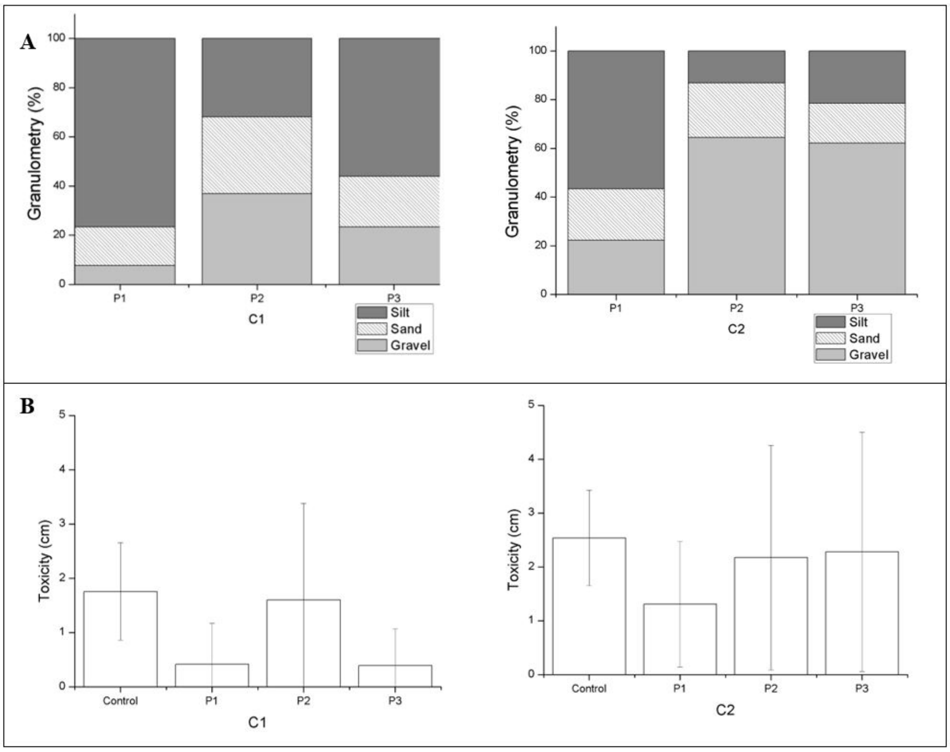

Figure 4. Granulometry (A) and toxicity (B) of sediment of the Ribeirão do Laranjal in rainy (C1) and dry (C2) seasons in the three sampling points: river mouth (P1), middle course (P2) and spring (P3).

Table 2. Metal content in Laranjal stream sediment in rainy (C1) and dry (C2) seasons in the sampling points at river mouth (P1), middle course (P2) and spring (P3).

	Metals (mg/kg)							
	Zn	Pb	Cd	Ni	Fe	Mn	Cu	Cr
P1, C1	171	90	22	66	7382	1877	19	6
P2, C1	330	105	21	56	7412	1817	58	1
P3, C1	85	97	17	41	322	1005	15	11
P1, C2	69	95	17	36	10917	3430	3	< 1
P2, C2	352	57	20	84	71275	1562	122	153
P3, C2	344	77	21	83	4445	1510	52	57
CONAMA 420/09	300	72	1.3	30	-	-	60	75

allowed by CONAMA 420/09 (Brasil, 2009). Although this legislation does not specify the maximum limits for Fe content, high concentrations of this element were found in P2 in the dry season. Fe is also present in P3 and P1 in the same season, but in lower concentrations.

Higher content of Pb was found in the sediments of the Ribeirão do Laranjal. The only exception was observed during the dry season (C2) in P2. The content of Cd and Ni were also higher than the maximum values allowed in both seasons and in all sampling points. The levels of Cu and Cr were lower than established by legislation in the rainy season (C1). In the dry season (C2), the results obtained in P2 were greater than permitted. Agricultural practices usually increase metals in soil and contribute to environmental deterioration from nonpoint source pollution (Atafar et al., 2010). The metals are, in general, constituted of impurities from fertilizers applied to agricultural soils. The metals As, Cd, Cu, Ni, Pb, V and Zn were found in superphosphate and urea fertilizer (Benson et al., 2014). Organic and mineral fertilizers, as well as corrective for soils, contain Zn as impurities (Kiekens, 1990). Heavy metals are also part of several agrochemical active ingredients and the use of Zn, Cu, Pb, As and Pb have a high level of soil contamination reflecting in human health (Muhibbullah et al., 2005). When metals reached an aquatic system, they can remain in the water column and can be incorporated by biota (bioaccumulation) or even sedimentary.

