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Effects of land use and sampling distance on water quality in tropical headwater springs (Pimenta creek, São Paulo State, Brazil)

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Abstract

The studies targeted to hydrology and water quality are scarce in tropical headwater streams. In these delicate ecosystems the comprehension of water quality can constitute a challenge, because the impact of land uses on stream dynamics is particularly severe in tropical areas. To fill this gap, an evaluation of water quality in a headwater streams (Pimenta creek, São Paulo State, Brazil) under tropical conditions was performed. The implementation of linear mixed models to water quality parameters allowed to know how and to what extent water flowing in these headwaters are influenced by: (i) the spatial variation of spring locations; (ii) the different land uses; and (iii) the state of conservation of the riparian vegetation. Both the land uses in the surroundings of water springs (native forest, degraded vegetation, agriculture and pasture) and the sampling points (exactly in the spring and 10, 30 and 50 metres downstream) were found to be factors able to explain water quality variability. Most of the analysed parameters, some of which strongly correlated each others (mainly electrical conductivity, Total Dissolved Solids and salinity, but also color, turbidity and iron concentrations), showed significant variations mainly due to the effects of the different land uses, but also to the distance from water spring. The instability of the water quality parameters in springs degraded from its headwater was also demonstrated. The water springs with developed riparian vegetation of natural forest (in a preserved or even disturbed conservation level) showed the best conditions in the aquatic environment (lower temperature, turbidity, color, nitrite and nitrate concentrations, neutral pH). Conversely, in the water springs with

pasture or agricultural activities a general worsening of water quality was detected (worse turbidity, color, pH, nitrate and nitrate concentrations). Overall, the study has confirmed how much aquatic environment is sensitive to changes in the environment.

Keywords: Land use; linear mixed model; pasture; riparian vegetation; tropical forest; water spring.

1. Introduction

Headwater streams (that is, the first- and second-order channels of a water course, Strahler, 1952), cumulatively constitute the great majority of channel length within a river network (Downing et al., 2012). Their importance within the ecology and health of a water course falls in the fact that headwater streams are the source of water, solutes, mineral sediment, and particulate organic matter (Schumm, 1977; Alexander et al., 2007; MacDonald and Coe, 2007; McClain and Naiman, 2008). These delicate ecosystems are strongly influenced by many disturbances factors, such as precipitation, morphology, land use, geology, vegetation, human impacts, which can affect the entire watershed supplied by their water flows (Wohl, 2017; Rodrigues et al., 2017). Furthermore, across diverse hydro-climatic regions, headwater streams tend to exhibit more spatial and temporal hydrologic variability than larger channels (Gomi et al., 2002; Richardson and Danehy, 2007), which strongly influences the river ecosystem. Given such stressing factors, it is necessary to pay attention to the physical, chemical, and biological functions of headwater streams and, in particular, to water quality. Recently, Wohl (2017) highlighted the importance of water chemistry analysis in headwater for at least two reasons: (i) headwater stream chemistry is highly influenced by upland flow paths and chemistry of incoming surface and ground waters; (ii) headwaters are the first line of defence against potential contaminants such as excess fine sediment or nutrients.
Unfortunately, the relatively small streams are currently rather ignored by legal protections (mostly extended to larger rivers) and are aggressively altered in connection with diverse land uses (Wohl, 2017), even though there has been a recent upsurge in interest in the restoration of riparian habitats, which is focusing attention on understanding and ameliorating such impacts (Bombino et al., 2007). Water quality of headwater streams is important, because not only it is highly influenced by both upland flow paths and incoming surface and groundwaters, but also due to the fact that headwaters are the first line of defense against potential contaminants such as excess fine sediment or nutrients and the first receiving point for organic matter (Alexander et al., 2007). Also land use has significant impacts on river water quality with complex mechanisms, as demonstrated by several comparative studies (e.g. Wear et al., 1998; Amiri et al., 2009; Ding et al., 2015). Although the

significant impact of land use on stream water quality has been well documented (Johnson and Gage, 1997; Allen, 2004; Hurley and Mazumder, 2013; Bu et al., 2014; Ye et al., 2014; Kändler et al., 2017), further study on the complex association should be considered as much as possible (Yu et al., 2016). Therefore, it is important to carry out specific monitoring activities about the effects of land use on water quality specifically targeted to water springs of headwater streams.

Many different papers have dealt with monitoring and modelling of water quality at catchment-scale in several environments (e.g. Emmett et al., 1994; Ferrier et al., 2001; Baker, 2003; Ahearn et al., 2005; Shrestha and Kazama, 2007; Amiri et al., 2009; Hurley et al., 2013; Bu et al., 2014; Ye et al., 2014; Viswanathan et al., 2015; Yu et al., 2016; Kändler et al., 2017). It has been highlighted that hydrology, light, temperature and water chemistry are controlled by regional factors such as geology, topography or climate (operating at spatial scales of catchments as well as ecoregions), and, in addition, that human land-use activities act to change both local and regional variables at an increasing rate (Bere and Tundisi, 2011). Therefore, it is evident that the analysis of water quality must be carried out by site-specific studies.

However, the studies targeted to hydrology and water quality in tropical catchments are in general scarce (Fujieda et al., 1997); in addition, the comprehension of water quality response of a tropical catchment can constitute a challenge, because hydrological processes in these areas are difficult to assess (Hunke et al., 2015a; 2015b). Moreover, if we consider that the impact of land uses on stream water quality dynamics is particularly severe in tropical areas due to a more rapid mineralization of tropical soil organic matter and often, high erosion than in temperate zones (Spaans et al. 1989; Malmer and Grip 1990; Hartemink et al., 2008), it is evident how important the evaluation of water quality and their variability factors under different land uses is in water spring of tropical headwater streams. In these contexts, the role of riparian vegetation tyipical of tropical forests must be also deepened. As a matter of fact, since riparian vegetation plays important hydrological and ecological functions in soil and natural resources protection, such as for instance stream water flow regularisation as well as conservation of river biodiversity and habitats (Tabacchi et al., 2000; Rocha et al., 2015), its role towards a greater stability of the physico-chemical characteristics of headwaters must be highlighted and enhanced.

Specific evaluations of water quality in Brazil are conducted at very few research stations, for example, clustered in the IBGE Reserve of the Federal District (Markewitz et al., 2006; Parron et al., 2010). Although more data are available from local and regional studies by local water managers or environmental protection agencies, they are not published in scientific journals and thus the impacts of land use on aquatic systems, that is, pollution from nutrients and pesticides, their in-stream processes, and their effects on aquatic habitats, are not well understood (Hunke et al., 2015a). Biome-specific water quality thresholds lack in Brazil (Hunke et al., 2015b), except for baselines for physical–chemical water parameters ranging from natural to very impacted conditions in the Cerrado area reported by Fonseca et al. (2014).

The objective of this work is the evaluation of water quality as influenced by the spatial variation of spring locations, the different land uses and state of conservation of the riparian vegetation in water springs of a headwater stream (São Paulo State, Brazil) typical of tropical conditions. More specifically, by applying linear mixed models the following questions are answered: (i) is water quality influenced by land use or distance from spring or both? (iii) to what extent water quality is influenced by these factors of change? (iii) are there any correlations among the water quality parameters? Identifying the spatial variability of land use impacts on water quality represents a significant challenge; addressing this issue is critical for assessing the potential risks of development and the cost-effectiveness of water management at the watershed scale (Ding et al., 2015).

2. Materials and methods

2.1. Study site description

The study was carried out in the headwater stream of Pimenta creek, a tributary of the Paraiso basin. The basin belongs to the São Manuel experimental farm (belonging to UNESP/FCA), in the central-western region of the state of São Paulo (Brazil) (Figure 1). The basin of the Pimenta creek is located between the geographic coordinates 22°46'07"S to 22°46'57"S and 48°33'49"W to 48°33'59"W at an average altitude of 779 meters. It covers an area of 22.8 ha and is covered by pasture (57.5%), native vegetation and bamboo (25.9%), exotic vegetation (5.5%), agriculture (10.1%) and infrastructure (1.0%); the main stream is 1620 metres long and its slope is of 2.6% up to 38.8%. The climate of the region of São Manuel is of the type Cwa, hot temperate climate (mesothermic). The wetter and colder period falls in the spring-summer seasons and the water shortage with warmer temperatures in the autumn-winter seasons (Cunha, 2009) (Figure 2). The floodplains of the water course show alluvial soils formed by sandy sediments (Lima, 2003). The soil of the basin, practically homogenous, is classified as Red-Dark Latosol, with sandy texture. It a soil in advanced stage of weathering, very evolved, as a result of notable transformations of the constitutive material.

