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Hydrobiogeochemistry of Two Catchments in Brazil Under Forest Recovery in an Environmental Services Payment Program

Ricardo de Oliveira Figueiredo · Matheus Martins Simioli · Talita de Varela Utsuni Camargo Jesus · Patrícia Porta Nova da Cruz · Gustavo Bayma · Sandra Furlan Nogueira · Timothy Richard Green · Plínio Barbosa de Camargo

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Abstract We investigated the fluvial geochemistry of two catchments at different stages in the forest recovery process which have been a focus of an Environmental Services Payment (ESP) program in Brazil. The Posses (PS) and Salto de Cima (SC) catchments (1200 ha and 1500 ha, respectively) are situated in the municipality of Extrema, Minas Gerais state. Their streams flow into the Jaguari River that supplies part of the water demand of the São Paulo metropolitan area. Samples were collected for chemical analysis and physical-chemical field measures every 2 weeks from January to December 2017. An important pollution point source was discovered in the PS stream related to bovine urine and feces, as well another unidentified source that can be related to a small food processing industry and/or a small fish farm. At the SC stream, on the other hand, there was clear evidence of domestic sewage input. This preliminary study confirmed a limited improvement of the stream water quality in response to recovery of the forest vegetation. Therefore, we recommend that in addition to enhanced monitoring to help distinguish biogeochemical sources and the benefits of land conservation practices, the ESP program should consider controlling point source pollution to accomplish its purpose.

Keywords Biogeochemical cycling · Ecosystem services · Land use change · Watershed management · Water quality · Water resources

R. de Oliveira Figueiredo (✉)
Embrapa Meio Ambiente, Rodovia SP 340, Km 127.5, Cx. Postal 69, Jaguariúna, SP 13.918-110, Brazil
e-mail: ricardo.figueiredo@embrapa.br

e-mail: rfigueiredo57@gmail.com

M. Martins Simioli
Embrapa Meio Ambiente, Jaguariúna, SP, Brazil
e-mail: matheussimas13@hotmail.com

T. de Varela Utsuni Camargo Jesus
Embrapa Meio Ambiente, Jaguariúna, SP, Brazil
e-mail: talitautsunivarela@hotmail.com

P. Porta Nova da Cruz
Embrapa Meio Ambiente, Jaguariúna, SP, Brazil
e-mail: pportanova@gmail.com

G. Bayma
Embrapa Meio Ambiente, Jaguariúna, SP, Brazil
e-mail: gustavo.bayma@embrapa.br

S. Furlan Nogueira
Embrapa Meio Ambiente, Jaguariúna, SP, Brazil
e-mail: sandra.nogueira@embrapa.br

T. Richard Green
USDA Agricultural Research Service (ARS), Fort Collins, CO, USA
e-mail: tim.green@usda.gov

P. Barbosa de Camargo
USP, Centro de Energia Nuclear na Agricultura, Piracicaba, SP, Brazil
e-mail: pcamargo@cena.usp.br

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Introduction

The Brazilian states of Minas Gerais and São Paulo faced an unusual water crisis in the years 2014–2015, which deeply affected and worried the urban and rural populations, agriculture and industry sectors, as well as the local, state, and federal governments. The inability to decisively link climate change or deforestation to such specific drought events does not mean that society can ignore the increase of the frequency of extreme events caused by global changes (Marengo et al. 2015).

Therefore, such crises have encouraged the science community to intensify studies regarding water sources that are vital for the Cantareira System, which is comprised of several reservoirs and channels that deliver 31,000 litters of water per second (31 m^3 s^{-1}, or 2.6 million m^3 d^{-1}) to supply 8.8 million inhabitants of the São Paulo metropolitan area. The Jaguari River, an important tributary of the Piracicaba River, is also fundamental in the water supply of the Cantareira System, and many of its headwaters are in the extreme south of Minas Gerais, especially in Camanducaia and Extrema municipalities. The Jaguari River basin has a total area of 4,320 km^2, of which 70.4% is located in the State of São Paulo and the remaining 29.6% km^2 in Minas Gerais.

In southern Minas Gerais, the topography is predominantly rugged and includes vast areas of the Mantiqueira Mountains, which in Tupi-Guarani indigenous language means "the place where water is born," due to the existence of numerous springs (Pereira et al. 2010). The landscape was originally Atlantic Forest vegetation. Currently, other than a few native forest remnants, catchment areas are primarily pastures interspersed with crops and planted forests. In this context, it is important to carry out studies to evaluate the impacts on water resources resulting from land use changes associated with reforestation and agricultural activities practiced in this region.

The municipality of Extrema is located in this Mantiqueira region and has adopted public policies that promote the provision of hydro-environmental services by means of environmental recovery in its catchments through the revegetation of the so-called "permanent preservation areas (PPAs)," the adoption of soil conservation practices, and the improvement of vicinal roads. In order to evaluate possible improvements in the quality of the water resources of these areas in their process of environmental recovery, a monitoring program of two contiguous, paired catchments was established and an environmental geodatabase was planned. As pointed by Cruz et al. (2017), the monitoring of such stream waters, together with the application of hydrological modeling, will be useful to evaluate the results of the forest recovery in this environmental public policy program using payments for environmental services as a system for recuperation of water resources in the studied region.

This monitoring activity comprised a fluvial biogeochemical characterization in the catchments, as proposed by Moldan and Cerný (1994) as a useful tool to evaluate the conditions for sustainability of productive activities in the rural environment and the impacts of land use changes. Therefore, the main objective of the present work was to do a preliminary evaluation of some hydrobiogeochemical variables considering the present state of agro-ecosystem conservation at two adjacent watersheds which are in different stages of forest recovery and that contribute to the Jaguari River Basin.

Materials and methods

Study area

The 1200-ha Posses (PS) catchment is located between latitudes 22°49'45"S and 22°53'30"S and longitudes 46°14'00"W and 46°15'30"W. The adjacent 1500-ha Salto de Cima (SC) catchment is located between latitudes 22°50'00"S and 22°53'00"S and longitudes 46°11'00"W and 46°14'15" W (Fig. 1). A Digital Elevation Model (DEM) with 5-m spatial resolution was obtained from the Secretary of Environment of Extrema (Cruz et al. 2017) and used to delineate the watersheds using WDAML (Watershed Delineation in ARC Macro Language) software (Green et al. 2014).

The climate at these catchments is subtropical with mild summers and drought periods during the winter, classified as Cwb type (Köppen). According to Lima (2013), the elevation in the PS ranges from 1144 to 1739 m. In PS the average temperature in winter is 13.1 °C and summer is 25.6 °C, and the average annual rainfall is 1477 mm (ANA 2008). In SC, mean annual rainfall is 1181 mm (ANA 2008), and the average elevation is 1130 m (Oliveira et al. 2012) ranging from 946 to 1558 m. We used rainfall data from the meteorological station of CIIAGRO (Integrated Center for Agrometeorological Information) located in the same municipality of Extrema (22°51'07.21"S and 46°19'34.64"W) as shown in Fig. 1.

