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Effects of land cover on chemical characteristics of streams in the Cerrado region of Brazil

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Abstract The Cerrado is the second largest Brazilian biome and contains the headwaters of three major hydrological basins in Brazil. In spite of the biological and ecological relevance of this biome, there is little information about how land use changes affect the chemistry of low-order streams in the Cerrado. To evaluate these effects streams that drain areas under natural, rural, and urban land cover were sampled near Brasília, Brazil. Water samples were collected between September 2004 and December 2006. Chemical concentrations generally followed the pattern of Urban > Rural > Natural. Median conductivity of stream water of 21.6 (interquartile: 22.7) µS/cm in urban streams was three and five-fold greater relative to rural and natural areas, respectively. In the wet season, despite of increasing discharge, concentration of many solutes were higher, particularly in rural and natural streams. Streams also presented higher total dissolved N (TDN) loads from natural to rural and urban although DIN:DON ratios did not differ significantly. In natural and urban streams TDN was 80 and 77% dissolved organic N, respectively. These results indicate that alterations in land cover from natural to rural and urban are changing stream water chemistry in the Cerrado with increasing solute concentrations, in addition to increased TDN output in areas under urban cover, with potential effects on ecosystem function.

Keywords Gallery forest · Nutrient fluxes · Savannas · Tropical catchments

Introduction

The Brazilian Cerrado is the second largest biome in South America, occupying approximately 2 million km^2 or 24% of the national territory (IBGE 2004). Land use conversion and consequent fragmentation of this important biome was stimulated by the construction of Brazil's new capital city, Brasília, in the early 1950s, and was accelerated in the 1970s with the expansion of the agricultural frontier into the Brazilian central plateau (Klink and Machado 2005). By 2002, approximately 39% of the original vegetative cover of the Brazilian Cerrado has been converted, mainly to cultivated pastures (26.5%) and agricultural crops (10.5%) (Sano et al. 2008).

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Changes in land use, such as those observed in the Cerrado, can impact the functioning of ecosystems. Studies in the Brazilan Amazon, which has suffered a cumulative deforestation in the last 10 years of $\sim 176{,}000\ \mathrm{km}^2$ (INPE 2009), demonstrate that land use change has affected the water balance (Salati and Vose 1984), biogeochemical cycling of elements (Melillo et al. 1996; Downing et al. 1999; Herpin et al. 2002), physical and chemical soil properties (Neill et al. 1995; McGrath et al. 2001; Markewitz et al. 2001), carbon cycling and the distribution of organic matter (Houghton 1990; Richey et al. 1997).

While studies evaluating the effects of changes in land use and land cover on the biogeochemistry of rivers in Brazil are relatively common in the Amazon (Williams and Melack 1997; Neill et al. 2001; Ballester et al. 2003; Biggs et al. 2002, 2004; Figueiredo et al. 2010), biogeochemical evaluations of the impacts of land use changes in the Cerrado region are still scarce in spite of its hydrological importance on a country-wide scale. Some of the most important hydrological basins in Brazil have their headwaters in the Cerrado: Araguaia-Tocantins, Paraná, and São Francisco basins. More than 70% of the discharge of these basins originates in the Cerrado region. Land use changes in the Cerrado, often coupled to increased fire frequency and invasion of exotic species, have generated profound changes in the vegetation structure and functioning of these ecosystems (Klink et al. 1995).