2.2. Sampling sites and water quality analyses

In the studied basin four headwaters with as many water springs were identified (henceforth indicated as "N1", "N2", "N3" and "N4") (Figure 3) and the land use characterised. The spring "N1" falls in a native tropical forest with a radius of 80 metres around the source. Riparian vegetation has the physiognomic characteristics of the semidecidual seasonal forest and Cerrado. Spring "N2" is covered by secondary riparian forest developed after a wildfire occurred 40 years ago with some pasture on the left bank. The headwater of the spring "N3" is mainly pastured and in some zones bamboo (*Bambusa* sp.) cover was artificially established for erosion control; 30 metres downstream of the headwater there is a narrow strip of riparian forest at its early stage. Around N3, domestic wastewater, treated and untreated, has been discharged for 50 years. In spring N4, pasture is cultivated around the spring with a cover of *Brachiaria* sp. In the rainy season, fertilizers and other chemical products are poured in the water course close to the spring, thus contributing for its degradation.

Stream discharges, measured in the channel immediately downstream of the four water springs, are higher between January and April (that is, during the wetter season, in which precipitation is concentrated) and lower during the drier period (particularly in August, when rainfall input is lower); on the average, the mean monthly values of stream discharge are quite similar among the four headwaters (from 0.17 L s^{-1} for N2 to 0.26 L s^{-1} for N3, Figure 4).

Close to these springs the riparian vegetation were characterised. Adopting the procedure described by Pinto (2005), the conservation level of the vegetation in the surroundings of each water spring was measured in four quadrants (up to a distance of about 10 metres from the thalweg), with the right and left margin oriented along the flow direction of the main course. In relation to this conservation level, the springs were classified as "preserved", "disturbed" or "degraded", accordingly to the criteria reported in the Brazilian forest code (Federal Law no. 12.651/2012). In more detail, the riparian vegetation is considered: (i) "preserved", when it exists in the surroundings of 50 metres from the spring without any signs of disturbance or degradation; (ii) "disturbed", if the spring does not show natural vegetation within a radius of 50 metres, but this space has a vegetation in good conditions and is covered partly by pasture or agriculture; (iii) "degraded", if the spring is subject to a high degree of disturbance, compacted soil, scarce and eroded vegetation. Therefore, the vegetation of springs "N1" and "N2" is "preserved forest" and "disturbed forest", respectively. Spring "N3" is a "degraded pasture", while vegetation of "N4" is classified as "degraded and agricultural").

In order to evaluate water quality, samples of water were collected systematically at four points for each of the four springs, with four measurements for each sampling point. In more detail, the first sampling point (henceforth "P1") was located exactly at spring source. The other samples were collected 10, 30 and 50 metres downstream of the water spring (indicated as "P2", "P3" and "P4", respectively); of course, each sampling point relates to a different distance from the source. Samples were collected throughout one year (from August 2012 to July 2013), distributed in monthly surveys.

In our study a limited but representative set of water quality parameters was selected. We excluded some measurements such as the concentrations of some cations (Ca^{++}, Mg^{++}, K^{+} and Na^{+}) and anions (HCO_3^-, SO_4^{--}, Cl^-), since water pollution by these elements/compounds was not suspected in the analysed springs, lacking in their surroundings mineral fertiliser use (containing some of the aforementioned cations) and industrial facilities (which may contaminate spring water with the anions above, beside heavy metals).

As regards the water quality parameters selected, the following determinations were made *in situ*:

- Electrical conductivity [µS cm^{-1}], total dissolved solids (TDS, [mg L^{-1}]) and salinity [mg L^{-1}], using the portable multimeters Extech PH 100 and EC 400;
- Temperature [°C] and pH [-] by a pH-meter (Extech PH 100).

At the Water Quality Laboratory of the Department of Rural Engineering at Campus Botucatu of the São Paulo State University, the following water parameters were determined:

- Color [mg L^{-1} Pt], by the colorimeter Aqua-Tester 611-A;
- Turbidity ([FAU], according to ISO Method 7027, attenuated radiation), nitrate [mg L^{-1}], nitrite [mg L^{-1}] and iron [mg L^{-1}], by the digital spectrophotometer Hach Model DR2010 were measured.

Phosphate concentration was not analysed in addition to nitrogen compounds, because the fertiliser used in the agricultural activities surrounding the analysed water springs is only animal manure, which, as well known, is rich in nitrogen and poor in phosphorous.

As reference limits for water quality evaluation and comparison, the standards issued by United States Environmental Protection Agency (USEPA) were adopted.

2.3. Statistical analysis

The water quality parameters were transformed to square root to fit the equity of variance and normal distribution, then the descriptive statistics for each variable were calculated. Subsequently, three Linear Mixed Models (henceforth indicated as "$LMM_{s \cdot d}$", "LMM_s" and "LMM_d") were applied to analyse whether there are any correlations (and their significance level) between the water quality parameters and: (i) spring characteristics (land use and conservation level of riparian vegetation) and distance from water spring (for $LMM_{s \cdot d}$); (ii) only spring characteristics (for LMM_s); (iii) only distance from water spring (LMM_d).

In order to find out which one of the three tested models best fits the data, the likelihood ratio test and the Akaike criterion were used. The results of the analyses performed for the three models were compared through the tables of analysis of variance. After the best LMM was defined, the Tukey test (at p-level < 0.05) was applied to compare water quality parameters between the sampling points of each source and the correlation analyses were performed using the Pearson method (Viswanathan et al., 2015).

3. Results

In general, all the measured parameters of water quality were under the criteria suggested by USEPA, except for iron concentration (in our study in the range 0.5-2.6 mg L^{-1} on the average against a limit of 0.3-1.0 mg L^{-1} reported by USEPA); this leads to consider the water quality of the analysed spring as good.

3.1. Water quality variations among water springs

Among the analysed water springs, "N1" showed the lowest mean temperature (19.3 °C ± 1.5), turbidity (12.6 FAU ± 6.1), nitrite (0.005 mg L^{-1} ± 0.003) and iron (0.3 mg L^{-1} ± 0.3), but the highest electrical conductivity (143.7 µS cm^{-1} ± 12.1), Total Dissolved Solids (100.7 mg L^{-1} ± 8.3), salinity (71.7 mg L^{-1} ± 5.7) and pH (7.3 ± 0.2). The spring "N2" had the lowest mean color (22.6 mg L^{-1} Pt ± 7.5) and nitrate (0.8 mg L^{-1} ± 0.3). For "N3" the lowest mean electrical conductivity (11.9 µS cm^{-1} ± 3.6), TDS (8.3 mg L^{-1} ± 2.5), salinity (5.8 mg L^{-1} ± 1.7) and pH (5.4 ± 0.3) together with the highest mean turbidity (173.3 FAU ± 78.1) and nitrite (0.1 mg L^{-1} ± 0.02) were measured. "N4" presented the highest mean temperature (23.1 °C ± 3), color (95.3 mg L^{-1} Pt ± 10.8), nitrate (4.8 mg L^{-1} ± 2.7) and iron (2.6 mg L^{-1} ± 0.6) (Table 1).

3.2. Comparison between linear mixed models

Table 2 reports the comparisons between the three linear mixed models (LMM) tested for analysing the water quality parameters in the Pimenta creek. The differences between $LMM_{s \cdot d}$ (based on spring characteristics and distance from the water spring) and LMM_d (based only on distance) were significant for all the studied parameters. $LMM_{s \cdot d}$ significantly differed from LMM_s (based on spring characteristics) only for two parameters (temperature and iron concentration), while LMM_s and LMM_d (this latter based only on distance) gave practically the same statistical values (Table 2).

3.3. Spatial variations of water quality in water springs

The spatial differences in temperature and iron concentrations between the sampling points of each spring were not significant (p-level > 0.9) (Table 3). Conversely, it was observed that in some points the electrical conductivity, Total Dissolved Solids, salinity, turbidity, color, pH, nitrate and nitrite were significantly influenced by the distance of water collection point from the spring. More than 90% of these differences were detected between "P1" and the other sampling points ("P2", "P3" and "P4"). The parameter pH was found to have the highest spatial variability among the sampling points (Table 3).

More specifically, for spring "N1" (preserved riparian forest), only pH had significant differences between the sampling points, except for the couples of points "P1"-"P2" and "P3"-"P4". Water sampled at spring "N2" (covered by natural forest in a disturbed state) had more significant difference in pH between points "P1" and "P3"-"P4" as well as "P2" and "P4" (Table 3). The spring "N3" (pasture with degraded vegetation) showed significant differences between the sampling point "P1" and the other points ("P2", "P3" and "P4") mainly for the Total Dissolved Solids, turbidity and color and in some couples of sampling points for pH, nitrate, nitrite and electrical conductivity). Finally, in the spring "N4" (with degraded vegetation as "N3", but agricultural) less significant differences (mainly in electrical conductivity, Total Dissolved Solids and salinity) were detected between the sampling point "P1" and the some other points at a distance from "P1" (Table 3).