Discharge at the outlets of the catchments was measured by the DAEE (Department of Water and Electric

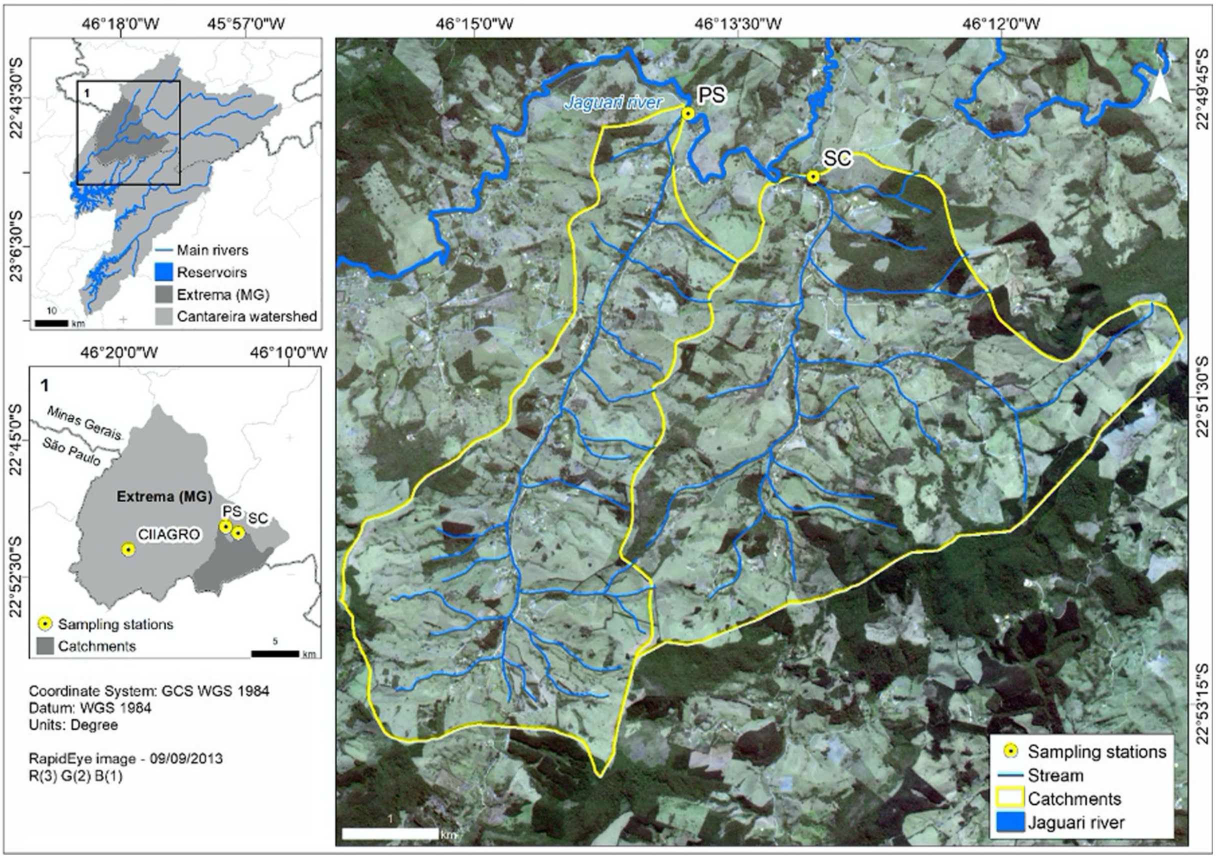


Fig. 1 Location of the streamwater sampling stations at the two studied catchments in the Jaguari River Basin—Posses (PS) and Salto de Cima (SC). The CIIAGRO meteorological station in the Extrema municipality in Minas Gerais (MG) is also shown in the regional inset map on the left

Power, State of São Paulo). However, the equipment used by the DAEE in the SC stream did not work satisfactorily during the study period, so that flow measurements were obtained only for the PS stream. Such discharge data were processed and provided by the IAG-USP (Institute of Astronomy, Geophysics and Atmospheric Sciences—University of São Paulo).

The main soil types are Ultisols, Cambisols, and Entisols (Lima 2013; Oliveira et al. 2012; Silva et al. 2008). As for native vegetation, Atlantic Forest and the semideciduous forests predominate (Leitão Filho 1982).

Both catchments are targets of an environmental recovery program and are at different stages in the environmental recovery process. The main practices adopted for the environmental recovery of microbasins are revegetation of the permanent preservation areas (PPAs), adoption of some soil conservation practices, and the improvement of vicinal roads in terms of generating hydrologic fluxes. The forest recovery in the PS, the most affected headwater basin in the municipality, began in 2007, while intervention practices in SC began in 2009 (Pereira et al. 2016).

Land use and land cover change (LULCC) analysis consisted firstly in obtaining Enhanced Thematic Mapper Plus (ETM+) and Operational Land Imager (OLI) images from Landsat-7 and Landsat-8 data, respectively, available in the "Earth Explorer" catalogue from the US Geological Survey (http://earthexplorer.usgs.gov/). We selected images with geometric correction "level 1–L1T." This product provides highly accurate digital elevation data by using ground control reference data of the land surface.

LULCC analysis considered changes between 2007 and 2017 at the PS and 2009 and 2017 at CS basins. For PS, we selected ETM+ Landsat-7 images from 2007 (August 8th, August 24th, and September 9th) and OLI Landsat-8 images from 2017 (February 16th, September 14th, and November 15th). For SC, we selected

ETM+ Landsat-7 images from 2009 (March 6th, August 13th, and August 29th). All Landsat image data were selected from path-row 219-76. ETM+ Landsat-7 selected bands were red (band 3, 0.63–0.69 μm); near infrared, NIR (band 4, 0.77–0.90 μm); and shortwave infrared, SWIR (band 5, 1.55–1.75 μm). OLI Landsat-8 selected bands were red (band 4, 0.64–0.67 μm); near infrared, NIR (band 5, 0.85–0.88 μm); and shortwave infrared, SWIR (band 5, 1.57-1.65 μm).

We used the Geographic Information System (GIS) software SPRING (Câmara et al. 1996) to create a geographical database and to process the selected images. As Landsat-7 and Landsat-8 images have 30-m spatial resolution, we applied the pan sharpening technique in each selected image to increase the spatial resolution to 15 m. The automatic polygon segmentation process was chosen to precisely delineate polygons in tandem with visual interpretation. Segmentation is a process where the image is divided into regions that must correspond to areas of interest of the application, represented by a set of continuous pixels (Nascimento and Almeida-Filho 1996; Sano et al. 2009).

The segments were exported as GIS shape files using SPRING and then classified by visual inspection in Quantum GIS (QGIS Development Team 2020). An interpretation key was established with auxiliary information for visual classification of forest (pristine and regrowth), forest plantation (pinus, eucalyptus), riparian vegetation (forest formation along water courses), pasture, and mosaic of occupation (areas where there is an association of different land use classes) using the method proposed by Gomes et al. (2012) and Espírito-Santo (2003). Temporal series of the enhanced vegetation index (EVI-2) (Jiang et al. 2008) provided by the Brazilian National Institute for Space Research (INPE) (Freitas et al. 2011) were also used for the interpretation key.

Table 1 shows the land use classification for each of the studied catchments in the year of 2017 and in the year when forest recovery began in each catchment. Pasture dominates both catchments, while forest, including the remnant native forest plus areas planted under the forest recovery process, comes in second place. This forest recovery is also the reason for the increase of riparian forest and the decrease of pasture areas at both catchments. Although the area of forest in PS more than doubled during the study period (2007–2017), the area of forest in SC remains greater by 4.1% of its total area.

Field and laboratory procedures

Four physical-chemical parameters of water quality were measured in two reaches immediately upstream of the two catchments outlets (avoiding the backflow of the Jaguari River) every two weeks from January 10 to December 20, 2017. We used a multiparametric probe (*YSI Professional Plus*) at 20 cm deep in the center of the streamflow to measure water temperature (T), electrical conductivity (EC), hydrogen ionic potential (pH), and dissolved oxygen (DO) (CETESB 1978). Additionally, on the same occasions, we collected water samples using 500-mL plastic bottles to determine the concentration of the total suspended sediment (TSS) as well as some cations and anions, total and organic dissolved nitrogen (TDN and DON), and dissolved organic and inorganic carbon (DOC and DIC). Additional samples for TDN and DOC analysis were collected using 500-mL amber glass bottles.

In the laboratory, TSS concentration of each water sample was performed according to ASTM (2000) by filtration of a known volume (ranging from 50 to 150 mL, depending on the amount of sediment in the sample), using an acidic prewashed polysulfone *Sterifil aseptic system* (*Millipore*) and a diaphragm vacuum pump (*Vacuubrand ME1C*). The sediment retained on a cellulose acetate membrane (pore size = 0.45 μm) was oven dried at 70 °C for 1 hour and calculated by the difference of the membrane weight before and after filtration, using an analytical balance (*Ohaus Adventure AR2140*).