In general, these changes in land use are first reflected in the biogeochemistry of small streams (Richey et al. 1997). Small streams are important biogeochemical elements in landscapes, as they connect the terrestrial environment with large rivers, and their chemistry is affected by biotic and abiotic processes such as climate, hydrology, soil properties, geomorphology, topography and land use (Thomas et al. 2004). Thus, the study of small catchments can integrate many processes in changing landscapes (Alexander et al. 2000; Campbell et al. 2004). For example, Neill et al. (2001) working in the western Amazon demonstrated changes in solute concentrations with lower nitrate concentrations and decrease in N:P ratios in streams draining pastures relative to forests, in addition to higher concentrations of total suspended solids, particulate organic carbon and particulate organic nitrogen in the dry season. The observed decrease in stream NO_3^- in pastures was consistent with previous studies that found lower extractable NO_3^- concentrations and lower rates of net N mineralization and net nitrification in the soils of the pasture watersheds compared with forest watersheds (Neill et al. 1995). Similarly, Forti et al. (2000), working in northeastern Amazonia, showed increased net export of all chemical species in a stream draining deforested portions of a 164 ha watershed, compared to pristine areas. Finally, Biggs et al. (2002), based on a synoptic sampling approach of 60 watersheds ranging from 18 to $12{,}500\ \mathrm{km}^2$ in southwestern Amazonia, observed an influence of deforestation, urbanization and soil type on stream solute concentrations. Seasonal differences in stream chemistry were also detected.

The present study evaluated the effects of different land covers (natural, rural and urban) and seasonality on nutrient concentrations and physical–chemical parameters of stream waters in the Cerrado region. It was hypothesized that: (1) given the dilute nature of natural streams in this region dissolved loads would readily respond to land conversion to agriculture (rural) or urbanization, with highest solute concentration in the streams draining rural and urban areas, (2) streams that drain urban areas will have the highest solute concentrations due to the point source release of effluents, (3) ion concentrations will be lower during the rainy season due to the dilution effect from higher discharge, and (4) nitrogen, a major limiting nutrient in Cerrado ecosystems, will shift from predominantly organic forms in natural systems to higher proportions of dissolved inorganic forms (NH_4^+, NO_2^- and NO_3^-) in rural and urban streams.

Materials and methods

Study area

This study was performed in small streams (1st to 3rd orders) in areas under natural, rural, and urban land covers around the Distrito Federal, Central Brazil (Fig. 1a). The climate in the region is classified as Aw according to the Köppen system. The average annual precipitation and mean air temperature in the last 10 years (1999–2009) were 1380 mm and 22.5°C, respectively.

The streams under natural cover ($N = 3$) were in protected areas (Fig. 1b and c). The Pitoco