The Principal Component Analysis (PCA; Table 3) showed that 92% of the environmental variables were explained by the first four axes (PC1 to PC4). The first factorial axis explained 47.76% of the data variance, while the second axis explained 18.01%. Axis 1 presented a higher contribution of Cu (0.64), toxicity (0.63), gravel (0.61) and IM (0.60), with negative correlation for silte (-0.64) and OM (-0.60). The vector with the greatest contribution in axis 2 was Ni (0.47), with negative correlation of Mn (-0.47), sand (-0.47) and conductivity (-0.45) (Table 3). The variance of the data on the first two axes of the PCA shows that the three sampling points (P1, P2 and P3) presented different contributions from the limnological variables. Axis 1 contributes to the similarities of the data regarding spatial distribution for P1 and P2, with C1 positioned in the negative quadrant, while data from the C2 (dry period), from the positive quadrant of PC1. The variance of the data of P3 was evidenced in axis 2, with the dry season in the positive quadrant and the rainy season in the negative quadrant, influenced by Mn, sand and conductivity.

The map of the land use and land occupation of the Ribeirão do Laranjal watershed (Figure 5) shows areas with the following activities: exposed soil, fish-farming,

Table 3. Correlation coefficients of the limnological variables with the first two axes of the PCA.

Limnological variable	PC1	PC2	PC3	PC4	PC5
Temperature	-0.54	0.16	-0.35	0.10	-0.19
Conductivity	0.29	-0.45	-0.38	0.13	0.20
Turbidity	-0.28	0.05	-0.63	-0.02	0.12
Dissolved oxygen	0.21	0.12	0.59	0.27	0.07
pH	0.16	-0.39	-0.26	0.44	-0.23
Density	0.57	-0.34	0.00	-0.12	-0.17
pH Sediment	0.53	-0.41	-0.11	0.16	-0.02
Organic matter	-0.60	0.24	0.03	0.24	-0.11
Inorganic matter	0.60	-0.24	-0.03	-0.24	0.11
Gravel	0.61	0.28	0.19	-0.02	-0.03
Sand	0.27	-0.47	0.09	-0.06	-0.43
Silt	-0.64	-0.16	-0.20	0.04	0.13
Toxicity	0.63	0.12	0.16	-0.22	0.08
Zn	0.56	0.23	-0.15	-0.22	-0.22
Pb	-0.48	-0.33	0.13	-0.24	-0.27
Cd	0.16	0.22	-0.54	-0.35	-0.09
Ni	0.45	0.45	-0.28	-0.09	0.03
Fe	0.55	-0.03	-0.20	0.35	0.14
Mn	-0.03	-0.47	0.05	-0.22	0.46
Cu	0.64	0.13	-0.16	0.15	-0.13
Cr	0.57	0.24	-0.08	0.29	0.11