The dissolved sample aliquots after such filtration were then kept frozen until performing ion chromatography and elemental analysis using an Ion Chromatographer (*Metrohm, model 861*) and a Total Organic Carbon Analyzer with a Nitrogen module (*Shimadzu TOC-V CSN*). The samples for TDN and DOC determinations were filtered through microfiber membranes (GFFs) using an acidic prewashed glass filtration system, and the filtered samples were kept in a refrigerator (~ 4 °C).

As for the chromatographic procedures, a cation column (*Metrosep C4*) packed with silica gel with carboxyl groups was used to determine calcium (Ca^{2+}), potassium (K^{+}), sodium (Na^{+}), magnesium (Mg^{2+}), and ammonium (NH_4^{+}) concentrations. For anionic separation, we used a *Metrosep A supp 5* column (packing material: polyvinyl alcohol with quaternaly ammonium groups) to determine chloride (Cl^{-}), sulfate (SO_4^{2-}), phosphate (PO_4^{3-}), and nitrate (NO_3^{-}) concentrations.

Table 1 Areas and percentages of land use classes for Posses and Salto de Cima Catchments from 2007 and 2009, respectively, to 2017

Land use class	Posses (PS) Catchment				Salto de Cima (SC) Catchment			
	2007		2017		2009		2017	
	ha	%	*ha*	%	*ha*	%	*ha*	%
Pasture	997.3	83.6	802.3	67.2	1064.8	70.0	896.8	59.0
Forest	99.8	8.4	205.9	17.3	284.8	18.7	326.2	21.4
Riparian forest	59.1	5.0	97.8	8.2	84.2	5.5	116.8	7.7
Forest plantation	29.5	2.5	69.7	5.8	75.2	4.9	155.0	10.2
Cropland	6.1	0.5	11.8	1.0	0.0	0.0	10.7	0.7
Mosaic of occupation	1.2	0.1	5.6	0.5	8.5	0.6	12.1	0.8
Water	0.0	0.0	0.0	0.0	3.3	0.2	3.3	0.2
Total	1193.0	100.0	1193.0	100.0	1520.8	100.0	1520.8	100.0

Using the TOC analyzer, we determined the concentrations of DOC and DIC as well as TDN. DON was calculated by subtracting the concentrations of the inorganic nitrogen species (NH_4^+ and NO_3^-) from the TDN concentration of each sample.

Hydrobiogeochemical data processing

The hydrobiogeochemical data, together with the discharge and rainfall data obtained by third parties, were tabulated in an electronic spreadsheet and plotted in graphs to display the temporal variation of these parameters in each of the studied catchments. These data were then analyzed statistically in the R software (R Core Team 2013) to generate box plots for each studied variable, thus facilitating the comparison of the results in each stream with respect to each variable separately.

In these box plots, quartiles of 25 and 75% are represented as a box. The median is shown as a horizontal line inside the box. The whiskers are drawn from the top of the box to the largest point that is less than 1.5 times the height of the inter-quartile range above the box (upper outer fence) and similarly below the box. Values outside the inner limits are shown as small circles.

Results and discussion

Hydrological data

Rainfall during the year 2017 registered at CIIAGRO station summed to 1258 mm, and monthly totals are plotted in Figure 2. At PS the 2017 annual discharge average based on daily data (provided by the IAG-USP team who used a Parshall flume) was 127 L s^{-1}. Monthly discharge average plotted ranged from 62 to 364 L s^{-1} (Figure 2). Rainfall and stream discharge had the highest values in January. Both tended to decline by April, but they had a slight increase of rainfall in March which delayed stream discharge from decreasing on this month. After a small increase in rainfall and discharge in May, there was a period of low values from June to September, including July with no rain. Discharge remained low until increasing after rains in October–December.

Field measurements

Water temperature (T), varying from 12.4 to 23.9 ^{o}C, tended to follow the seasonal variability of the air temperature, registering higher T values in summer and lower T values in winter (Table 2 and Figure 3). Both streams showed the same magnitude of T values during the field campaigns, with only one exception in the beginning of November when SC experienced an atypical lower T. Median values for PS and SC for the study period were 19.3 and 18.8 ^{o}C, respectively. Figure 4 illustrates the similarity of water temperature patterns at both streams.

Dissolved oxygen (DO), varying from 48 to 12.5 mg L^{-1}, presented the inverse pattern of T, registering lower DO concentrations in summer and higher ones in winter (Table 2 and Fig. 3). Except for a few sampling dates, stream DO values of PS and SC followed similar

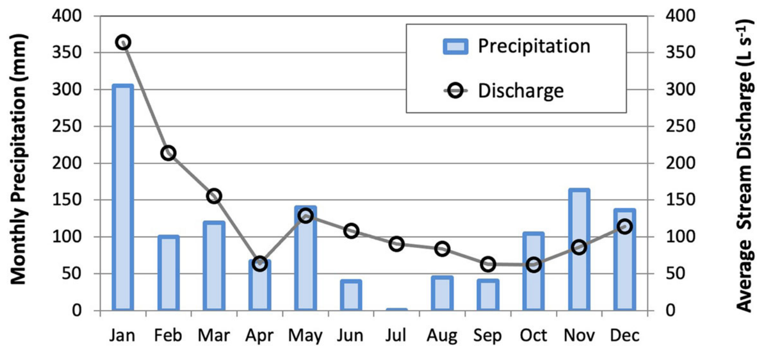


Fig. 2 Monthly rainfall totals and average discharge at the outlet of the Posses catchment during the study period (January to December 2017).

patterns. However, atypically high DO concentration in June at SC did not affect the magnitude of the median at SC (7.2 mg L^{-1}) compared with PS (7.8 mg L^{-1}) (Table 2). The box plots (Fig. 4) include DO concentration medians and the variability of the values, which illustrate similarity in the DO patterns at both streams.

Table 2 Hydrobiogeochemical parameters values (median, minimum, maximum) in Posses (PS) and Salto de Cima (SC) catchments.

Variables (units)	PS			SC		
	med	min	max	med	min	max
TSS (mg L^{-1})	6.5	1.3	375.0	8.4	5.0	416.7
TDS (mg L^{-1})	39.3	25.3	143.7	34.8	29.3	48.1
T (°C)	19.3	12.4	23.0	18.8	12.7	23.9
DO (mg L^{-1})	7.8	5.0	10.8	7.2	4.8	12.5
EC (µS cm^{-1})	61	39	221	54	45	74
pH	6.77	5.60	7.44	6.40	5.77	7.27
Na (µM)	210	60	1562	189	88	385
K (µM)	71	10	262	80	0	151
Ca (µM)	184	50	284	190	81	274
Mg (µM)	379	155	561	339	121	530
NH_4^+ (µM)	0.00	0.00	105.05	6.98	0.00	31.56
NO_3^- (µM)	8.05	0.00	38.44	15.22	0.85	50.49
PO_4^{3-} (µM)	0.00	0.00	8.18	0.00	0.00	0.00
SO_4^{2-} (µM)	6	2	14	9	5	19
Cl^- (µM)	105	38	2092	65	35	3227
DON (µM)	18	0	54	17	0	55
TN (µM)	29	21	94	34	27	89
DOC (mg L^{-1})	6.86	4.51	14.45	7.19	1.92	9.67
IC (mg L^{-1})	4.75	0.25	7.04	4.18	0.82	6.69
TC (mg L^{-1})	12.71	5.87	19.00	11.56	5.98	14.50

Electrical conductivity (EC) varied from 39 to 221 µS cm^{-1} at PS but displayed much less variation at SC. At PS, higher values occurred during lower discharge periods. As presented in Table 2, the median EC was a little higher (13%) in PS (61 µS cm^{-1}) compared with SC (54 µS cm^{-1}), although two unusual peaks (221 and 364 µS cm^{-1}) of EC were measured at PS in August and October, respectively, during low discharge at PS (Figs. 2 and 3). These EC peaks in PS caused a high 75% quartile as well as an expansion of the top whisker and a few extreme values (Fig. 4).

