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

3  
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14  
15 **Abstract**

16  
17 The studies targeted to hydrology and water quality are scarce in tropical headwater streams. In  
18 these delicate ecosystems the comprehension of water quality can constitute a challenge, because  
19 the impact of land uses on stream dynamics is particularly severe in tropical areas. To fill this gap,  
20 an evaluation of water quality in a headwater streams (Pimenta creek, São Paulo State, Brazil)  
21 under tropical conditions was performed. The implementation of linear mixed models to water  
22 quality parameters allowed to know how and to what extent water flowing in these headwaters are  
23 influenced by: (i) the spatial variation of spring locations; (ii) the different land uses; and (iii) the  
24 state of conservation of the riparian vegetation. Both the land uses in the surroundings of water  
25 springs (native forest, degraded vegetation, agriculture and pasture) and the sampling points  
26 (exactly in the spring and 10, 30 and 50 metres downstream) were found to be factors able to  
27 explain water quality variability. Most of the analysed parameters, some of which strongly  
28 correlated each others (mainly electrical conductivity, Total Dissolved Solids and salinity, but also  
29 color, turbidity and iron concentrations), showed significant variations mainly due to the effects of  
30 the different land uses, but also to the distance from water spring. The instability of the water  
31 quality parameters in springs degraded from its headwater was also demonstrated. The water  
32 springs with developed riparian vegetation of natural forest (in a preserved or even disturbed  
33 conservation level) showed the best conditions in the aquatic environment (lower temperature,  
34 turbidity, color, nitrite and nitrate concentrations, neutral pH). Conversely, in the water springs with

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

38

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

40

## 41 **1. Introduction**

42

43 Headwater streams (that is, the first- and second-order channels of a water course, Strahler, 1952),  
44 cumulatively constitute the great majority of channel length within a river network (Downing et al.,  
45 2012). Their importance within the ecology and health of a water course falls in the fact that  
46 headwater streams are the source of water, solutes, mineral sediment, and particulate organic matter  
47 (Schumm, 1977; Alexander et al., 2007; MacDonald and Coe, 2007; McClain and Naiman, 2008).  
48 These delicate ecosystems are strongly influenced by many disturbances factors, such as  
49 precipitation, morphology, land use, geology, vegetation, human impacts, which can affect the  
50 entire watershed supplied by their water flows (Wohl, 2017; Rodrigues et al., 2017). Furthermore,  
51 across diverse hydro-climatic regions, headwater streams tend to exhibit more spatial and temporal  
52 hydrologic variability than larger channels (Gomi et al., 2002; Richardson and Danehy, 2007),  
53 which strongly influences the river ecosystem. Given such stressing factors, it is necessary to pay  
54 attention to the physical, chemical, and biological functions of headwater streams and, in particular,  
55 to water quality. **Recently, Wohl (2017) highlighted the importance of water chemistry analysis in  
56 headwater for at least two reasons: (i) headwater stream chemistry is highly influenced by upland  
57 flow paths and chemistry of incoming surface and ground waters; (ii) headwaters are the first line of  
58 defence against potential contaminants such as excess fine sediment or nutrients.**

59 Unfortunately, the relatively small streams are currently rather ignored by legal protections (mostly  
60 extended to larger rivers) and are aggressively altered in connection with diverse land uses (Wohl,  
61 2017), even though there has been a recent upsurge in interest in the restoration of riparian habitats,  
62 which is focusing attention on understanding and ameliorating such impacts (Bombino et al., 2007).  
63 Water quality of headwater streams is important, because not only it is highly influenced by both  
64 upland flow paths and incoming surface and groundwaters, but also due to the fact that headwaters  
65 are the first line of defense against potential contaminants such as excess fine sediment or nutrients  
66 and the first receiving point for organic matter (Alexander et al., 2007). Also land use has  
67 significant impacts on river water quality with complex mechanisms, as demonstrated by several  
68 comparative studies (e.g. Wear et al., 1998; Amiri et al., 2009; Ding et al., 2015). Although the

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

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

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

97 Specific evaluations of water quality in Brazil are conducted at very few research stations, for  
98 example, clustered in the IBGE Reserve of the Federal District (Markewitz et al., 2006; Parron et  
99 al., 2010). Although more data are available from local and regional studies by local water  
100 managers or environmental protection agencies, they are not published in scientific journals and  
101 thus the impacts of land use on aquatic systems, that is, pollution from nutrients and pesticides, their  
102 in-stream processes, and their effects on aquatic habitats, are not well understood (Hunke et al.,

103 2015a). Biome-specific water quality thresholds lack in Brazil (Hunke et al., 2015b), except for  
104 baselines for physical–chemical water parameters ranging from natural to very impacted conditions  
105 in the Cerrado area reported by Fonseca et al. (2014).

106 The objective of this work is the evaluation of water quality as influenced by the spatial variation of  
107 spring locations, the different land uses and state of conservation of the riparian vegetation in water  
108 springs of a headwater stream (São Paulo State, Brazil) typical of tropical conditions. More  
109 specifically, by applying linear mixed models the following questions are answered: (i) is water  
110 quality influenced by land use or distance from spring or both? (ii) to what extent water quality is  
111 influenced by these factors of change? (iii) are there any correlations among the water quality  
112 parameters? Identifying the spatial variability of land use impacts on water quality represents a  
113 significant challenge; addressing this issue is critical for assessing the potential risks of  
114 development and the cost-effectiveness of water management at the watershed scale (Ding et al.,  
115 2015).