3.4. Correlations among water quality parameters

As expected, electrical conductivity, Total Dissolved Solids and salinity were strongly correlated each another (r > 0.99) and this suggests that they express very similar water quality parameters and processes. All these parameters were not significantly correlated with temperature, nitrate and nitrite (r < 0.20). Finally, color has a very strong correlation with turbidity (r = 0.85) and iron (r = 0.87) and these latter parameters are also noticeably correlated each other (r = 0.76) (Figure 5). Also Rodrigues et al. (2017) found a high correlation between iron and turbidity in the same tropical environment.

4. Discussions

Tropical catchments, such as the focus of this investigation, are precisely characterized by strong seasonality of climate with pronounced wet and dry seasons (Perez Hernandez and Lopez, 1998); moreover, also the generation of surface runoff, which influences water quality parameters, is a seasonal phenomenon, largely affected by land use and climate within the basin (Singh et al., 2004). Tropical streams differ ecologically from temperate ones, since streams in the tropics typically receive higher solar radiation and more intense rainfall, with warmer water and often relatively predictable floods; moreover, they show a higher biodiversity than their temperate equivalents (Dudgeon, 1999), which suggested to investigate the water quality of tropical streams as affected by natural and human-induced stresses.

In general, from the noticeable variations of the physico-chemical parameters of water quality related to the effects of land use, it is evident that water courses are very sensitive to changes in the environment and this is particularly true in the portions of the stream where vegetation is removed or increasingly modified. Also this study revealed a significant incidence of the different land uses and conservation levels of riparian vegetation as well as the distance of sampling points on water quality, as indicated by the significant differences detected in the majority of the analysed parameters.

First of all, the implementation and reciprocal comparison of three different LMMs showed that, when water quality is monitored in tropical streams, not only the land use of the spring surroundings, but also the sampling distance can play an influence. As a matter of fact, if LMM_s take into account as variability factor only sampling point or land use effects, the difference in water quality parameters are always not significant (see comparison of LMM_s and LMM_d models in Table 2). Viceversa, a 2-level LMM highlights correctly the variability of water quality which depend on both land use and distance from water source (see $LMM_{s \cdot d}$ in Table 2).

As regards the effects of land use on water quality parameters, the study has demonstrated that water temperature and iron concentration were not significantly variable among forest (spring "N1"), disturbed vegetation ("N2"), pasture ("N3") and agricultural land uses ("N4"); however, the water springs with riparian vegetation showed slightly low temperature throughout the year (even though not significantly) because of the shadowing of forest canopies. The spring "N4", unprotected from vegetation, and "N3", with small vegetation, were exposed to direct solar radiation and consequently the temperatures rise up (Arcova and Cicco, 1999).

In comparison to the international standards (e.g. those of USEPA), the water quality of the analysed spring was generally good with the exception of iron concentration. This element, an important indicator of geogenic conditions, becomes soluble by redox processes in soils and sediment (Vuori, 1995) and, thus, the stream water concentration tends to depend on the particular hydrological situation rather than on land use (Kändler et al. 2017). The iron concentration of Pimenta creek showed some variations among the springs, even though not significantly: water quality of spring "N1" was similar as "N2" and these latter springs differed from "N3" and "N4". The values of iron concentration measured at the springs "N1" and "N2" highlighted that the presence of the riparian vegetation, preserved or even disturbed, influenced this parameter of spring water; on the contrary, the degraded vegetation of spring "N4" and bamboo with a small strip of degraded vegetation in "N3" showed that the absence or low strips of riparian complexes in a degraded state resulted in an increase of iron values, able to overcome the acceptance limits (suggested by USEPA standards) for this water quality parameter.

Compared to water springs with riparian vegetation (preserved, "N1", or degraded, "N2"), turbidity, color, pH and nitrate concentrations were much higher (that is, in "N3" and "N4"). The water pH was close to neutrality in the springs with riparian vegetation (accordingly to Donadio et al., 2005, who found pH close to 7 in water springs with tropical natural vegetation), showing a more preserved aquatic environment, while water was quite acid (due to organic acid pouring with wastewater of indigenous origin) in the other springs, which indicated possible water pollution. At the downstream sampling points, an increase of the concentration of color, turbidity and suspended solids was observed related with agricultural ditches triggering the coupling of agricultural hillslopes and stream (Slattery et al., 2002). In tropical forest environments, also Primavesi et al. (2002) and Donadio et al. (2005) reported higher values of turbidity in microbasins with agricultural land use than in forested areas, thus evidencing the function of the riparian forest in reducing solids supply from sources to stream water. The increase in turbidity values due to the scarcity of riparian forest were also observed in the study of Arcova and Cicco (1999) in a tropical and agricultural microbasin, which showed also higher color values and suspended sediments in water of the stream interfering with the presence of a road (as in spring "N4" of our study). Also Donadio et al. (2005) found lower values of the water color in tropical streams of riparian forest compared to other land uses. Many Authors reported that farmland is responsible for water pollution, while, on the contrary, forested areas show negative correlations with most ions (e.g. Bahar et al., 2008; Zhou et al., 2012; Xia et al., 2012; Kändler et al., 2017). As Keesstra et al. (2012) found, the riparian zone has a significant effect on water and sediment transport in headwater catchments, since high roughness in natural rivers due to vegetation and geomorphological attributes may generate drag on flowing water. This is also in accordance with Gao (2008), who showed that the riparian vegetation in headwater catchments play an important role in the resulting water and sediment dynamics of rivers further downstream; in general, vegetation of riparian zones has a demonstrated buffer capacity for avoiding the transfer of diffuse contaminants to surface waters (Connolly et al., 2015). Since headwater streams are particularly closely coupled with adjacent riparian and terrestrial environments, because of the higher ratio of aquatic-riparian interface and the sensitivity of riparian zones towards river basin ecohydrology (Bombino et al., 2014; Wohl, 2017), riparian buffer strips and their structure are critical for maintaining water functions and minimising eutrophication (Boëchat et al., 2013; Parron et al., 2010; Fernandes et al., 2014; Hinke et al., 2015b). Thus, under the catchment management point of view, riparian vegetation should be promoted in stream channels and intensive agricultural uses in adjacent areas should be avoided, in order to not alter water quality (Rodrigues et al., 2017).

Differences in Electrical conductivity, Total Dissolved Solids and salinity (all of them strongly correlated each other, as highlighted above) among the different land uses close to the four water springs do not seem to be in relation to human-induced changes (affecting "N3" and "N4") or lower disturbance in headwaters (as in "N1" and "N2"); as a matter of fact, the highest values were surveyed in the preserved spring, while the lowest parameters were measured in the partially degraded headwaters. The determinant factor for the electrical conductivity values may be the geology of the sites, that, for instance, is constituted by rocks resistant to weathering, such as granites and gneisses, in "N1" (highest electrical conductivity), and soils in advanced stage of weathering in "N2" (lowest EC) (Arcova and Cicco, 1999). Extremely weathered, undisturbed watersheds are characterized by very low in-stream ionic concentrations (and therefore electrical conductivity) often dominated by the Calcium ion (Markewitz et al., 2006).

Nutrients such as inorganic nitrogen (ammonia, nitrate and nitrite) are important factors affecting water quality, since they play, together the bioavailable forms of phosphorous, an important role in the eutrophication process in surface waters (Soulsby et al., 2001; Sener et al., 2017). The higher concentrations of nitrites and mainly of nitrates in springs "N3" (pastured) and "N4" (cropped) - even though low compared to USEPA water quality standards - can be explained, as for pH, by the fact that the sites were heterogeneous in land use and these parameters are sensitive to denudation of riparian vegetation and nitrogen-based fertilizer use, since fertilizers and animal manure (rich in nitrogen) is usually transported downstream by surface runoff to the waterways. The spring "N3" had a domestic sewage at its headwater; this fact may have contributed to the spatial variation of turbidity and color, increasing the presence of suspended solids in water and the sediment transport downstream, which interfere with light penetration through the water. Effluents pouring into streams is in fact an important factor that controls water quality parameters (Castro and Mendonça, 2004). Many different studies have shown that agricultural land uses at catchment scale is a primary predictor for water quality compounds (Smart et al., 1998; Ferrier et al., 2001; Ahearn et al., 2005). An increase in electrical conductivity and inorganic N-forms in surface water was detected in most reviewed studies due to anthropogenic inputs from fertilisation and liming. Silva et al. (2011) detected higher nitrite concentrations and water conductivity in tropical rural streams compared to natural low order catchments and concluded that agricultural land use had a measurable impact on solute loads in the river system (Hunke et al., 2015b). These latter Authors from their water sampling results demonstrated the significant impact of agricultural use on water quality, especially for nitrate and nitrite concentrations. For small first-order pasture catchments, Gücker et al. (2009) found significantly higher electrical conductivities and NO_3 compared with natural streams. The concentrations of NO_3 and NO_2 in rural streams were as much as 1.5 times higher, and they differed significantly from natural streams (Hunke et al., 2015a). Fonseca et al. (2013) presented similar findings in low-order pristine streams.