A pH range of 5.6–7.4 was measured and with some similarity in pattern between the two streams (Table 2). However, PS had higher pH values during almost all of the study period and also a larger seasonal variability compared with SC, as well as higher pH median (6.77) while the median value at SC was 6.40 (Table 2 and Fig. 3). This pattern can also be seen in the pH box plot in Fig. 4c as the PS median plotted higher than values of the SC quartiles box.

Total Dissolved Solids (TDS) range of 25.3–143.7 mg L^{-1} was measured, showing very little seasonal variation at SC. However, at PS some higher TDS values were measured during the year that do not follow seasonal patterns or relate to discharge effects (Fig. 5); however, these spikes contributed to a slightly higher median (39.3 mg L^{-1}) compared with SC (34.8 mg L^{-1}) (Table 2).

Laboratory chemical results

Total suspended sediment (TSS) varied from 1 to 417 mg L^{-1}. Higher TSS values were observed in the beginning of the year as a response to large rainfall and discharge at the two catchments. Except for sharp responses of an extreme rainfall event in November at both streams, there was little seasonal variation during the rest of year, and TSS median values were not very

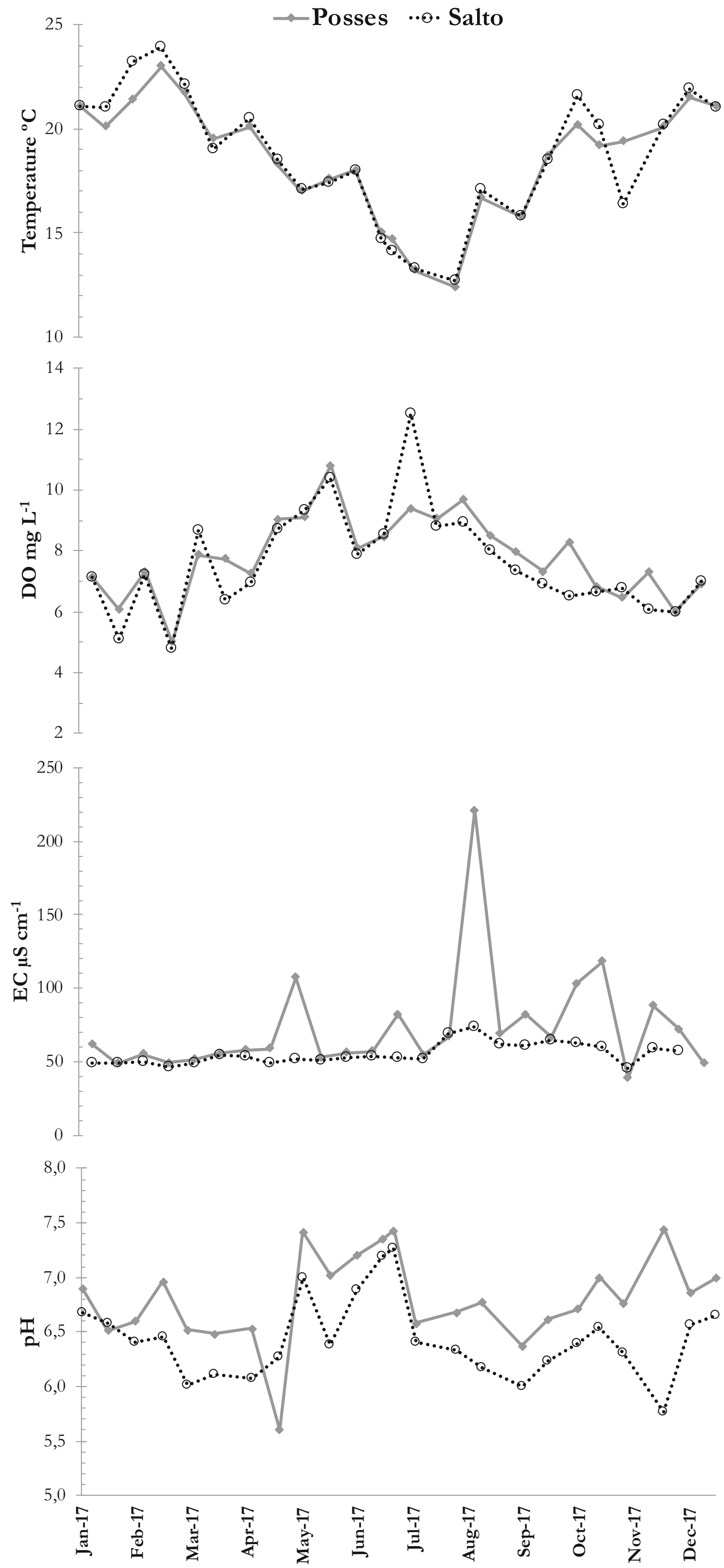


Fig. 3 Temporal variations of pH, EC, DO, and water temperature at Posses (PS) and Salto de Cima (SC) catchments

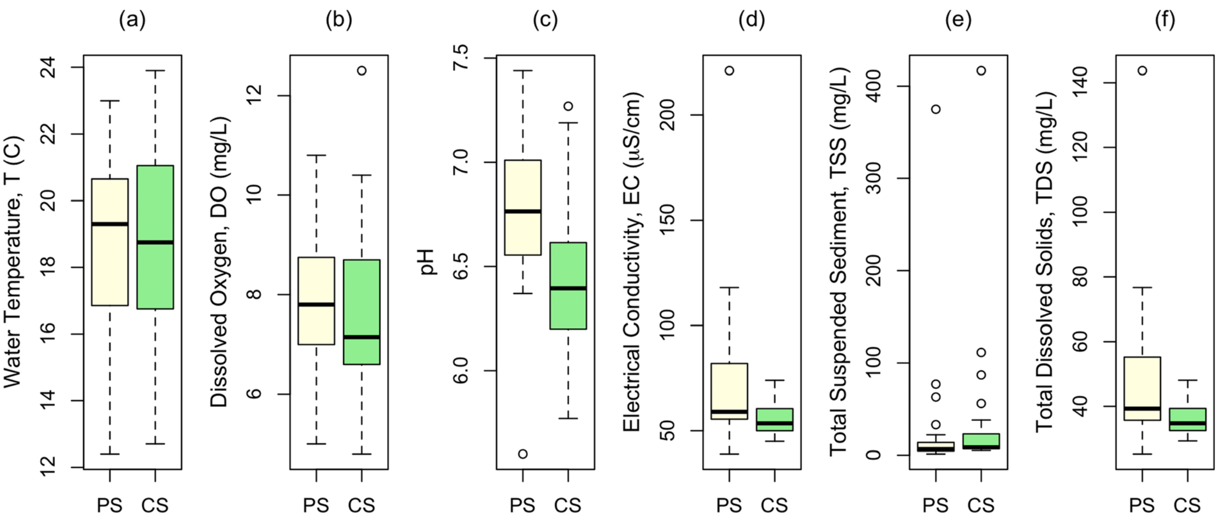
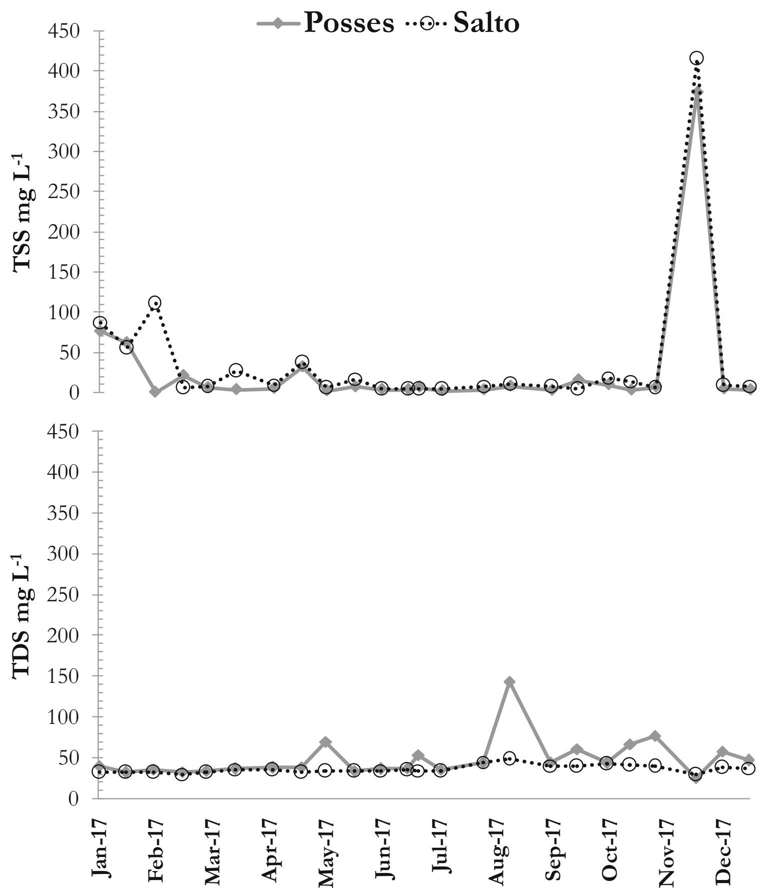