116

## 117 **2. Materials and methods**

118

### 119 *2.1. Study site description*

120

121 The study was carried out in the headwater stream of Pimenta creek, a tributary of the Paraiso basin.  
122 The basin belongs to the São Manuel experimental farm (belonging to UNESP/FCA), in the central-  
123 western region of the state of São Paulo (Brazil) (Figure 1). The basin of the Pimenta creek is  
124 located between the geographic coordinates 22°46'07"S to 22°46'57"S and 48°33'49"W to  
125 48°33'59"W at an average altitude of 779 meters. It covers an area of 22.8 ha and is covered by  
126 pasture (57.5%), native vegetation and bamboo (25.9%), exotic vegetation (5.5%), agriculture  
127 (10.1%) and infrastructure (1.0%); the main stream is 1620 metres long and its slope is of 2.6% up  
128 to 38.8%. The climate of the region of São Manuel is of the type Cwa, hot temperate climate  
129 (mesothermic). The wetter and colder period falls in the spring-summer seasons and the water  
130 shortage with warmer temperatures in the autumn-winter seasons (Cunha, 2009) (Figure 2). The  
131 floodplains of the water course show alluvial soils formed by sandy sediments (Lima, 2003). The  
132 soil of the basin, practically homogenous, is classified as Red-Dark Latosol, with sandy texture. It a  
133 soil in advanced stage of weathering, very evolved, as a result of notable transformations of the  
134 constitutive material.

135

### 136 *2.2. Sampling sites and water quality analyses*

137

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

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

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

169 In order to evaluate water quality, samples of water were collected systematically at four points for  
170 each of the four springs, with four measurements for each sampling point. In more detail, the first

171 sampling point (henceforth "P1") was located exactly at spring source. The other samples were  
172 collected 10, 30 and 50 metres downstream of the water spring (indicated as "P2", "P3" and "P4",  
173 respectively); of course, each sampling point relates to a different distance from the source. Samples  
174 were collected throughout one year (from August 2012 to July 2013), distributed in monthly  
175 surveys.

176 In our study a limited but representative set of water quality parameters was selected. We excluded  
177 some measurements such as the concentrations of some cations ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$  and  $\text{Na}^+$ ) and  
178 anions ( $\text{HCO}_3^-$ ,  $\text{SO}_4^-$ ,  $\text{Cl}^-$ ), since water pollution by these elements/compounds was not suspected in  
179 the analysed springs, lacking in their surroundings mineral fertiliser use (containing some of the  
180 aforementioned cations) and industrial facilities (which may contaminate spring water with the  
181 anions above, beside heavy metals).

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

- 183 - Electrical conductivity [ $\mu\text{S cm}^{-1}$ ], total dissolved solids (TDS, [ $\text{mg L}^{-1}$ ]) and salinity [ $\text{mg L}^{-1}$ ],  
184 using the portable multimeters Extech PH 100 and EC 400;  
185 - Temperature [ $^{\circ}\text{C}$ ] and pH [-] by a pH-meter (Extech PH 100).

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

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

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

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

196

### 197 2.3. Statistical analysis

198

199 The water quality parameters were transformed to square root to fit the equity of variance and  
200 normal distribution, then the descriptive statistics for each variable were calculated. Subsequently,  
201 three Linear Mixed Models (henceforth indicated as "LMM<sub>s,d</sub>", "LMM<sub>s</sub>" and "LMM<sub>d</sub>") were  
202 applied to analyse whether there are any correlations (and their significance level) between the  
203 water quality parameters and: (i) spring characteristics (land use and conservation level of riparian

204 vegetation) and distance from water spring (for  $LMM_{s,d}$ ); (ii) only spring characteristics (for  
205  $LMM_s$ ); (iii) only distance from water spring ( $LMM_d$ ).

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

212

### 213 **3. Results**

214

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

219

#### 220 *3.1. Water quality variations among water springs*

221

222 Among the analysed water springs, "N1" showed the lowest mean temperature ( $19.3\text{ }^{\circ}\text{C} \pm 1.5$ ),  
223 turbidity ( $12.6\text{ FAU} \pm 6.1$ ), nitrite ( $0.005\text{ mg L}^{-1} \pm 0.003$ ) and iron ( $0.3\text{ mg L}^{-1} \pm 0.3$ ), but the  
224 highest electrical conductivity ( $143.7\text{ }\mu\text{S cm}^{-1} \pm 12.1$ ), Total Dissolved Solids ( $100.7\text{ mg L}^{-1} \pm 8.3$ ),  
225 salinity ( $71.7\text{ mg L}^{-1} \pm 5.7$ ) and pH ( $7.3 \pm 0.2$ ). The spring "N2" had the lowest mean color ( $22.6$   
226  $\text{mg L}^{-1}\text{ Pt} \pm 7.5$ ) and nitrate ( $0.8\text{ mg L}^{-1} \pm 0.3$ ). For "N3" the lowest mean electrical conductivity  
227 ( $11.9\text{ }\mu\text{S cm}^{-1} \pm 3.6$ ), TDS ( $8.3\text{ mg L}^{-1} \pm 2.5$ ), salinity ( $5.8\text{ mg L}^{-1} \pm 1.7$ ) and pH ( $5.4 \pm 0.3$ ) together  
228 with the highest mean turbidity ( $173.3\text{ FAU} \pm 78.1$ ) and nitrite ( $0.1\text{ mg L}^{-1} \pm 0.02$ ) were measured.  
229 "N4" presented the highest mean temperature ( $23.1\text{ }^{\circ}\text{C} \pm 3$ ), color ( $95.3\text{ mg L}^{-1}\text{ Pt} \pm 10.8$ ), nitrate  
230 ( $4.8\text{ mg L}^{-1} \pm 2.7$ ) and iron ( $2.6\text{ mg L}^{-1} \pm 0.6$ ) (Table 1).