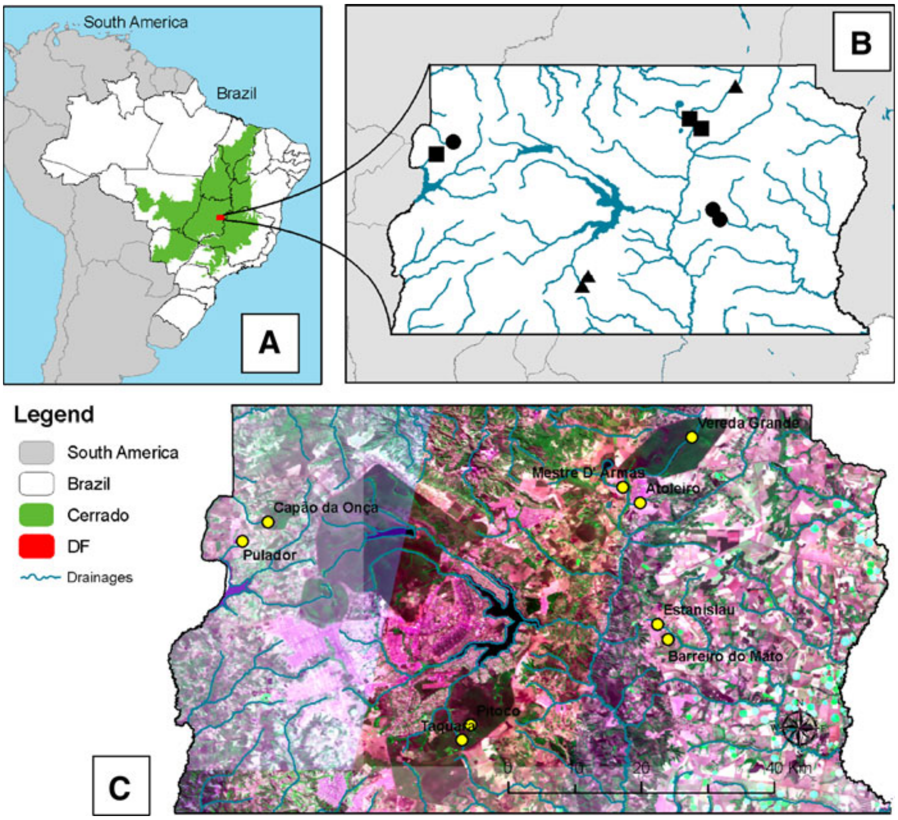

Fig. 1 **a** Distribution of the Cerrado Biome in the Brazilian territory; **b** distribution of the drainages in the Federal District, with the sampling points highlighted (*triangles* correspond to natural cover, *circles* to rural cover and *square* urban cover); **c** satellite image (CBERS) of the Federal District, with the location of sampling points

(15°55′52″S and 47°52′40″W) and Taquara (15°57′06″S and 47°53′21″W) streams were located at the Ecological Reserve of the Brazilian Institute of Geography and Statistics (RECOR-IBGE). The basin encompassing the Pitoco and Taquara streams is ~30 km^2, with almost 100% under natural cover. The Vereda Grande stream (15°32′33″S and 47°34′42″W) at the Águas Emendadas Ecological Station is situated in a basin that has approximately 39 km^2, with 79.4% under natural cover, 20.3% under rural use and 0.3% under urban cover (Table 1).

The streams under rural cover ($N = 3$) were located in small farms surrounded by pastures and large agricultural fields, mainly soybean and maize (Fig. 1c). The Estanislau (15°47′41.6″S and 47°37′29.7″W) and Barreiro do Mato (15°48′56.3″S and 47°36′38″W) streams are located in a watershed of 39.5 km^2, with 85% under agricultural cover and the rest under natural cover. The Capão da Onça (15°38′29.5″S and 48°10′53″W) stream is located in another watershed of 45.8 km^2, near the city of Brazlândia. This basin has 48% agricultural cover, 44% natural cover, 7% under silviculture and 1% urban cover.

Sampling points in urban streams ($N = 3$) were located near recent centers of urbanization (Fig. 1c). Atoleiro (15°37′50.1″S and 47°38′53.2″W) and Mestre D'Armas (15°36′35.3″S and 47°40′18.5″W) streams were located in the city of Planaltina. The basin containing these streams has 77.7 km^2, with 14.0, 58.7, and 27.3% of its area under urban, natural, and rural cover, respectively. The basin of the Pulador stream (15°40′56.7″S and 48°11′09.3″W) is located close to Brazlândia. This 19.1 km^2 basin has 6.0, 77.0, and 17.0% under urban, rural and natural cover, respectively.

Soils in uplands of the Cerrado are predominantly well-drained, highly-weathered Latossolos, according to the Brazilian Soil Classification, which corresponds to Oxisols in the US soil classification. Downslope well-drained but less well-developed soil profiles may be encountered, which are classified as Cambissolos (Inceptisols in US Soil Taxonomy). In the Federal District the Oxisols occupy 54.5% of the territory, while Cambissolos cover approximately

Table 1 Catchment basin characteristics for streams that drain areas under predominantly natural, rural and urban land cover in Federal District, Brasilia, Brazil (2007)

Stream class	Stream	Drainage area (km^2)	Upper stream (km^2)	Natural cover (%)	Rural cover (%)	Urban cover (%)
Natural	Pitoco	13.3	0.8	100	–	–
	Taquara	16.1	1.5	100	–	–
	Vereda Grande	38.5	38.5	79.4	20.3	0.3
Rural	Estanislau and Barreiro do Mato	39.3	3.9 2.5	11.5 16.7	88.5 83.3	– –
	Capão da Onça	45.8	7.2	49.5	50.5	–
Urban	Pulador	19.1	1.7	17	77	6
	Mestre D'Armas	57.4	57.4	63	27	10
	Atoleiro	20.3	20.3	46.2	27.1	26.7

31% (Reatto et al. 2004). In the catchments in the present study, Oxisols are in the dominant soil type. Near streams, however, Gleissolos are common (there is no analogous order in US Soil Taxonomy but the Aquox suborder would be similar). According Silva (2008) and Spera et al. (2006) the riparian zones of Pitoco, Taquara, Estanislau, Barreiro do Mato and Pulador Gleissolos are typically of high clay content (>60%) like the upland Oxisols but are highly reduced presenting gleyed colors.