Fig. 4 Box plots of water quality variables **a** water temperature, **b** dissolved oxygen, **c** pH, **d** electrical conductivity, **e** total suspended solids, and **f** total dissolved solids at Posses (PS) and Salto de Cima (SC) catchments. See also Table 2

different, 6.5 mg L^{-1} at PS and 8.4 mg L^{-1} at SC (Table 2 and Fig. 5). Moreover, we observe in Fig. 4 that the box plots of PS and SC are very similar.

Major cation concentrations (Na^+, K^+, Ca^{2+}, and Mg^{2+}; Fig. 6) varied more widely at PS than at SC. For Na^+ a few concentration peaks were detected at

Fig. 5 Temporal variations of total suspended sediment (TSS) and total dissolved solids (TDS) at Posses (PS) and Salto de Cima (SC) catchments



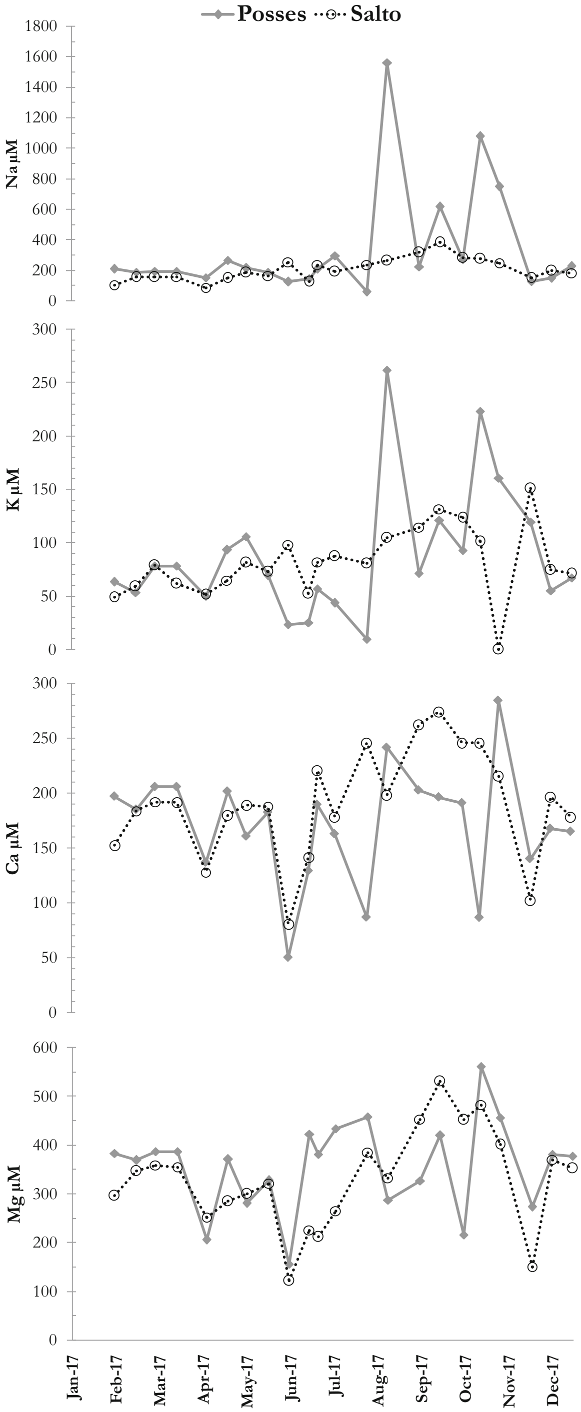


Fig. 6 Temporal variations of the major cation concentrations (in µM)—sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+})—at Posses (PS) and Salto de Cima (SC) catchments

PS, but no peaks at SC. The different Na^+ patterns at PS are also displayed in Figure 7, with four values outside the inner limits (small circles).

Major anion concentrations (Cl^- and SO_4^{2-}; Fig. 8) followed two distinct and synchronous peaks at SC. The highest peak in June coincided with the peak in Cl^- at PS, but SO_4^{2-} did not have a peak at PS. Except for these two occasions, Cl^- concentration was usually higher at PS than at SC during most of the study period. On the other hand, SO_4^{2-} concentrations were higher at SC than at PS. Cl^- concentrations at PS varied more than at SC, and SO_4^{2-} concentrations were higher at SC than at PS (Fig. 9).

Dissolved nitrogen species concentrations (NH_4^+, NO_3^-, DON, and TN) are shown in Fig. 10. For NH_4^+ the PS catchment showed a series of very low values but also had the two highest concentration values compared with concentrations at SC. A constant increasing NO_3^- concentration was observed during the study period, but decaying at end of the year, with one important concentration peak at each catchment on two different occasions. DON variation presented two high concentration peaks at each catchment but during different periods of the year. Peaks in TN appeared random and were not synchronized between PS and SC.

Box plots (Fig. 11) highlight the presence of high-top whiskers for NH_4^+ at PS and a narrow range of values distribution at SC, while for NO_3^- at PS the range of values is as narrow as it is at SC. On the other hand, the distributions of DON and TN concentrations are more similar across the two catchments.

Temporal variations of the dissolved carbon species (DOC, DIC, and TC; Fig. 12) demonstrate that DOC values were higher than DIC values in both catchments during the entire study period. As for TC, it was a little higher at PS than at SC from August to November. Moreover, important concentration peaks for DOC and TC were measured in November at PS. Also, the box plots presented in Fig. 11 reveal that the magnitudes of dissolved carbon species concentrations did not present important differences.