231

#### 232 *3.2. Comparison between linear mixed models*

233

234 Table 2 reports the comparisons between the three linear mixed models (LMM) tested for analysing  
235 the water quality parameters in the Pimenta creek. The differences between  $LMM_{s,d}$  (based on  
236 spring characteristics and distance from the water spring) and  $LMM_d$  (based only on distance) were  
237 significant for all the studied parameters.  $LMM_{s,d}$  significantly differed from  $LMM_s$  (based on

238 spring characteristics) only for two parameters (temperature and iron concentration), while LMM<sub>s</sub>,  
239 and LMM<sub>d</sub> (this latter based only on distance) gave practically the same statistical values (Table 2).

240

### 241 *3.3. Spatial variations of water quality in water springs*

242

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

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

260

### 261 *3.4. Correlations among water quality parameters*

262

263 As expected, electrical conductivity, Total Dissolved Solids and salinity were strongly correlated  
264 each another ( $r > 0.99$ ) and this suggests that they express very similar water quality parameters and  
265 processes. All these parameters were not significantly correlated with temperature, nitrate and  
266 nitrite ( $r < 0.20$ ). Finally, color has a very strong correlation with turbidity ( $r = 0.85$ ) and iron ( $r =$   
267  $0.87$ ) and these latter parameters are also noticeably correlated each other ( $r = 0.76$ ) (Figure 5). Also  
268 Rodrigues et al. (2017) found a high correlation between iron and turbidity in the same tropical  
269 environment.

270

271

#### 272 **4. Discussions**

273

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

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

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

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

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

317 Compared to water springs with riparian vegetation (preserved, "N1", or degraded, "N2"), turbidity,  
318 color, pH and nitrate concentrations were much higher (that is, in "N3" and "N4"). The water pH  
319 was close to neutrality in the springs with riparian vegetation (accordingly to Donadio et al., 2005,  
320 who found pH close to 7 in water springs with tropical natural vegetation), showing a more  
321 preserved aquatic environment, while water was quite acid (due to organic acid pouring with  
322 wastewater of indigenous origin) in the other springs, which indicated possible water pollution. At  
323 the downstream sampling points, an increase of the concentration of color, turbidity and suspended  
324 solids was observed related with agricultural ditches triggering the coupling of agricultural  
325 hillslopes and stream (Slattery et al., 2002). In tropical forest environments, also Primavesi et al.  
326 (2002) and Donadio et al. (2005) reported higher values of turbidity in microbasins with agricultural  
327 land use than in forested areas, thus evidencing the function of the riparian forest in reducing solids  
328 supply from sources to stream water. The increase in turbidity values due to the scarcity of riparian  
329 forest were also observed in the study of Arcova and Cicco (1999) in a tropical and agricultural  
330 microbasin, which showed also higher color values and suspended sediments in water of the stream  
331 interfering with the presence of a road (as in spring "N4" of our study). Also Donadio et al. (2005)  
332 found lower values of the water color in tropical streams of riparian forest compared to other land  
333 uses. Many Authors reported that farmland is responsible for water pollution, while, on the  
334 contrary, forested areas show negative correlations with most ions (e.g. Bahar et al., 2008; Zhou et  
335 al., 2012; Xia et al., 2012; Kändler et al., 2017). As Keesstra et al. (2012) found, the riparian zone  
336 has a significant effect on water and sediment transport in headwater catchments, since high  
337 roughness in natural rivers due to vegetation and geomorphological attributes may generate drag on

338 flowing water. This is also in accordance with Gao (2008), who showed that the riparian vegetation  
339 in headwater catchments play an important role in the resulting water and sediment dynamics of  
340 rivers further downstream; **in general, vegetation of riparian zones has a demonstrated buffer  
341 capacity for avoiding the transfer of diffuse contaminants to surface waters (Connolly et al., 2015).**  
342 Since headwater streams are particularly closely coupled with adjacent riparian and terrestrial  
343 environments, because of the higher ratio of aquatic-riparian interface and the sensitivity of riparian  
344 zones towards river basin ecohydrology (Bombino et al., 2014; Wohl, 2017), riparian buffer strips  
345 and their structure are critical for maintaining water functions and minimising eutrophication  
346 (Boëchat et al., 2013; Parron et al., 2010; Fernandes et al., 2014; Hinke et al., 2015b). **Thus, under  
347 the catchment management point of view, riparian vegetation should be promoted in stream  
348 channels and intensive agricultural uses in adjacent areas should be avoided, in order to not alter  
349 water quality (Rodrigues et al., 2017).**

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

361 **Nutrients such as inorganic nitrogen (ammonia, nitrate and nitrite) are important factors affecting  
362 water quality, since they play, together the bioavailable forms of phosphorous, an important role in  
363 the eutrophication process in surface waters (Soulsby et al., 2001; Sener et al., 2017).** The higher  
364 concentrations of nitrites and mainly of nitrates in springs "N3" (pastured) and "N4" (cropped) -  
365 **even though low compared to USEPA water quality standards** - can be explained, as for pH, by the  
366 fact that the sites were heterogeneous in land use and these parameters are sensitive to denudation  
367 of riparian vegetation and nitrogen-based fertilizer use, since fertilizers and animal manure (rich in  
368 nitrogen) is usually transported downstream by surface runoff to the waterways. The spring "N3"  
369 had a domestic sewage at its headwater; this fact may have contributed to the spatial variation of  
370 turbidity and color, increasing the presence of suspended solids in water and the sediment transport  
371 downstream, which interfere with light penetration through the water. Effluents pouring into

372 streams is in fact an important factor that controls water quality parameters (Castro and Mendonça,  
373 2004). Many different studies have shown that agricultural land uses at catchment scale is a primary  
374 predictor for water quality compounds (Smart et al., 1998; Ferrier et al., 2001; Ahearn et al., 2005).  
375 An increase in electrical conductivity and inorganic N-forms in surface water was detected in most  
376 reviewed studies due to anthropogenic inputs from fertilisation and liming. Silva et al. (2011)  
377 detected higher nitrite concentrations and water conductivity in tropical rural streams compared to  
378 natural low order catchments and concluded that agricultural land use had a measurable impact on  
379 solute loads in the river system (Hunke et al., 2015b). These latter Authors from their water  
380 sampling results demonstrated the significant impact of agricultural use on water quality, especially  
381 for nitrate and nitrite concentrations. For small first-order pasture catchments, Gücker et al. (2009)  
382 found significantly higher electrical conductivities and  $\text{NO}_3$  compared with natural streams. The  
383 concentrations of  $\text{NO}_3$  and  $\text{NO}_2$  in rural streams were as much as 1.5 times higher, and they differed  
384 significantly from natural streams (Hunke et al., 2015a). Fonseca et al. (2013) presented similar  
385 findings in low-order pristine streams.