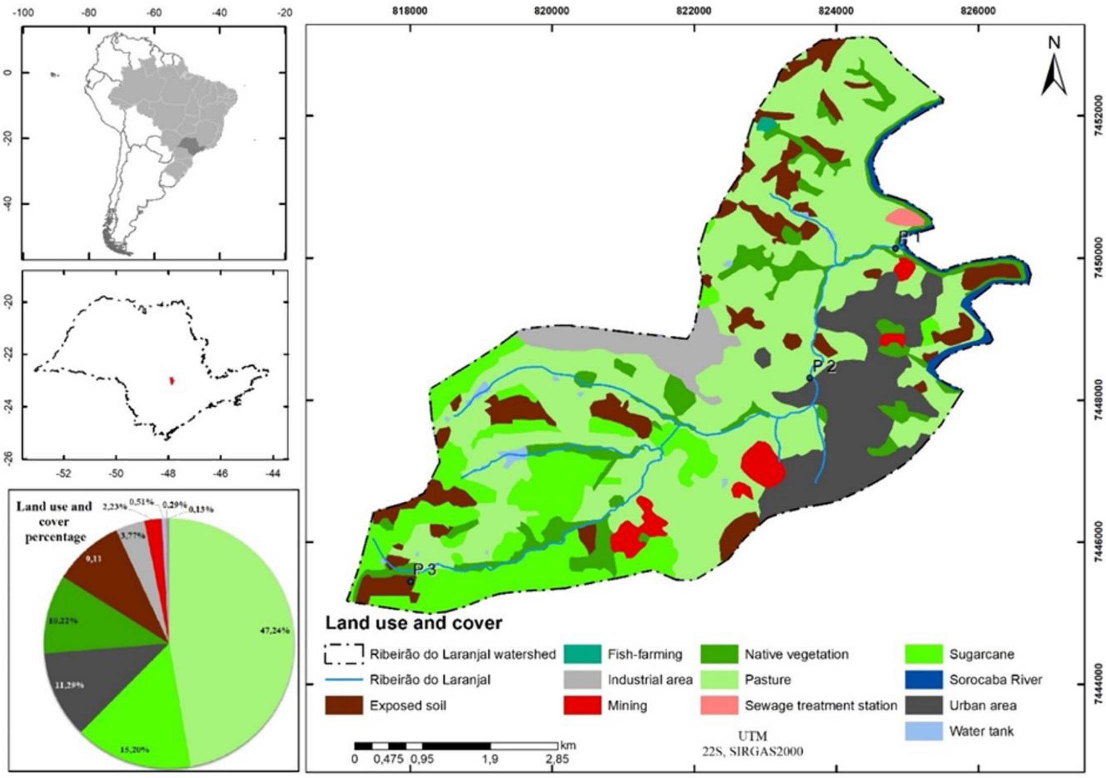

Figure 5. Land use and land cover of Ribeirão do Laranjal watershed in 2012.

industrial and urban areas, mining, native vegetation, pasture, sewage treatment station, sugarcane and water tank.

The Laranjal stream watershed has 3418.32ha with a huge area of pastures (47.24%), sugarcane (15.20%), urban area (11.29%), native vegetation (10.22%) and exposed soil (9.11%). Considering that sugarcane is a semi-perennial crop, the exposed soil areas traced may represent a post-harvest situation. There are areas of mining (2.23%) which extract clay for the manufacture of tiles, one of the economic bases of the municipality.

There is also a small area of water tanks (0.91%), which has the function of providing water for livestock. Some of these tanks occur near to Ribeirão do Laranjal. Near to the urban area is located the Pedra Brasil quarry, characterized as a mining area, which is disactivated since early 2000s and that accumulates water with a different hue because of the remnants of chemicals used for the extraction of stones in the past. The native vegetation, i.e., Permanent Protection Area and Legal Reserves, represent 10.22% of the total basin area, which represents a non-impacted environmental, consequently, a high conservation of local biodiversity.

CONCLUSION

The water EC indicates that the Ribeirão do Laranjal watershed is subjected to non planning input of sewage associated to erosion points due to the lack of riparian vegetation. The other variables are in accordance with Brazilian legislation (CONAMA 357/05 and CONAMA 420/09). The sediment from the stream presented high particle size and were predominantly inorganic. In general, the stream sediments displayed a high concentration of Cd, Ni and Cu. This concentration is due to the land use and occupation of the surrounding areas, wherein the anthropic pressure (e.g., intensive farming use surrounding P1 and P3) is responsible for the input of these elements. Considering the environmental degradation around the stream bank, was diagnosed the removal of the riparian vegetation in all points and the adduction of liquid and solid sewage in P2 proceeding from the urban area. Independent of season (rainy or dry), P1 showed the highest toxicity. The values of Cd and Ni were greater than allowed by the legislation in both seasons; the Pb value was larger in wet season and Cu and Cr had a greater value in P2 at dry season (C2). As for the land use and land occupation of the watershed, there was a predominance of the pasture, following by sugarcane and urban area. From the obtained results, we conclude that it is essential that the public administration take the necessary providences for the improvement of water quality, land use and land cover, and plan the occupation surrounding the Ribeirão do Laranjal, while maintaining the integrity of the water body that crosses Laranjal Paulista.

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