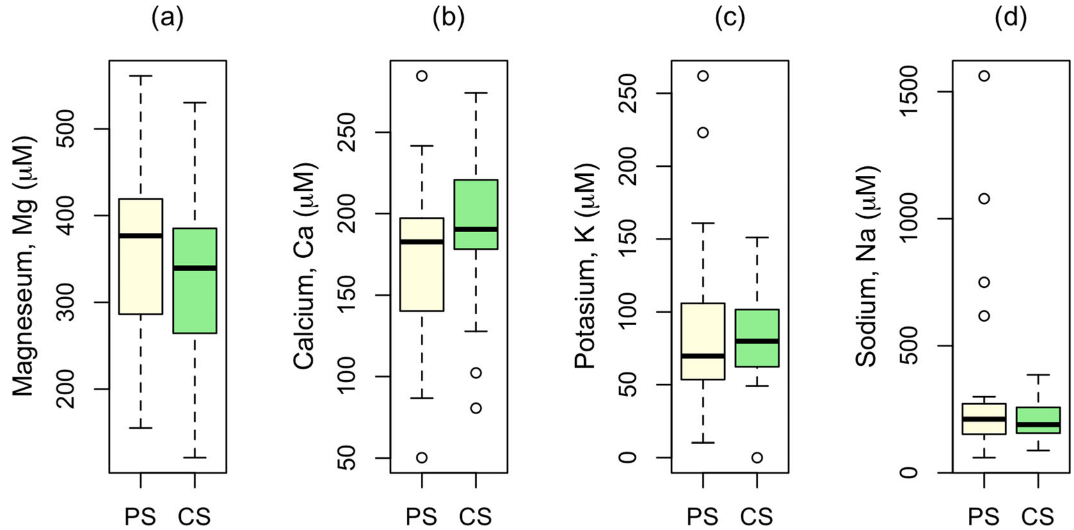
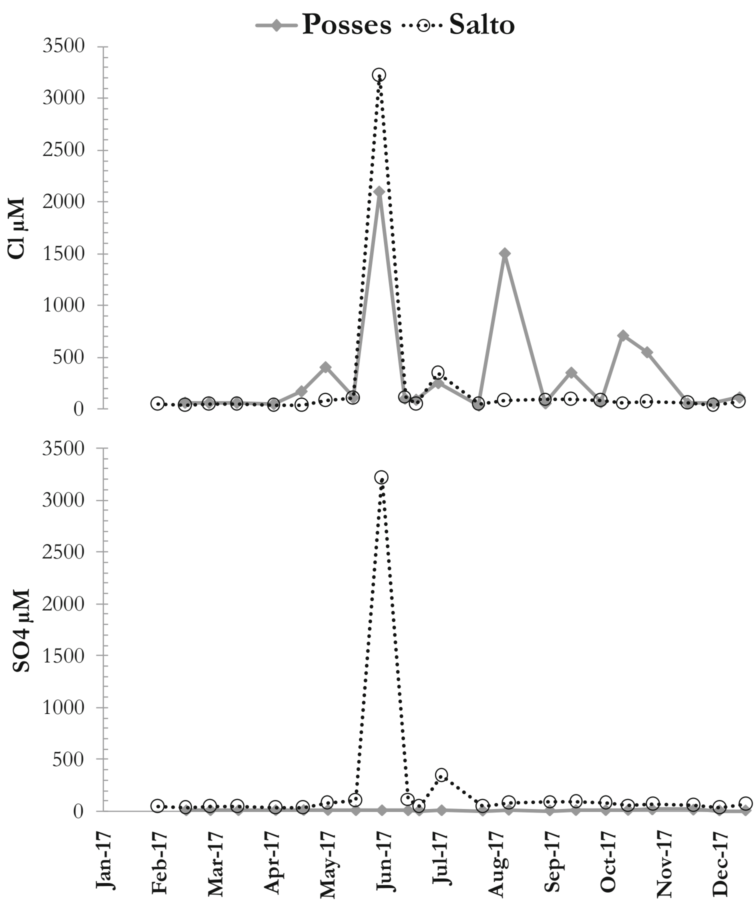


Fig. 7 Box plots of the major cation concentrations (in μM) for (a) sodium (Na^+), (b) potassium (K^+), (c) calcium (Ca^{2+}), and (d) magnesium (Mg^{2+}) at Posses (PS) and Salto de Cima (SC) catchments

Fig. 8 Temporal variations of the major anion concentrations (in μM)—chloride (Cl^-) and sulfate (SO_4^{2-})—at Posses (PS) and Salto de Cima (SC) catchments



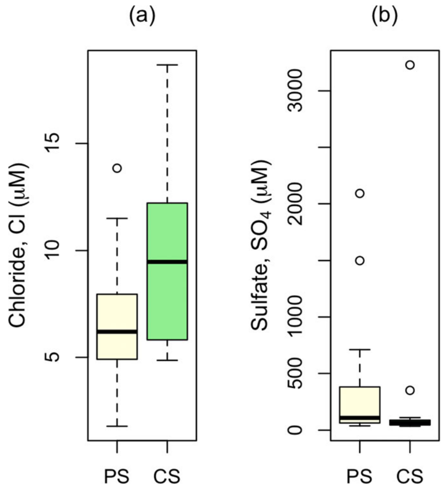


Fig. 9 Box plots of the major anion concentrations (in µM)—(a) chloride (Cl^-) and (b) sulfate (SO_4^{2-})—at Posses (PS) and Salto de Cima (SC) catchments

Streamwater quality responses to forest vegetation recovery

Results of physical-chemical parameters of water quality in general were a quite similar at PS and SC as expected for paired catchments situated in the same pedogeological and climate conditions despite the large difference in percentage of forest cover (Table 1). In fact, TSS, T, pH, and DO were in a range of magnitude that might confirm this (Table 2; Fig. 4). However, EC values differed substantially between PS and SC. This behavior stems from data collections at discrete times (grab samples) during the studied period as can be observed in their temporal variations (Fig. 3).

Previously during 2015 at the same PS reach, Reis (2018) measured T, EC, and pH annual mean values slightly higher (20.2 °C, 73.6 µS cm^{-1} and 7.8, respectively) than the median values measured by the present work (Table 2). Such modification from 2015 to 2017 may indicate a small improvement of stream water quality toward recovery. Further measurements and statistical analyses are needed to establish significant changes (or lack thereof). Decreases in water temperature may generally relate to shading provided by riparian vegetation. Moreover, decreased EC may reflect lower nutrient inputs in the stream, and lower pH may be an indicator of soils enriched by organic matter originating from forests.

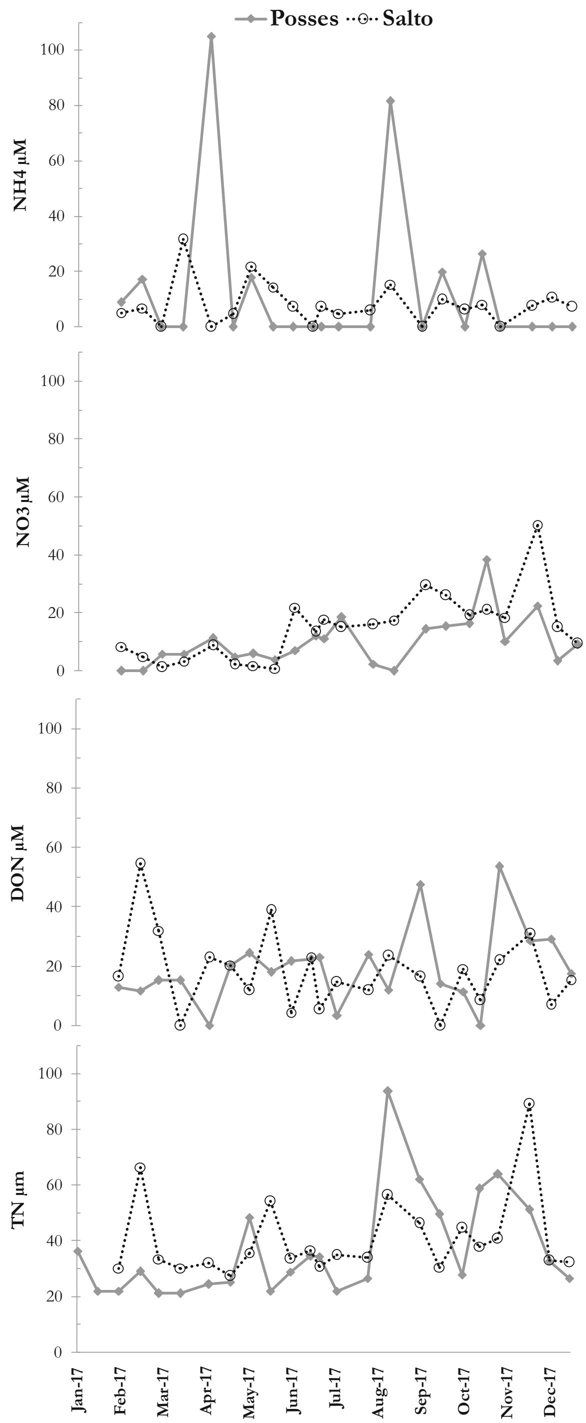


Fig. 10 Temporal variations of dissolved nitrogen species concentrations (in µM)—ammonium (NH_4^+), nitrate (NO_3^-), organic nitrogen (DON), and total nitrogen (TN)—at Posses (PS) and Salto de Cima (SC) catchments