386 Conversely, an improvement in the water quality is usually observed in relation to the amount of  
387 nitrate and nitrite in the microcatchments with dense vegetation cover and in an advanced  
388 regeneration phase. Nitrate concentrations in surface water of Brazilian forests (e.g. in Cerrado)  
389 were orders of magnitude lower compared with concentrations measured in European rivers under  
390 land use change (Hunke et al., 2015a). In a stream with gallery forest within an ecological reserve  
391 near Brasília, Parron et al. (2010) found only very low N concentrations, whereas nitrates were not  
392 detectable, due to the fact that forest has a high filtering capacity. Moreover, a dilution effect of  
393  $\text{NaNO}_2$ ,  $\text{NO}_2$  and  $\text{NO}_2\text{-N}$  as well as Total Dissolved Solids (and, as a consequence, of electrical  
394 conductivity and salinity) was observed downstream of tropical rivers (Rodrigues et al., 2017).  
395 Analyzing the impacts of human activities in reforested basins, Castro and Mendonça (2004) found  
396 an improvement in the quality of in relation to the amount of nitrate and nitrite in microbasins with  
397 dense vegetation cover and in advanced regeneration phase. The same Authors also recorded higher  
398 amounts of nitrate due to agricultural practices and soil exposure by low effective protection  
399 coverage, in addition to that of fertilizers.

400 **As different studies have demonstrated, land use changes (i.e. from forest to agricultural land uses)**  
401 **may alter and increase water and sediment connectivity, thus changing water quality along streams**  
402 **(Parsons et al., 2015; Masselink et al., 2017a; Masselink et al., 2017b).** From the study it was  
403 evident that most of the water quality parameters in agriculture-dominated sites had higher  
404 concentrations than those in forest-dominated sites, as also stated by Dong et al. (2015). Therefore,  
405 the land use type had a significant weight not only in the correlation coefficients for each water

406 quality characteristic but also in the degree of influence of land use itself on each water quality  
407 variable (Yu et al., 2016). However, some important caveats apply to studies of the relationship  
408 between land use and stream water quality: when conducting a Pearson's correlation analysis on  
409 this type of relationship, the conclusion that the land use type was the primary driver of stream  
410 water quality must be made with caution (Yu et al., 2016). In addition, forecasting changes in  
411 stream water quality in response to changes in land use type may run the risk that the relationship  
412 would alter over time owing to changes in some specific practices or the environment itself (Allen,  
413 2004).

414 With reference to the water quality variability as function of the sampling distance from the spring,  
415 the spatial variations were significant for the majority of the couples of points in relation to pH,  
416 demonstrating the heterogeneity of the site and the sensitivity of this parameter, but not for  
417 temperature and iron concentrations. Water temperature and iron concentrations remained unaltered  
418 within each spring (that is, within the same land use) regardless of the distance of sample collection.  
419 Nitrate concentration as well as Electrical conductivity, Total Dissolved Solids and salinity had  
420 significant spatial variations only in the two water springs considered to be degraded ("N3" and  
421 "N4"), as direct consequence of both human-induced changes (pasture, agriculture and wastewater  
422 pouring) and lower presence of riparian vegetation. Water color and turbidity significantly differed  
423 according to the distance only in pastured spring. The noticeable relation between flow quality and  
424 the effect of the distance was detected also by Castro and Mendonça (2004) and Rodrigues et al.  
425 (2017), who found an important relationship between discharge and the distance effect on water  
426 quality parameters: the study of these latter Authors indicated that the measured water quality  
427 parameters varied among the different sampling points from the headwater sampling point (0 m) to  
428 the last downstream sampling point (2500 m).

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

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

450

## 451 **5. Conclusions**

452

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

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

473 The study can serve as a monitoring model in compared to other impacted watersheds (Arcova and  
474 Cicco, 1999) and **the values of the water quality parameters achieved may represent a reliable**  
475 **database to support the development of conservation and management strategies for tropical**  
476 **headwaters**. However, it should be noted that the use of water as a qualitative indicator requires  
477 further studies to verify that the other factors that may interfere with its quality.  
478 Finally, the monitoring activities of water quality allow us to know and interpret the actual  
479 influences played by factors of change (such as land use, spatial and temporal changes) on water  
480 quality and riparian ecology. Understanding the relationships between water quality and their  
481 variability and land use as is necessary to diagnose information on the health of water springs and  
482 headwater streams and to support the adoption of the best management strategy (Lessels and  
483 Bishop, 2013).