Conversely, an improvement in the water quality is usually observed in relation to the amount of nitrate and nitrite in the microcatchments with dense vegetation cover and in an advanced regeneration phase. Nitrate concentrations in surface water of Brazilian forests (e.g. in Cerrado) were orders of magnitude lower compared with concentrations measured in European rivers under land use change (Hunke et al., 2015a). In a stream with gallery forest within an ecological reserve near Brasilía, Parron et al. (2010) found only very low N concentrations, whereas nitrates were not detectable, due to the fact that forest has a high filtering capacity. Moreover, a dilution effect of $NaNO_2$, NO_2 and NO_2-N as well as Total Dissolved Solids (and, as a consequence, of electrical conductivity and salinity) was observed downstream of tropical rivers (Rodrigues et al., 2017). Analyzing the impacts of human activities in reforested basins, Castro and Mendonça (2004) found an improvement in the quality of in relation to the amount of nitrate and nitrite in microbasins with dense vegetation cover and in advanced regeneration phase. The same Authors also recorded higher amounts of nitrate due to agricultural practices and soil exposure by low effective protection coverage, in addition to that of fertilizers.

As different studies have demonstrated, land use changes (i.e. from forest to agricultural land uses) may alter and increase water and sediment connectivity, thus changing water quality along streams (Parsons et al., 2015; Masselink et al., 2017a; Masselink et al., 2017b). From the study it was evident that most of the water quality parameters in agriculture-dominated sites had higher concentrations than those in forest-dominated sites, as also stated by Dong et al. (2015). Therefore, the land use type had a significant weight not only in the correlation coefficients for each water quality characteristic but also in the degree of influence of land use itself on each water quality variable (Yu et al., 2016). However, some important caveats apply to studies of the relationship between land use and stream water quality: when conducting a Pearson's correlation analysis on this type of relationship, the conclusion that the land use type was the primary driver of stream water quality must be made with caution (Yu et al., 2016). In addition, forecasting changes in stream water quality in response to changes in land use type may run the risk that the relationship would alter over time owing to changes in some specific practices or the environment itself (Allen, 2004).

With reference to the water quality variability as function of the sampling distance from the spring, the spatial variations were significant for the majority of the couples of points in relation to pH, demonstrating the heterogeneity of the site and the sensitivity of this parameter, but not for temperature and iron concentrations. Water temperature and iron concentrations remained unaltered within each spring (that is, within the same land use) regardless of the distance of sample collection. Nitrate concentration as well as Electrical conductivity, Total Dissolved Solids and salinity had significant spatial variations only in the two water springs considered to be degraded ("N3" and "N4"), as direct consequence of both human-induced changes (pasture, agriculture and wastewater pouring) and lower presence of riparian vegetation. Water color and turbidity significantly differed according to the distance only in pastured spring. The noticeable relation between flow quality and the effect of the distance was detected also by Castro and Mendonça (2004) and Rodrigues et al- (2017), who found an important relationship between discharge and the distance effect on water quality parameters: the study of these latter Authors indicated that the measured water quality parameters varied among the different sampling points from the headwater sampling point (0 m) to the last downstream sampling point (2500 m).

Overall, the study showed that, for a preserved water spring covered by riparian forest, more or less preserved (as the spring "N1" and "N2" are), only pH of water may suffer from some alterations between the surroundings of spring (points "P1" and "P2") and other zones at a distance from the source ("P3" and "P4"), being the differences among the other water quality parameters practically not appreciable. Conversely, the significant variations of parameters detected for the agricultural spring (e.g. turbidity, color, total suspended solids) demonstrate the increase of instability of water quality parameters with distance in a spring degraded from its headwater. Finally, in the last spring (degraded as the previous one) the lower differences (mainly in electrical conductivity, Total Dissolved Solids and salinity) in the surveyed paramters evidenced less noticeable spatial variations of water quality in pasture.

Our results are in tune with those of studies carried out in temperate systems, which have demonstrated that riparian forest buffers act on water quality, by filtering sediment and nutrients from agricultural runoff and providing shade that moderates stream temperatures and regulates instream primary production (Karr and Schlosser, 1978; Peterjohn and Correll, 1984; Osborne and Kovacic, 1993). However, although riparian forest buffers are expected to provide similar functions in tropical systems, studies documenting relationships between forest buffers and river ecosystem components in the tropics are conspicuously lacking (Lorion and Kennedy, 2009); our study tried to fill this gap, suggesting how, in tropical headwaters of Mata Atlantica (one of the most threatened biome in Brazil, SOS Mata Atlantica and INPE, 2013), forested riparian zones could significantly reduce the impacts of deforestation - by agricultural and pasture activities - on tropical streams (Pringle and Scatena, 1999; Benstead et al., 2003).

5. Conclusions

In spite of a generally good water quality (except for the iron concentration), the monitoring of water quality in a small headwater of the tropical environment showed a large variability of many parameters among the different land uses and sampling points. Both these factors play an important role in explaining water quality variability, as showed by the comparison among three linear mixed models. Among the analysed parameters, some of which strongly correlated each other (mainly electrical conductivity, Total Dissolved Solids and salinity, but also color, turbidity and iron concentrations), pH was found to be the water quality parameter with the highest spatial variability among sampling points. The other parameters evaluated showed variations mainly due to the effects of the different land uses, but also to the distance from water spring. In general, the study demonstrated the instability of the water quality parameters in spring degraded from its headwater. The water springs with developed riparian vegetation of natural forest (in a preserved or even disturbed conservation level) showed the best conditions in the aquatic environment (lower temperature, turbidity, color, nitrite and nitrate concentrations, neutral pH). Conversely, compared to vegetated surroundings, in the water springs with pasture or agricultural activities a general worsening of water quality was detected (worse turbidity, color, pH, nitrite and nitrate concentrations).

On the whole, the study has demonstrated how much aquatic environment is sensitive to changes in the environment, confirming findings of literature. It has also been highlighted the importance of riparian vegetation effects for conservation of water quality of tropical headwater catchments, where, instead, agriculture and pasture may represent a threat against natural resource preservation.

The study can serve as a monitoring model in compared to other impacted watersheds (Arcova and Cicco, 1999) and the values of the water quality parameters achieved may represent a reliable database to support the development of conservation and management strategies for tropical headwaters. However, it should be noted that the use of water as a qualitative indicator requires further studies to verify that the other factors that may interfere with its quality.

Finally, the monitoring activities of water quality allow us to know and interpret the actual influences played by factors of change (such as land use, spatial and temporal changes) on water quality and riparian ecology. Understanding the relationships between water quality and their variability and land use as is necessary to diagnose information on the health of water springs and headwater streams and to support the adoption of the best management strategy (Lessels and Bishop, 2013).

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TABLES

Table 1. Descriptive statistics of water quality parameters of water spring in the Pimenta creek (São Paulo State, Brazil).

Water spring sampling point	**Mean**	**Maximum**	**Minimum**	**Std. Dev.**	**CV**	**Water spring sampling point**	**Mean**	**Maximum**	**Minimum**	**Std. Dev.**	**CV**
	Temperature (ºC)						**Electrical Conductivity (µS cm^{-1})**				
N1P1	19,2	21,3	16,6	1,6	8,4	N1P1	147,3	165,7	125,4	13,7	9,3
N1P2	19,3	21,3	16,7	1,5	7,8	N1P2	140,0	154,3	121,3	11,4	8,2
N1P3	19,3	21,0	16,8	1,5	7,6	N1P3	142,4	155,3	121,5	11,8	8,3
N1P4	19,3	21,4	16,8	1,5	7,9	N1P4	145,1	161,6	129,0	11,3	7,8
Mean	*19,3*	*21,3*	*16,7*	*1,5*	*7,9*	*Mean*	*143,7*	*159,2*	*124,3*	*12,1*	*8,4*
N2P1	20,0	23,2	17,2	1,8	8,8	N2P1	49,3	67,9	41,0	8,1	16,4
N2P2	19,9	22,8	17,3	1,7	8,4	N2P2	44,8	56,5	37,9	6,5	14,5
N2P3	19,8	22,4	17,3	1,6	8,3	N2P3	44,3	59,9	38,1	6,7	15,1
N2P4	19,7	22,3	17,3	1,7	8,7	N2P4	45,3	55,5	39,0	6,2	13,6
Mean	*19,9*	*22,7*	*17,3*	*1,7*	*8,6*	*Mean*	*45,9*	*60,0*	*39,0*	*6,9*	*14,9*
N3P1	21,4	24,5	18,2	2,0	9,3	N3P1	14,6	19,7	11,6	2,2	14,7
N3P2	21,8	24,7	18,2	1,9	8,9	N3P2	11,5	18,5	5,0	4,2	36,2
N3P3	21,7	25,6	18,2	2,1	9,8	N3P3	10,5	19,9	6,1	4,7	44,5
N3P4	21,6	25,0	18,1	2,2	10,1	N3P4	10,9	19,9	7,1	3,4	31,4
Mean	*21,6*	*25,0*	*18,2*	*2,1*	*9,5*	*Mean*	*11,9*	*19,5*	*7,5*	*3,6*	*31,7*
N4P1	23,5	30,2	18,3	3,6	15,3	N4P1	111,3	153,3	93,0	16,9	15,1
N4P2	23,1	28,3	18,4	3,0	13,1	N4P2	98,6	116,0	80,0	10,3	10,4
N4P3	23,1	28,1	18,7	2,8	12,1	N4P3	100,5	136,7	82,1	15,2	15,1
N4P4	22,7	27,3	18,0	2,7	12,0	N4P4	93,9	106,3	81,3	7,9	8,4
Mean	*23,1*	*28,5*	*18,4*	*3,0*	*13,1*	*Mean*	*101,1*	*128,1*	*84,1*	*12,5*	*12,3*
	Total dissolved solids (mg L^{-1})						**Salinity (mg L^{-1})**				
N1P1	103,6	115,9	89,7	9,2	8,9	N1P1	73,0	81,2	64,1	5,9	8,0
N1P2	97,6	108,0	84,6	8,2	8,4	N1P2	69,7	77,3	60,5	5,9	8,4
N1P3	99,3	108,9	85,4	7,7	7,7	N1P3	71,1	77,8	61,5	5,5	7,7
N1P4	102,2	113,4	91,4	8,1	7,9	N1P4	72,9	80,6	65,3	5,8	7,9
Mean	*100,7*	*111,6*	*87,8*	*8,3*	*8,2*	*Mean*	*71,7*	*79,2*	*62,9*	*5,7*	*8,0*
N2P1	34,5	47,5	28,9	5,8	16,7	N2P1	24,5	34,0	20,6	4,1	16,5