Sample collection and analysis

Stream water samples were collected in previously acid-washed 250-ml polypropylene bottles in the nine streams (three in each land cover) from September 2004 to December 2006 every 2 weeks during the wet season (October to April), and monthly, during the dry season (May to September).

Pressure transducers (Data Logger—Global Water) were installed in the Pitoco (November-2005 to December-2006) and Taquara (November-2005 to September-2006) streams (Natural areas), and Barreiro do Mato (December-2006 to January-2008) stream (Rural area) in order to determine the seasonal variation in the stage height of these streams (Figs. 2, 3, and 4).

The water samples were collected under base flow conditions except for five collections made during the wet season under storm flow conditions (three times in natural streams (Mar/2006; Dec/2006; Jan/2007) and twice in rural streams (Dec/2006 and Jan/2007). Bottles with water samples were placed in a cooler until returning to the laboratory. A subsample was taken for immediate determinations (alkalinity and turbidity), and another one was filtered through cellulose acetate filters (nominal pore size 0.45 µm) and stored at −4°C until analysis.

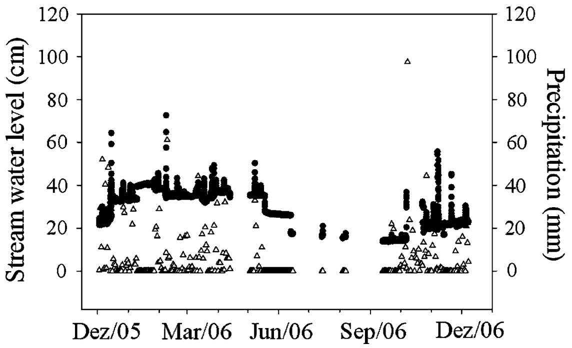

Fig. 2 Stage height for the upper reach of the Pitoco stream and precipitation measurements, Federal District, Brazil (*circles* correspond to stage height and *triangles* to precipitation)

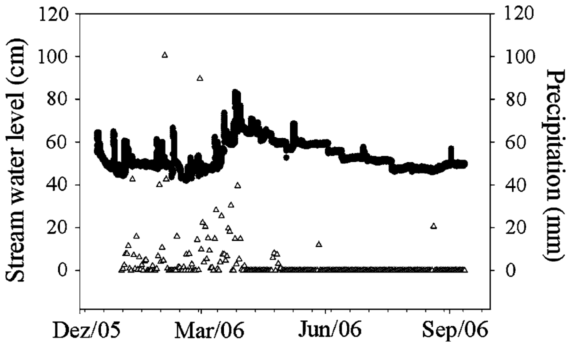

Fig. 3 Stage height for the upper reach of the Taquara stream and precipitation measurements, Federal District, Brazil (*circles* correspond to stage height and *triangles* to precipitation)

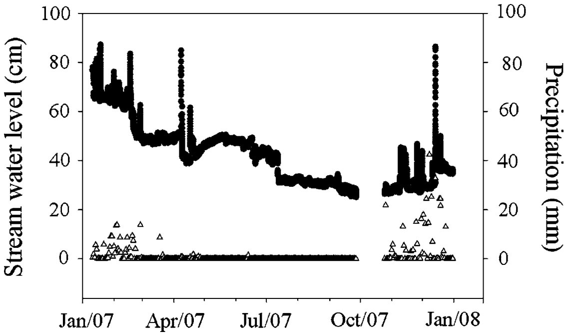

Fig. 4 Stage height for the Barreiro do Mato stream and precipitation measurements, Federal District, Brazil (*circles* correspond to stage height and *triangles* to precipitation)

Measurements of pH (H^+ concentrations), electrical conductivity and dissolved oxygen were performed in situ with a Oakton 10 series meter (glass combination electrode) and an oxygen electrode (64—Fisher Scientific), respectively.