484

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486

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493

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1 **TABLES**

2

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

4

Water spring sampling point	Mean	Maximum	Minimum	Std. Dev.	CV	Water spring sampling point	Mean	Maximum	Minimum	Std. Dev.	CV
	Temperature (°C)						Electrical Conductivity (µS cm <sup>-1</sup> )				
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
<i>Mean</i>	<i>19,3</i>	<i>21,3</i>	<i>16,7</i>	<i>1,5</i>	<i>7,9</i>	<i>Mean</i>	<i>143,7</i>	<i>159,2</i>	<i>124,3</i>	<i>12,1</i>	<i>8,4</i>
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
<i>Mean</i>	<i>19,9</i>	<i>22,7</i>	<i>17,3</i>	<i>1,7</i>	<i>8,6</i>	<i>Mean</i>	<i>45,9</i>	<i>60,0</i>	<i>39,0</i>	<i>6,9</i>	<i>14,9</i>
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
<i>Mean</i>	<i>21,6</i>	<i>25,0</i>	<i>18,2</i>	<i>2,1</i>	<i>9,5</i>	<i>Mean</i>	<i>11,9</i>	<i>19,5</i>	<i>7,5</i>	<i>3,6</i>	<i>31,7</i>
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
<i>Mean</i>	<i>23,1</i>	<i>28,5</i>	<i>18,4</i>	<i>3,0</i>	<i>13,1</i>	<i>Mean</i>	<i>101,1</i>	<i>128,1</i>	<i>84,1</i>	<i>12,5</i>	<i>12,3</i>
	Total dissolved solids (mg L <sup>-1</sup> )						Salinity (mg L <sup>-1</sup> )				
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
<i>Mean</i>	<i>100,7</i>	<i>111,6</i>	<i>87,8</i>	<i>8,3</i>	<i>8,2</i>	<i>Mean</i>	<i>71,7</i>	<i>79,2</i>	<i>62,9</i>	<i>5,7</i>	<i>8,0</i>
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
<i>Mean</i>	<i>32,0</i>	<i>41,5</i>	<i>26,9</i>	<i>4,8</i>	<i>15,0</i>	<i>Mean</i>	<i>22,9</i>	<i>29,8</i>	<i>19,5</i>	<i>3,4</i>	<i>15,0</i>
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
<i>Mean</i>	<i>8,3</i>	<i>13,4</i>	<i>5,1</i>	<i>2,5</i>	<i>30,7</i>	<i>Mean</i>	<i>5,8</i>	<i>8,9</i>	<i>3,5</i>	<i>1,7</i>	<i>31,2</i>
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
<i>Mean</i>	<i>67,0</i>	<i>81,9</i>	<i>57,3</i>	<i>7,1</i>	<i>10,2</i>	<i>Mean</i>	<i>47,5</i>	<i>59,6</i>	<i>38,1</i>	<i>6,4</i>	<i>12,8</i>
	<b>Turbidity (FAU)</b>						<b>Color (mg L<sup>-1</sup> Pt)</b>				
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
<i>Mean</i>	<i>12,6</i>	<i>22,8</i>	<i>2,3</i>	<i>6,1</i>	<i>48,6</i>	<i>Mean</i>	<i>23,8</i>	<i>42,5</i>	<i>14,4</i>	<i>8,7</i>	<i>37,1</i>
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
<i>Mean</i>	<i>15,9</i>	<i>45,0</i>	<i>0,8</i>	<i>12,4</i>	<i>78,8</i>	<i>Mean</i>	<i>22,6</i>	<i>37,5</i>	<i>13,1</i>	<i>7,5</i>	<i>33,0</i>
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
<i>Mean</i>	<i>173,3</i>	<i>291,8</i>	<i>47,3</i>	<i>78,1</i>	<i>45,3</i>	<i>Mean</i>	<i>86,6</i>	<i>100,0</i>	<i>51,3</i>	<i>17,4</i>	<i>21,7</i>
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
<i>Mean</i>	<i>159,4</i>	<i>240,3</i>	<i>91,5</i>	<i>41,2</i>	<i>25,5</i>	<i>Mean</i>	<i>95,3</i>	<i>100,0</i>	<i>65,0</i>	<i>10,8</i>	<i>11,4</i>
	<b>pH (-)</b>						<b>Nitrate (mg L<sup>-1</sup>)</b>				
N1P1	7,0	7,4	6,7	0,2	3,2	N1P1	1,2	1,9	0,3	0,5	42,7



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
<i>Mean</i>	<i>0,0</i>	<i>0,1</i>	<i>0,0</i>	<i>0,0</i>	<i>62,8</i>	<i>Mean</i>	<i>2,6</i>	<i>3,0</i>	<i>1,4</i>	<i>0,6</i>	<i>24,6</i>

5

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 ( $> \chi^2$ )		
	LMM <sub>s-d</sub> vs LMM <sub>s</sub>	LMM <sub>s-d</sub> vs LMM <sub>d</sub>	LMM <sub>s</sub> vs LMM <sub>d</sub>
Temperature	0.94	<b>&lt;0.001***</b>	1
Electrical conductivity	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Total Dissolved Solids	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Salinity	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Turbidity	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Color	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
pH	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Nitrate	<b>&lt;0.001***</b>	<b>&lt;0.001***</b>	1
Nitrite	<b>0.01*</b>	<b>&lt;0.001***</b>	1
Iron	0.34	<b>&lt;0.001***</b>	1

Notes: in bold characters the significant differences are highlighted; \*, \*\*, \*\*\* significant difference at  $p < 0.05$ , 0.01 and 0.001, respectively; LMM<sub>s-d</sub> = linear mixed model applied to both water spring and sampling point; LMM<sub>s</sub> = linear mixed model applied to water spring; LMM<sub>d</sub> = linear mixed model applied to sampling point.