N2P2	31,2	39,5	26,5	4,3	13,9	N2P2	22,5	29,1	18,9	3,3	14,8
N2P3	30,8	39,4	26,9	4,4	14,2	N2P3	22,0	28,0	19,1	3,0	13,8
N2P4	31,4	39,4	25,3	4,8	15,3	N2P4	22,6	28,2	19,3	3,4	14,8
Mean	*32,0*	*41,5*	*26,9*	*4,8*	*15,0*	*Mean*	*22,9*	*29,8*	*19,5*	*3,4*	*15,0*
N3P1	10,4	13,9	8,0	1,6	15,2	N3P1	7,1	8,3	5,1	0,9	12,4
N3P2	8,3	16,2	3,5	3,7	45,1	N3P2	5,8	10,1	2,6	2,6	43,9
N3P3	7,1	12,6	4,5	2,6	36,4	N3P3	5,2	9,7	3,0	2,2	41,4
N3P4	7,2	10,9	4,5	1,9	26,0	N3P4	5,1	7,5	3,1	1,4	27,0
Mean	*8,3*	*13,4*	*5,1*	*2,5*	*30,7*	*Mean*	*5,8*	*8,9*	*3,5*	*1,7*	*31,2*
N4P1	73,4	106,5	60,9	13,0	17,7	N4P1	54,5	80,1	35,1	13,3	24,4
N4P2	67,5	80,4	55,2	7,4	11,0	N4P2	47,0	57,3	39,3	5,2	11,0
N4P3	63,5	70,1	56,2	3,6	5,6	N4P3	44,8	50,8	39,8	3,0	6,6
N4P4	63,8	70,4	56,8	4,3	6,7	N4P4	43,9	50,3	38,1	4,1	9,3
Mean	*67,0*	*81,9*	*57,3*	*7,1*	*10,2*	*Mean*	*47,5*	*59,6*	*38,1*	*6,4*	*12,8*
	Turbidity (FAU)						**Color (mg L^{-1} Pt)**				
N1P1	12,3	23,0	2,0	6,3	51,3	N1P1	19,4	35,0	10,0	8,9	46,1
N1P2	14,2	22,0	4,0	5,1	36,0	N1P2	25,4	40,0	17,5	7,1	28,1
N1P3	12,3	25,0	0,0	8,6	69,3	N1P3	24,6	40,0	15,0	7,8	31,5
N1P4	11,6	21,0	3,0	4,4	37,7	N1P4	25,8	55,0	15,0	11,0	42,5
Mean	*12,6*	*22,8*	*2,3*	*6,1*	*48,6*	*Mean*	*23,8*	*42,5*	*14,4*	*8,7*	*37,1*
N2P1	11,9	34,0	0,0	10,3	86,6	N2P1	19,4	30,0	10,0	5,8	29,7
N2P2	18,8	56,0	0,0	15,5	82,7	N2P2	21,9	35,0	10,0	8,9	40,5
N2P3	16,5	46,0	1,0	11,4	68,8	N2P3	22,9	35,0	15,0	6,6	28,6
N2P4	16,3	44,0	2,0	12,6	76,9	N2P4	26,3	50,0	17,5	8,8	33,4
Mean	*15,9*	*45,0*	*0,8*	*12,4*	*78,8*	*Mean*	*22,6*	*37,5*	*13,1*	*7,5*	*33,0*
N3P1	70,9	119,0	20,0	33,3	46,9	N3P1	63,3	100,0	40,0	24,6	38,9
N3P2	219,2	362,0	38,0	99,3	45,3	N3P2	91,7	100,0	50,0	19,5	21,2
N3P3	205,3	366,0	60,0	101,5	49,5	N3P3	96,3	100,0	55,0	13,0	13,5
N3P4	197,9	320,0	71,0	78,4	39,6	N3P4	95,0	100,0	60,0	12,4	13,1
Mean	*173,3*	*291,8*	*47,3*	*78,1*	*45,3*	*Mean*	*86,6*	*100,0*	*51,3*	*17,4*	*21,7*
N4P1	144,0	191,0	91,0	29,9	20,8	N4P1	94,2	100,0	60,0	12,4	13,2
N4P2	155,4	230,0	100,0	37,0	23,8	N4P2	92,9	100,0	60,0	13,6	14,6
N4P3	176,1	284,0	75,0	57,4	32,6	N4P3	95,8	100,0	60,0	11,7	12,2
N4P4	161,9	256,0	100,0	40,3	24,9	N4P4	98,3	100,0	80,0	5,8	5,9
Mean	*159,4*	*240,3*	*91,5*	*41,2*	*25,5*	*Mean*	*95,3*	*100,0*	*65,0*	*10,8*	*11,4*
	pH (-)						**Nitrate (mg L^{-1})**				
N1P1	7,0	7,4	6,7	0,2	3,2	N1P1	1,2	1,9	0,3	0,5	42,7