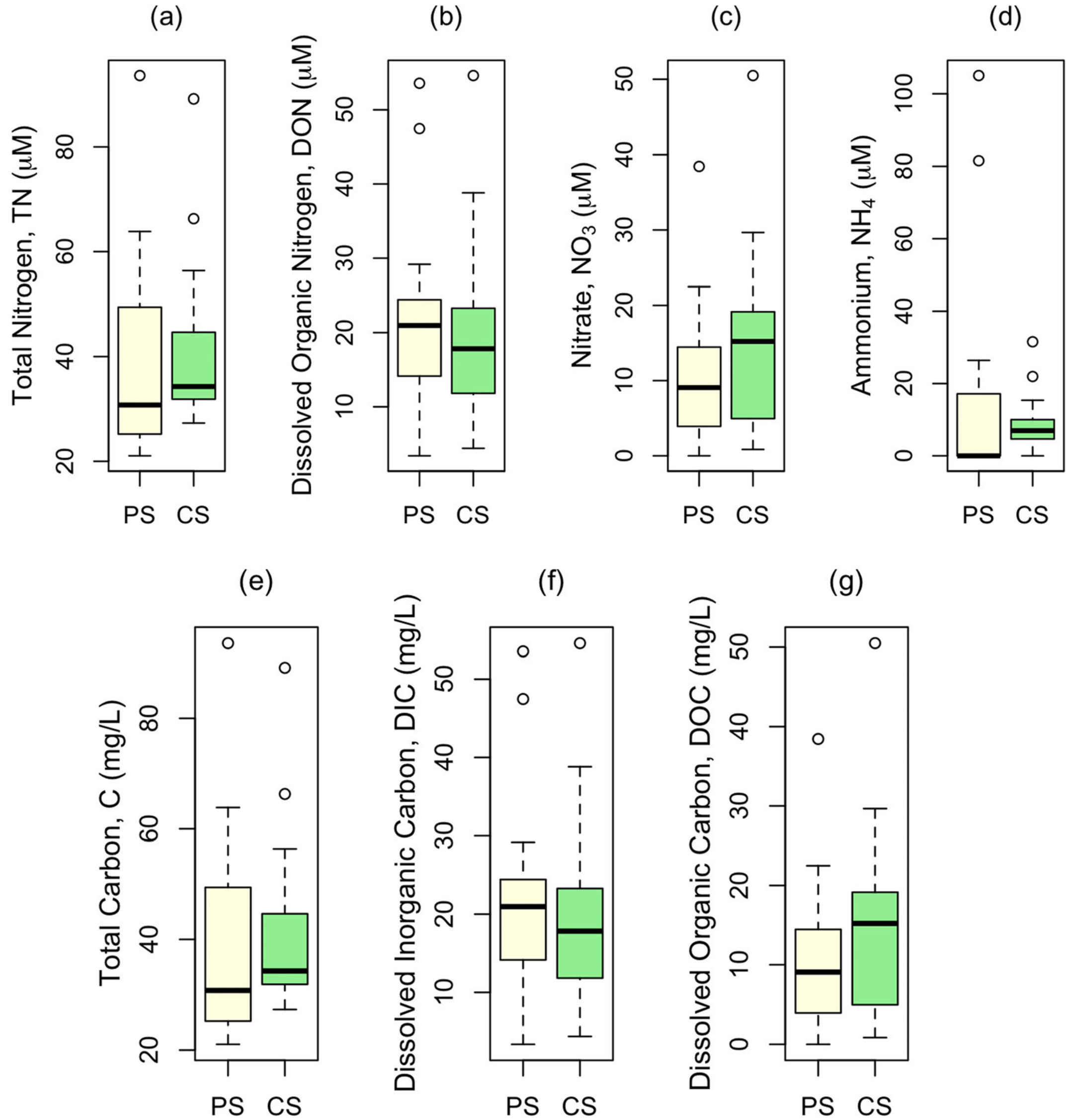


Fig. 11 Box plots of the concentrations of dissolved nitrogen species (in μM)—(a) total nitrogen (TN), (b) dissolved organic nitrogen (DON), (c) nitrate (NO_3^-), and (d) ammonium (NH_4^+) and dissolved carbon species (in mg L^{-1})—(e) total carbon (TC), (f) dissolved inorganic carbon (DIC), and (g) dissolved organic carbon (DOC) at Posses (PS) and Salto de Cima (SC) catchments

The TDS and EC behavior at PS during our study were likely caused by point pollution sources. Vercellino et al. (2015) also related EC to point-source pollution studying effects of the effluent discharge at the Piracimirim Stream located in Piracicaba, São Paulo State. Our observation about TDS and EC is corroborated by concentration peaks for several major ions (Na^+, K^+, Mg^{2+}, and Cl^-) at PS (Fig. 6) that cannot be explained by the natural inputs from pedogeological sources, vegetation dynamics, or agriculture practices as they are punctual and they have appeared as input pulses (Panno et al. 2002). The natural or non-point agricultural inputs usually change stream hydrogeochemistry more gradually and do not produce sharp increases as such observed peaks at PS but not at SC.

Mullaney et al. (2009) also communicated that increased Cl^- concentrations in surface waters could be related to wastewater discharges with high Cl^- during a low-flow period, as in the case of two monitoring stations in Illinois, USA. Moreover, Biggs et al. (2004) detected that urbanization promoted Cl^- concentration