Table 3. Pairwise comparisons (by the linear mixed model LMM<sub>s,d</sub>) 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	<b>&lt;0.01***</b>	-2.08	0.78	7.93	<b>&lt;0.01***</b>
N3P1	N3P3	0.65	1	-3.56	<b>0.03*</b>	-4.01	<b>&lt;0.01**</b>	-2.86	0.23	73.31	<b>&lt;0.01***</b>
N3P1	N3P4	0.3	1	-3.06	0.1	3.84	<b>0.01*</b>	-2.95	0.19	7.21	<b>&lt;0.01***</b>
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	<b>0.05*</b>	-2.37	0.57	-3.37	0.06	0.58	1
N4P1	N4P3	-0.88	1	-2.95	0.2	-4	<b>&lt;0.01**</b>	-4.44	<b>&lt;0.01***</b>	1.5	0.98
N4P1	N4P4	-1.85	0.9	-4.74	<b>&lt;0.01*</b>	-3.9	<b>&lt;0.01**</b>	-4.97	<b>&lt;0.01***</b>	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	Pr(> z )	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	<b>&lt;0.01***</b>	-0.57	1	0.39	1	-2.49	0.48
N1P1	N1P4	2.15	0.73	5.26	<b>&lt;0.01***</b>	-0.36	1	0.47	1	-1.69	0.95
N1P2	N1P3	0.29	1	4.27	<b>&lt;0.01***</b>	-0.01	1	0.97	0.99	-1.29	0.99
N1P2	N1P4	-0.01	1	3.96	<b>&lt;0.01***</b>	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	<b>&lt;0.01***</b>	-0.12	1	0.8	1	0.05	1
N2P1	N2P4	2.19	0.71	5.25	<b>&lt;0.01***</b>	-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	<b>&lt;0.01***</b>	-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	<b>&lt;0.01***</b>	3.03	0.16	1.77	0.93	2.16	0.73	-1.54	0.98
N3P1	N3P3	6	<b>&lt;0.01***</b>	5.97	<b>&lt;0.01***</b>	4.72	<b>&lt;0.01***</b>	3.93	<b>&lt;0.01**</b>	-0.35	1
N3P1	N3P4	5.81	<b>&lt;0.01***</b>	6.38	<b>&lt;0.01***</b>	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	<b>0.02*</b>	-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	<b>&lt;0.01*</b>	1.92	0.87	0.98	1
N4P1	N4P4	0.71	1	3.62	<b>0.02*</b>	1.97	0.84	0.85	1	1.74	0.94
N4P2	N4P3	0.48	1	0.13	1	5.24	<b>&lt;0.01***</b>	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.

1 **FIGURE CAPTIONS**

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

5

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

8

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

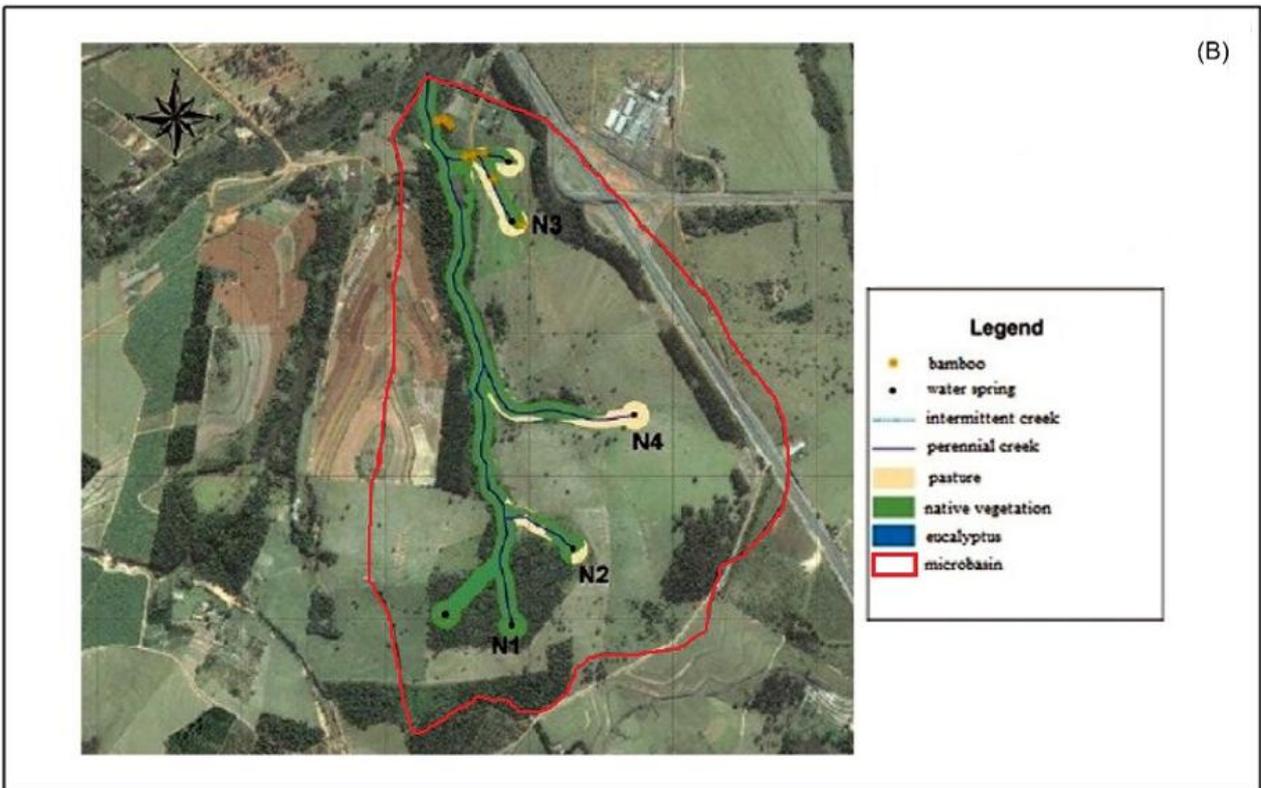
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12 Figure 4. Stream discharge and precipitation records (mean  $\pm$  std. dev., years 2012-2013) at water  
13 springs (N1, ..., N4) of Pimenta creek (São Paulo State, Brazil).

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15 Figure 5. Correlation matrix of the water quality parameters of four springs in the Pimenta creek  
16 (São Paulo State, Brazil).