N1P2	7,1	7,6	6,8	0,2	2,8	N1P2	1,1	1,9	0,4	0,5	46,7
N1P3	7,5	7,9	6,9	0,3	3,7	N1P3	1,1	1,8	0,1	0,5	43,4
N1P4	7,5	7,7	7,0	0,2	2,5	N1P4	1,1	1,4	0,4	0,3	24,1
Mean	*7,3*	*7,6*	*6,9*	*0,2*	*3,1*	*Mean*	*1,1*	*1,8*	*0,3*	*0,4*	*39,2*
N2P1	6,9	7,3	6,6	0,2	2,9	N2P1	0,8	1,4	0,3	0,3	36,7
N2P2	7,0	7,4	6,7	0,3	3,7	N2P2	0,9	1,3	0,3	0,4	41,4
N2P3	7,3	7,6	6,4	0,4	5,2	N2P3	0,8	1,6	0,2	0,5	58,8
N2P4	7,4	7,6	6,9	0,2	3,1	N2P4	0,7	1,0	0,3	0,3	38,2
Mean	*7,2*	*7,5*	*6,7*	*0,3*	*3,7*	*Mean*	*0,8*	*1,3*	*0,3*	*0,3*	*43,8*
N3P1	5,1	6,0	4,7	0,4	6,9	N3P1	2,2	3,8	1,1	0,7	33,8
N3P2	5,3	5,6	5,1	0,2	3,4	N3P2	3,2	5,6	1,5	1,4	43,1
N3P3	5,6	6,1	5,1	0,3	5,2	N3P3	5,5	14,9	2,5	4,1	74,9
N3P4	5,6	6,2	5,1	0,3	5,5	N3P4	2,8	6,4	1,3	1,3	47,7
Mean	*5,4*	*6,0*	*5,0*	*0,3*	*5,3*	*Mean*	*3,4*	*7,7*	*1,6*	*1,9*	*49,9*
N4P1	6,5	7,3	5,8	0,4	5,7	N4P1	3,6	6,6	2,3	1,3	37,4
N4P2	6,7	7,0	6,3	0,2	2,8	N4P2	3,2	6,9	1,9	1,4	44,7
N4P3	6,7	7,2	6,2	0,3	4,6	N4P3	7,5	16,0	2,3	5,3	69,8
N4P4	6,8	7,1	6,5	0,2	3,1	N4P4	5,1	11,5	2,1	3,0	58,3
Mean	*6,7*	*7,2*	*6,2*	*0,3*	*4,1*	*Mean*	*4,8*	*10,3*	*2,2*	*2,7*	*52,5*
	Nitrite (mg L^{-1})						**Iron (mg L^{-1})**				
N1P1	0,0	0,0	0,0	0,0	40,0	N1P1	0,4	0,9	0,1	0,3	70,5
N1P2	0,0	0,0	0,0	0,0	75,0	N1P2	0,3	0,5	0,1	0,2	55,2
N1P3	0,0	0,0	0,0	0,0	40,0	N1P3	0,2	0,7	0,1	0,2	104,8
N1P4	0,0	0,0	0,0	0,0	66,7	N1P4	0,3	0,9	0,0	0,3	100,0
Mean	*0,0*	*0,0*	*0,0*	*0,0*	*55,4*	*Mean*	*0,3*	*0,8*	*0,1*	*0,3*	*82,6*
N2P1	0,0	0,0	0,0	0,0	75,0	N2P1	0,5	1,0	0,2	0,3	61,7
N2P2	0,0	0,0	0,0	0,0	233,3	N2P2	0,5	0,8	0,2	0,2	47,9
N2P3	0,0	0,0	0,0	0,0	50,0	N2P3	0,5	1,0	0,1	0,3	63,3
N2P4	0,0	0,0	0,0	0,0	140,0	N2P4	0,5	0,9	0,1	0,3	62,2
Mean	*0,0*	*0,0*	*0,0*	*0,0*	*124,6*	*Mean*	*0,5*	*0,9*	*0,1*	*0,3*	*58,8*
N3P1	0,0	0,0	0,0	0,0	43,8	N3P1	2,7	3,0	1,1	0,7	25,4
N3P2	0,0	0,1	0,0	0,0	63,0	N3P2	2,3	3,0	0,6	0,8	35,8
N3P3	0,4	0,1	0,0	0,0	7,1	N3P3	2,6	3,0	1,3	0,7	28,6
N3P4	0,0	0,0	0,0	0,0	52,4	N3P4	2,5	3,0	1,5	0,6	25,1
Mean	*0,1*	*0,1*	*0,0*	*0,0*	*41,6*	*Mean*	*2,5*	*3,0*	*1,1*	*0,7*	*28,7*
N4P1	0,0	0,0	0,0	0,0	41,7	N4P1	2,4	3,0	1,1	0,8	31,3
N4P2	0,0	0,1	0,0	0,0	65,2	N4P2	2,4	3,0	0,8	0,8	34,6

N4P3	0,0	0,1	0,0	0,0	84,2	N4P3	2,7	3,0	1,7	0,5	20,0
N4P4	0,0	0,1	0,0	0,0	60,0	N4P4	2,8	3,0	2,1	0,4	12,4
Mean	*0,0*	*0,1*	*0,0*	*0,0*	*62,8*	*Mean*	*2,6*	*3,0*	*1,4*	*0,6*	*24,6*

Note: N refers to the water spring number, while P to the water sampling point; CV = coefficient of variation (std. dev./mean, [%]).

Table 2. Comparison between linear mixed models (LMM) applied to water quality parameters of water springs in Pimenta creek (São Paulo State, Brazil).

Water quality parameters	**Pr (> χ^2)**		
	$LMM_{s \cdot d}$ vs LMM_s	**$LMM_{s \cdot d}$ vs LMM_d**	**LMM_s vs LMM_d**
Temperature	0.94	**<0.001*** **	1
Electrical conductivity	**<0.001*** **	**<0.001*** **	1
Total Dissolved Solids	**<0.001*** **	**<0.001*** **	1
Salinity	**<0.001*** **	**<0.001*** **	1
Turbidity	**<0.001*** **	**<0.001*** **	1
Color	**<0.001*** **	**<0.001*** **	1
pH	**<0.001*** **	**<0.001*** **	1
Nitrate	**<0.001*** **	**<0.001*** **	1
Nitrite	**0.01* **	**<0.001*** **	1
Iron	0.34	**<0.001*** **	1

Notes: in bold characters the significant differences are highlighted; *, **, *** significant difference at $p < 0.05$, 0.01 and 0.001, respectively; $LMM_{s \cdot d}$ = linear mixed model applied to both water spring and sampling point; LMM_s = linear mixed model applied to water spring; LMM_d = linear mixed model applied to sampling point.

Table 3. Pairwise comparisons (by the linear mixed model $LMM_{s \cdot d}$) between sampling points (P1, ..., P4) of water quality parameters in the four analysed water springs (N1, ..., N4) in the Pimenta creek (São Paulo State, Brazil).

Water spring/ sampling point		**Temperature**		**Electrical conductivity**		**Total Dissolved Solids**		**Salinity**		**Turbidity**	
		z value	**Pr(>|z|)**	**z value**	**Pr(>|z|)**	**z value**	**Pr(>|z|)**	**z value**	**Pr(>|z|)**	**z value**	**Pr(>|z|)**
N1P1	N1P2	0.2	1	-1.7	0.9	-2.08	0.77	-1.38	0.99	0.41	1
N1P1	N1P3	0.3	1	-1.14	0.9	-1.45	0.98	-0.79	1	0.35	1
N1P1	N1P4	0.22	1	-0.5	1	-0.46	1	-0.05	1	0.05	1
N1P2	N1P3	0.09	1	0.55	1	0.59	1	-23.68	1	0.76	1
N1P2	N1P4	0.02	1	1.2	0.9	1.62	0.97	-25.18	0.99	-0.46	1
N1P3	N1P4	-0.08	1	0.64	1	1.03	0.99	0.75	1	0.3	1
N2P1	N2P2	-0.31	1	-1.85	0.9	-1.99	0.83	-1.44	0.99	1.09	0.99
N2P1	N2P3	-0.61	1	-2.05	0.8	-2.25	0.66	1.8	0.99	0.99	1
N2P1	N2P4	-0.96	0.9	-1.59	0.9	-1.86	0.89	-1.36	0.92	0.87	1
N2P2	N2P3	-0.3	1	-0.2	1	-0.25	1	0.35	1	-0.09	1
N2P2	N2P4	-0.65	1	0.26	1	0.14	1	0.08	1	-0.21	1
N2P3	N2P4	-0.36	1	0.46	1	0.38	1	0.44	1	-0.12	1
N3P1	N3P2	0.89	1	-2.64	0.4	-2.81	**<0.01*** **	-2.08	0.78	7.93	**<0.01*** **
N3P1	N3P3	0.65	1	-3.56	**0.03***	-4.01	**<0.01****	-2.86	0.23	73.31	**<0.01*** **
N3P1	N3P4	0.3	1	-3.06	0.1	3.84	**0.01***	-2.95	0.19	7.21	**<0.01*** **
N3P2	N3P3	-0.24	1	-0.92	0.9	1.27	0.99	-0.79	1	-0.62	1
N3P2	N3P4	-0.6	1	-0.42	1	-1.03	0.99	-0.87	1	-0.71	1
N3P3	N3P4	0.36	1	0.5	1	0.24	1	-0.84	1	-0.1	1
N4P1	N4P2	-1.09	0.9	-3.43	**0.05***	-2.37	0.57	-3.37	0.06	0.58	1
N4P1	N4P3	-0.88	1	-2.95	0.2	-4	**<0.01****	-4.44	**<0.01*** **	1.5	0.98
N4P1	N4P4	-1.85	0.9	-4.74	**<0.01***	-3.9	**<0.01****	-4.97	**<0.01*** **	0.9	1
N4P2	N4P3	0.2	1	0.48	1	-1.63	0.96	-1.07	0.99	0.92	1
N4P2	N4P4	-0.76	1	-1.31	0.9	-1.53	0.98	-1.6	0.97	0.32	1
N4P3	N4P4	-0.96	0.9	-1.79	0.92	0.1	1	-0.53	1	-0.6	1
Water spring/ sampling point		**Color**		**pH**		**Nitrate**		**Nitrite**		**Iron**	
		z value	**Pr(>|z|)**	**z value**	**Pr(>|z|)**	**z value**		**z value**	**Pr(>|z|)**	**z value**	**Pr(>|z|)**
N1P1	N1P2	2.16	0.73	1.3	0.99	-0.55	1	-0.56	1	-1.28	0.99
N1P1	N1P3	1.87	0.89	5.57	**<0.01*** **	-0.57	1	0.39	1	-2.49	0.48
N1P1	N1P4	2.15	0.73	5.26	**<0.01*** **	-0.36	1	0.47	1	-1.69	0.95
N1P2	N1P3	0.29	1	4.27	**<0.01*** **	-0.01	1	0.97	0.99	-1.29	0.99
N1P2	N1P4	-0.01	1	3.96	**<0.01*** **	0.19	1	1.05	0.99	-0.41	1
N1P3	N1P4	0.28	1	-0.31	1	0.21	1	0.09	1	0.8	1
N2P1	N2P2	0.7	1	1.27	0.99	0.21	1	-0.82	1	0.22	1
N2P1	N2P3	1.2	0.99	4.36	**<0.01*** **	-0.12	1	0.8	1	0.05	1
N2P1	N2P4	2.19	0.71	5.25	**<0.01*** **	-0.4	1	0.69	1	-0.22	1
N2P2	N2P3	0.5	1	3.01	0.13	-0.33	1	1.63	0.96	-0.16	1
N2P2	N2P4	1.49	0.98	3.98	**<0.01*** **	-0.61	1	1.51	0.98	-0.43	1
N2P3	N2P4	0.99	1	0.89	1	-0.29	1	-0.12	1	-0.27	1
N3P1	N3P2	5.16	**<0.01*** **	3.03	0.16	1.77	0.93	2.16	0.73	-1.54	0.98
N3P1	N3P3	6	**<0.01*** **	5.97	**<0.01*** **	4.72	**<0.01*** **	3.93	**<0.01****	-0.35	1
N3P1	N3P4	5.81	**<0.01*** **	6.38	**<0.01*** **	1.04	0.99	1.11	0.99	-0.58	1
N3P2	N3P3	0.84	1	2.95	0.19	2.95	0.19	1.77	0.92	1.19	0.99
N3P2	N3P4	0.65	1	3.35	0.06	-0.73	1	-1.04	0.99	0.97	1