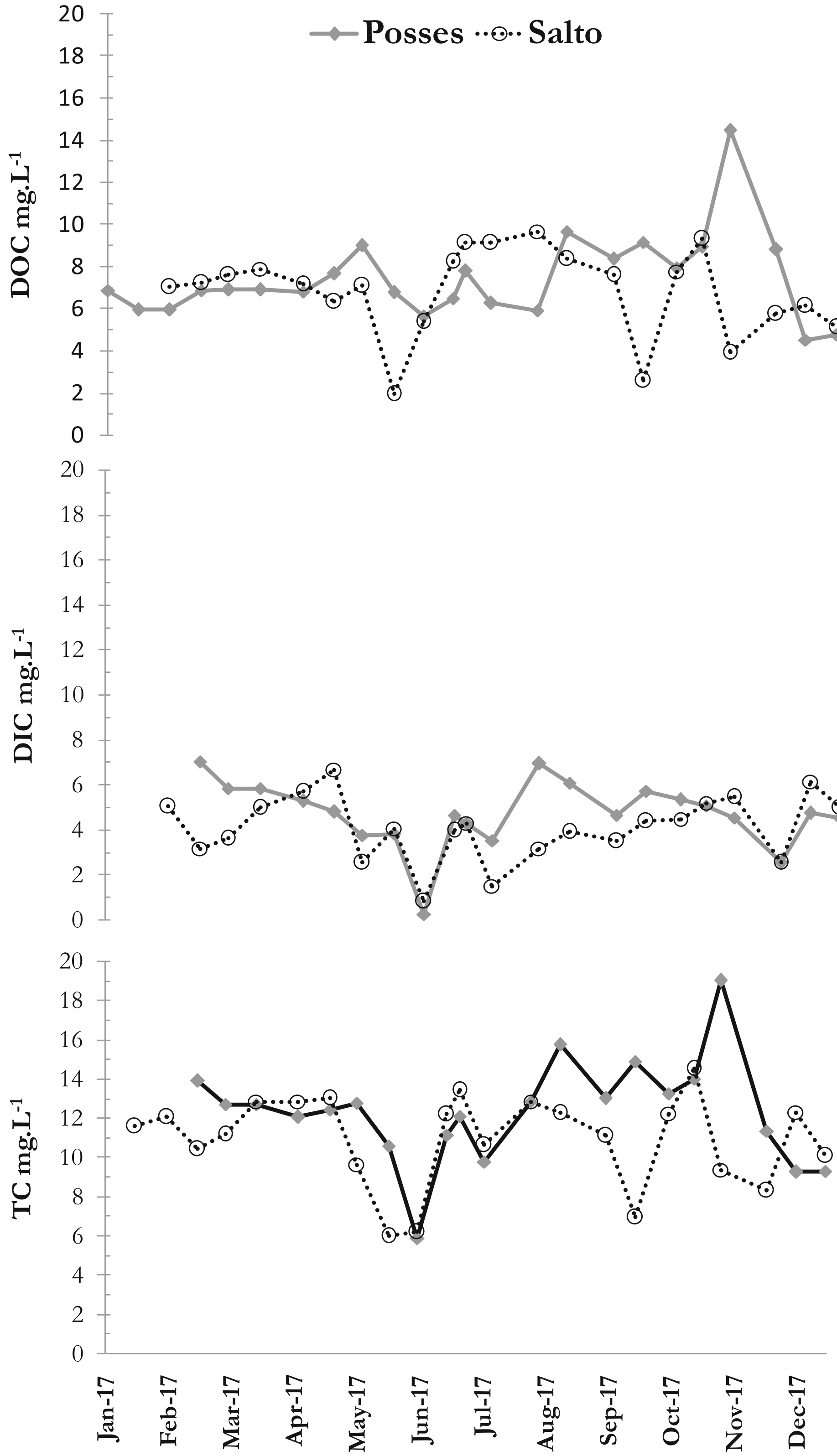


Fig. 12 Temporal variations of dissolved carbon species concentrations (in mg L^{-1})—organic carbon (DOC), inorganic carbon (DIC), and total carbon (TC)—at Posses (PS) and Salto de Cima (SC) catchments

increasing for all watershed sizes they evaluated in a land use change study in an Amazonian Brazilian state. Thus, we suspect that the high Cl^- peak at SC (Fig. 8) may be related to domestic sewage input as we observed houses around this stream reach.

As for the other major ions, Ca^{2+} was very similar at both catchments, increasing during low flow periods. Thus, as expected, despite the land use and soils characteristics, the effect of discharge on Ca^{2+} concentration increase is large as demonstrated by Markewitz et al. (2011) for streams in Brazil of the Amazon and Cerrado biomes. On the other hand, during our study, SO_4^{2-} had two peaks at SC and a tendency to have higher concentrations than the ones at PS (Fig. 8). A likely explanation would be a point pollution source related to a tiny urbanization (domestic sewage already mentioned before) at this lower part of the watershed, which is not contemplated at land use classification (Table 1) considering they are very small areas related to the catchment area. In a previous study of Amazonian watersheds, Biggs et al. (2001) concluded that population density strongly affected SO_4^{2-} stream concentrations in both seasons of the year.

Considering the results of Reis (2018) for the monitoring from January 2015 to January 2016 regarding the magnitudes of major ions, the differences of the present work conducted in 2017 is that Na^+, K^+, Mg^{2+}, and Cl^- concentrations in 2017 have peaks that were not observed before. Therefore, it seems that the mentioned point sources of pollution became more frequent in 2017. Considering all these results and the detected point source inputs, the recommendation of Santos (2014) was not confirmed for the use of EC as an indicator of the effects of the ESP program activities, which are restricted to farming and reforestation practices, for water quality improvement.

Regarding N, P, and C, we highlight that possibly because of larger forest areas, SC was more enriched in NO_3^- than PS (Tables 1 and 2; Fig. 11), which was also observed by Santos (2014) comparing these two catchments in 2011–2013. As has been shown in many publications, NO_3^- dynamics are more intense in forest soils than in pasture soils reflecting in the stream chemistry. For example, Neill et al. (2001) studied small catchments in an area of agricultural expansion in the Brazilian Amazon, where they concluded that NO_3^- concentrations in stream water were correlated with high NO_3^- production in forest soils and lower NO_3^- production in pasture soils.

Germer et al. (2009) evaluated net fluxes of inorganic N within a small pastoral area in the southwestern part of the Amazon Basin, wherein they identified net N sinks. Another study in southeastern Brazil (Salemi et al. 2015) stated that older pastures in the Atlantic Rainforest displayed dynamic patterns of N which are similar to the present N dynamics for Amazonian watersheds. In particular, both studies demonstrate N accumulation via greater annual input loads of N in rainfall than the annual output N loads generated in stream discharge.

Low availability of soil inorganic N is inferred by the main forms of N measured in water being organic N. Thus, addition of fertilizers to such mature pastures provides a source of inorganic N to receiving stream reaches.

NH_4^+ concentration peaks in PS (Fig. 10) can be explained by the presence of cattle seen in the field close to the sampling station in a place without fencing. PO_4^{3-} was only detected once in the water samples (that is the reason no graph of PO_4^{3-} is presented) and it was in PS which may be related to this same cattle influence (Table 2).

At SC we measured NH_4^+ concentrations generally higher than in PS, with the exception of the described peaks at PS (Fig. 10). As this SC sampling station has more houses in the vicinity, such NH_4^+ values can be a response to improper domestic sewage disposal, even though this very tiny urban neighborhood was not considered in the land use classification as commented regarding to PS (Table 1). Perhaps at SC this has more effect over the NH_4^+ concentrations than the presence of the grass in the riparian zone as mentioned by Reis (2018) who related this land cover at PS to higher NH_4^+ values.

Thus, it was evident that there was a point pollution source, probably related to a small food industry and/or a small fish farm present at the lower reach of the PS stream, as well as signals of bovine urine and feces regarding to cattle visits to this stream. Such factors affected streamwater quality at PS catchment, and domestic sewage input has also affected SC water quality, which needs to be considered in the strategy of this PES program in the Extrema municipality. In fact, Martinelli et al. (2002) already highlighted that domestic sewage, as a point source for instance, has caused severe alterations in water bodies in the São Paulo State, including the Piracicaba river basin.

Therefore, forest recovery as well as landscape and management soil practice effects on the water resources can have overlapping benefits for such discovered pollution sources. Otherwise, all the efforts to improve water quality can be diminished as it is targeted by the local PES program, as pointed out by Santos (2014), who concluded that the forest recovery would reduce the effects of nutrient, sediments and organic compounds carried by the hydric terrestrial flows and consequently collaborating for the water resources conservation in the region.

Conclusion

We found limited improvement of the measured water quality in streams of both Posses and Salto de Cima catchments in response to recovering the forest vegetation. However, we detected some infrequent signals of point sources of pollution at the Posses stream outlet on seemingly random dates and times. Consequently, we recommend considering anthropic effluents and other watershed management practices as part of the Extrema Environmental Services Payment program. Confidence in the contribution of these catchments with good water quality entering into the Jaguari River, and consequently to the Cantareira Reservoir, can be assured only after taking such actions. Although this is a preliminary evaluation, the present data and analyses provide a baseline and strong foundation for assessing cumulative effects of both diffuse agricultural management and wastewater mitigation efforts affecting future water quality in these upland catchments. Despite the different stages of the forest recovery process between Posses and Salto de Cima catchments, the general water quality results were similar enough to detect potential differences in the progression over longer periods in these paired catchments. Future work may help us distinguish the impacts of ESP distributed across these catchments from punctual sources of contamination in space and time.

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