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



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24 Figure 1. Location (A) and aerial photo (B) of the Pimenta creek basin (São Paulo State, Brazil)

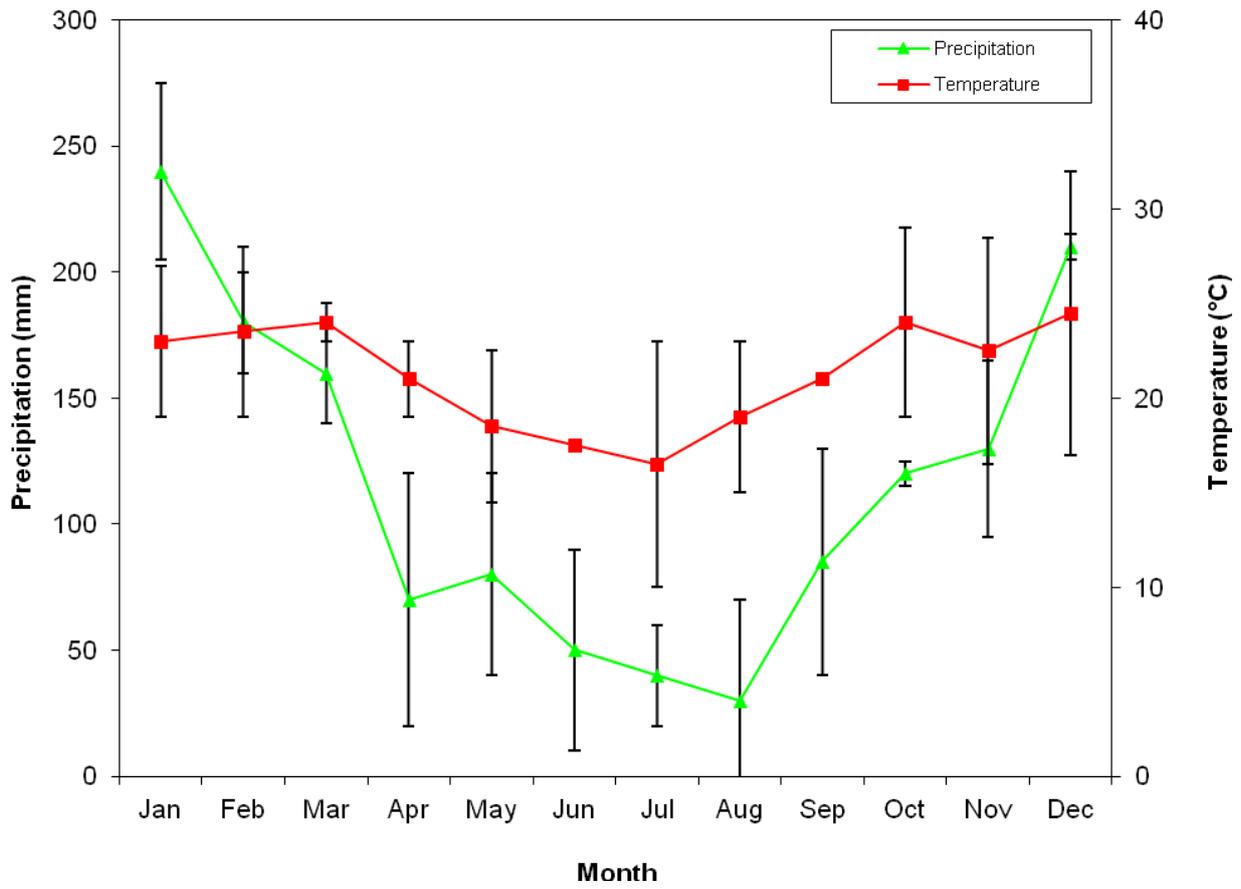
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(source: adapted from Lima, 2003).

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

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Figure 3. Environment of the four water springs in the Pimenta creek (São Paulo State, Brazil).

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(Water springs A = "N1"; B = "N2"; C = "N3"; D = "N4").