N3P3	N3P4	-0.19	1	0.4	1	-3.68	**0.02***	-2.82	0.26	-0.23	1
N4P1	N4P2	-0.21	1	2.29	0.63	-0.68	1	-0.31	1	-0.11	1
N4P1	N4P3	0.27	1	2.42	0.53	4.57	**<0.01***	1.92	0.87	0.98	1
N4P1	N4P4	0.71	1	3.62	**0.02***	1.97	0.84	0.85	1	1.74	0.94
N4P2	N4P3	0.48	1	0.13	1	5.24	**<0.01*****	2.23	0.68	1.09	0.99
N4P2	N4P4	0.92	1	1.33	0.99	2.64	0.37	1.16	0.99	1.85	0.9
N4P3	N4P4	0.44	1	1.2	0.99	-2.6	0.4	-1.07	0.99	0.76	1

Notes: in bold characters the significant differences are highlighted; *, **, *** significant difference at p < 0.05, 0.01 and 0.001, respectively.

FIGURE CAPTIONS

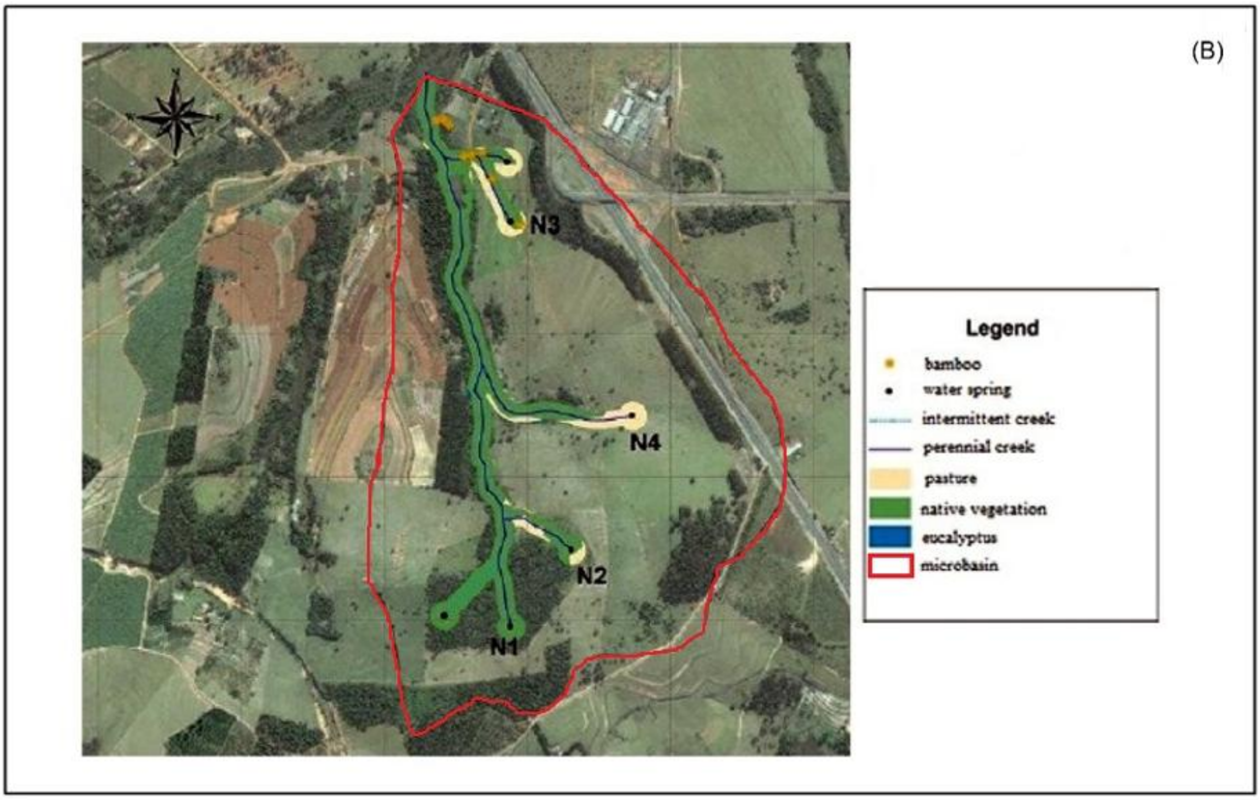
Figure 1. Location (A) and aerial photo (B) of the Pimenta creek basin (São Paulo State, Brazil) (source: adapted from Lima, 2003).

Figure 2. Precipitation and temperature records (mean ± std. dev., years 1971-2011) at São Manuel experimental farm (São Paulo State, Brazil).

Figure 3. Environment of the four water springs in the Pimenta creek (São Paulo State, Brazil). (Water springs A = "N1"; B = "N2"; C = "N3"; D = "N4").

Figure 4. Stream discharge and precipitation records (mean ± std. dev., years 2012-2013) at water springs (N1, ..., N4) of Pimenta creek (São Paulo State, Brazil).

Figure 5. Correlation matrix of the water quality parameters of four springs in the Pimenta creek (São Paulo State, Brazil).
(Notes: charts on the matrix diagonal reports the values of the water quality parameters measured in the headwater springs; charts in the left-bottom side reports correlations between measurements of couples of parameters – red lines indicates possible interpolating equations; numbers in the right-up side are the coefficients of determinations of these equations).



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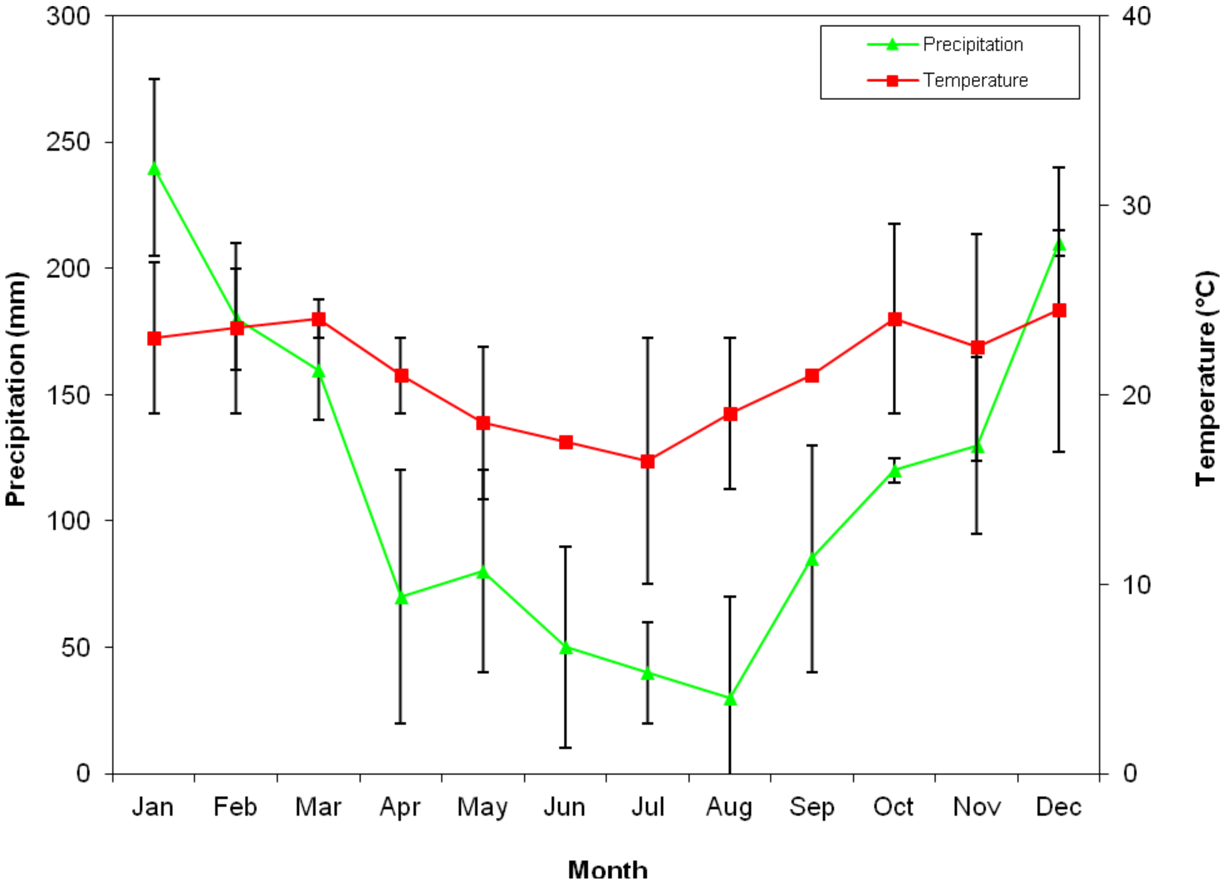