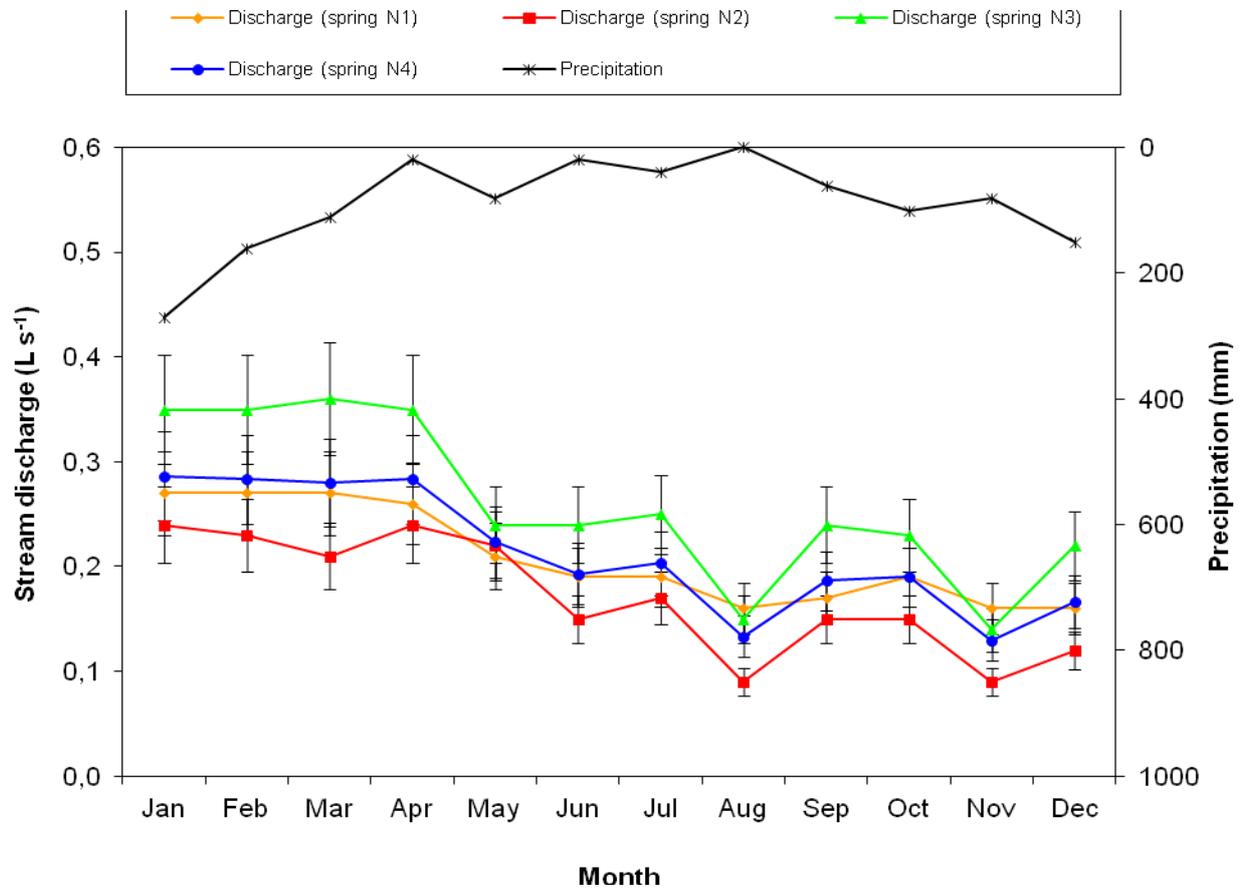
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Figure 4. Stream discharge and precipitation records (mean  $\pm$  std. dev., years 2012-2013) at water springs (N1, ..., N4) of Pimenta creek (São Paulo State, Brazil).

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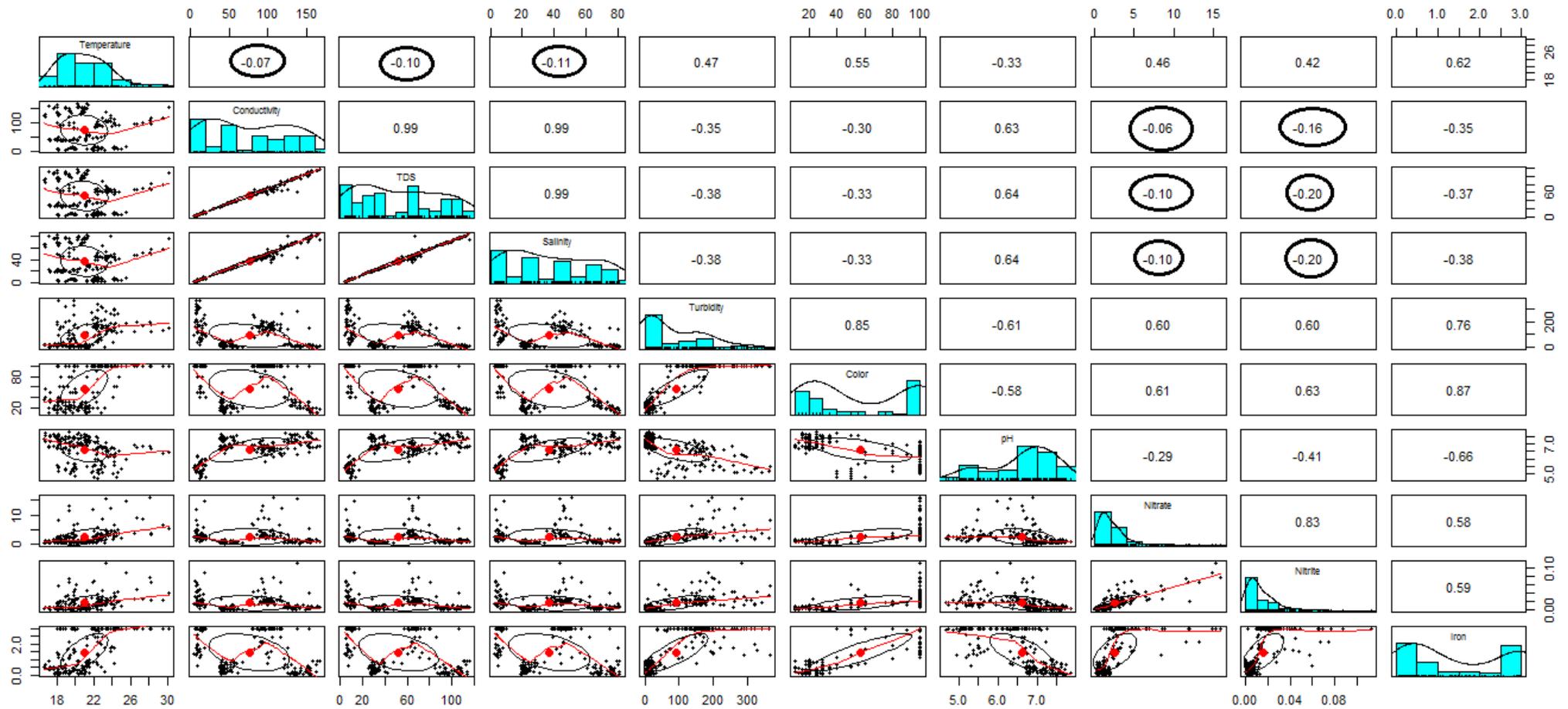


Figure 5. Correlation matrix of the water quality parameters of four springs in the Pimenta creek (São Paulo State, Brazil) - circles highlight negative correlations among water quality parameters.

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