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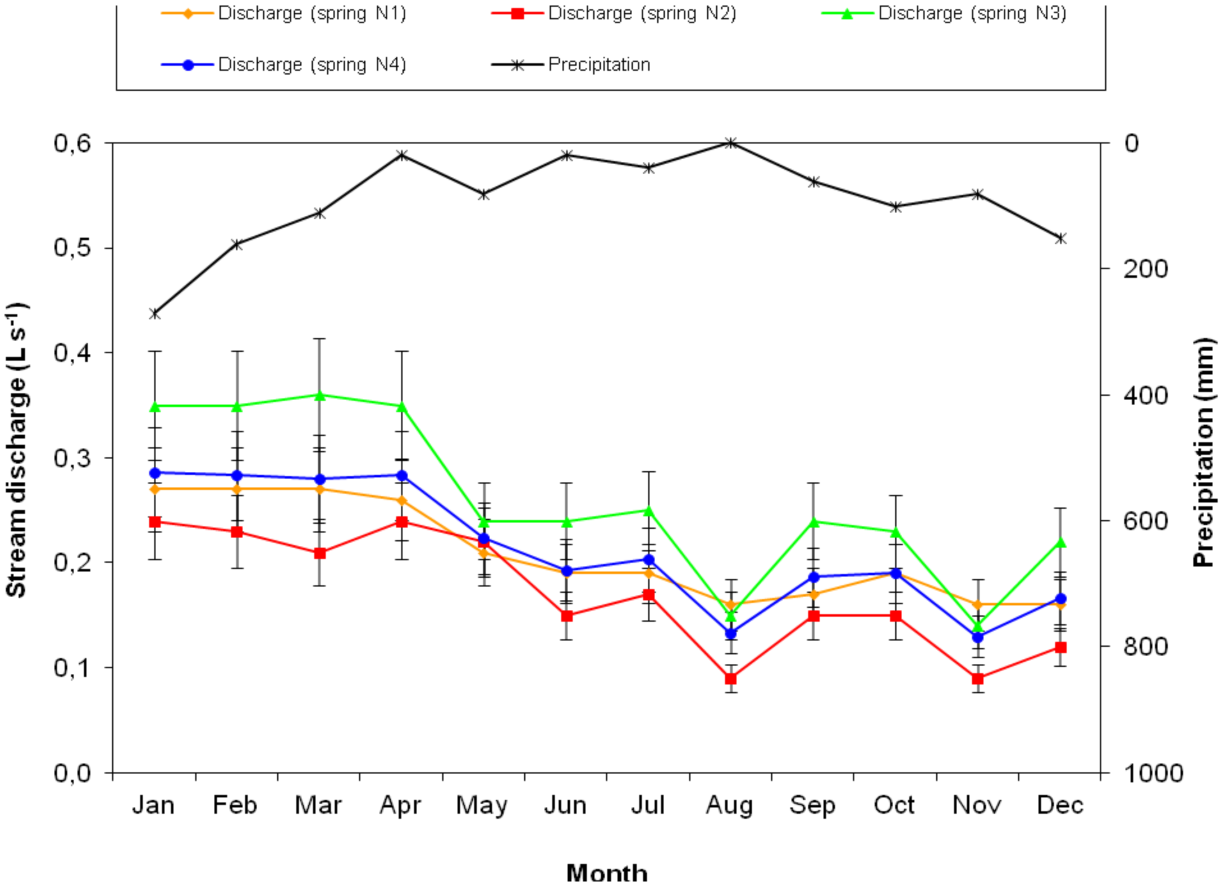

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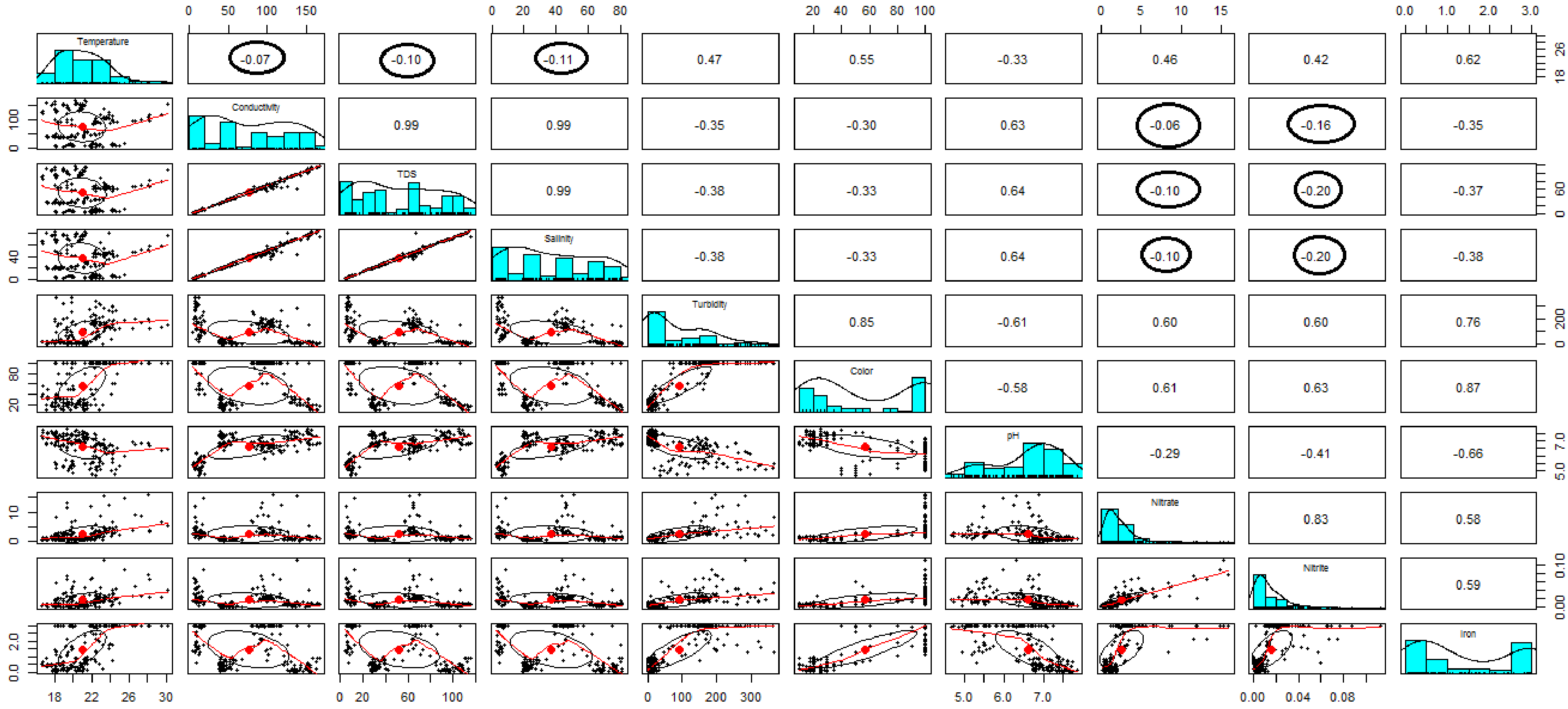

Figure 5. Correlation matrix of the water quality parameters of four springs in the Pimenta creek (São Paulo State, Brazil) - circles highlight negative correlations among water quality parameters.

(Notes: charts on the matrix diagonal reports the values of the water quality parameters measured in the headwater springs; charts in the left-bottom side reports correlations between measurements of couples of parameters – red lines indicates possible interpolating equations; numbers in the right-up side are the coefficients of determinations of these equations).