Alkalinity was determined in the laboratory on the same day of collection using endpoint titrations with 0.002 N H_2SO_4 to pH 4.5 (Clesceri et al. 1998). A HACH 2001 NA turbidimeter was used for turbidity determinations. Water samples were analyzed for dissolved organic carbon (DOC) (Shimadzu TOC 5000, Columbia, MD) and total dissolved nitrogen (TDN) (persulphate digestion, following Koroleff 1983). Cations (NH_4^+, Ca^{+2}, Mg^{+2}, K^+ and Na^+) and anions (NO_2^-, NO_3^-, PO_4^{-3}, Cl^- and SO_4^{-2}) were analyzed by ion chromatography (Dionex DX500, Sunnyvale, CA). Filtered samples were used for major ions, DOC and TDN determinations.

Statistical analysis

As normality of the data was rejected by the Kolmogorov–Smirnov test, non-parametric statistical tests were performed using the statistical package SPSS 10.0. The concentrations of solutes (not flux-weighted) in streams under natural cover, rural and urban areas were compared by a Kruskal–Wallis test, while seasonality (wet and dry seasons) was compared by a Mann–Whitney test. In order to test the interactions between land cover and seasonality effects, data were log transformed to approximate a normal distribution, and a two way-ANOVA was performed using $p < 0.05$ to indicate significant effects.

Results

The values of H^+ concentration, alkalinity and electrical conductivity differed significantly ($p = 0.000$) among land cover types, with streams in urban areas showing the highest median values for alkalinity 111.3 μM (Interquartile Range: 84.9 μM) and electrical conductivity 21.6 (22.7) μS/cm, followed by rural and natural areas (Fig. 5). On the other hand, H^+ concentrations were lower 1.0 (1.3) μM) in urban areas and higher in streams from natural areas 9.3 (11) μM). Streams draining through rural areas showed intermediate values. Turbidity was also significantly higher in urban streams (median 12.6 (22.9) NTU; $p = 0.000$), while values in rural streams did not differ from those of streams in natural areas (Fig. 5). Seasonal differences for alkalinity, with higher values in the rainy season, were observed only in natural and rural streams ($p = 0.017$ and 0.00, respectively), while in urban streams there were seasonal variations for H^+ concentration ($p = 0.019$) and turbidity ($p = 0.050$), with higher values also observed during the rainy season (Table 2). Significant interactions between the effects of land cover and seasonality ($p = 0.006$) were only observed for alkalinity values.

The streams in urban areas presented the highest dissolved oxygen median concentrations 8.1 (2.1) mg/L ($p = 0.000$), with 90% oxygen saturation (Fig. 5), while rural streams showed the lowest median concentrations 6.5 (1.8) mg/L, ($p = 0.000$) with approximately 74% saturation. Streams in natural areas also presented good oxygenation with saturation around 85%. Dissolved oxygen concentrations differed significantly between seasons, with highest concentrations in the dry season in the studied streams (natural and rural $p = 0.000$; and urban $p = 0.008$) (Table 2).

Urban streams had larger total dissolved nitrogen (TDN) in relation to median concentrations 33.0 (24.1) μM, approximately 85% higher, than natural and rural streams ($p = 0.000$) which did not differ from each other (Fig. 6). Urban and rural streams presented the highest concentrations for NH_4^+ (median = 4.3 (5.4) and 5.0 (7.1) μM, respectively; $p = 0.000$ and 0.049, respectively;) (Fig. 6). The concentrations of NO_2^- and NO_3^- in water samples for natural, rural, and urban streams also differed significantly ($p = 0.000$) with the highest values in

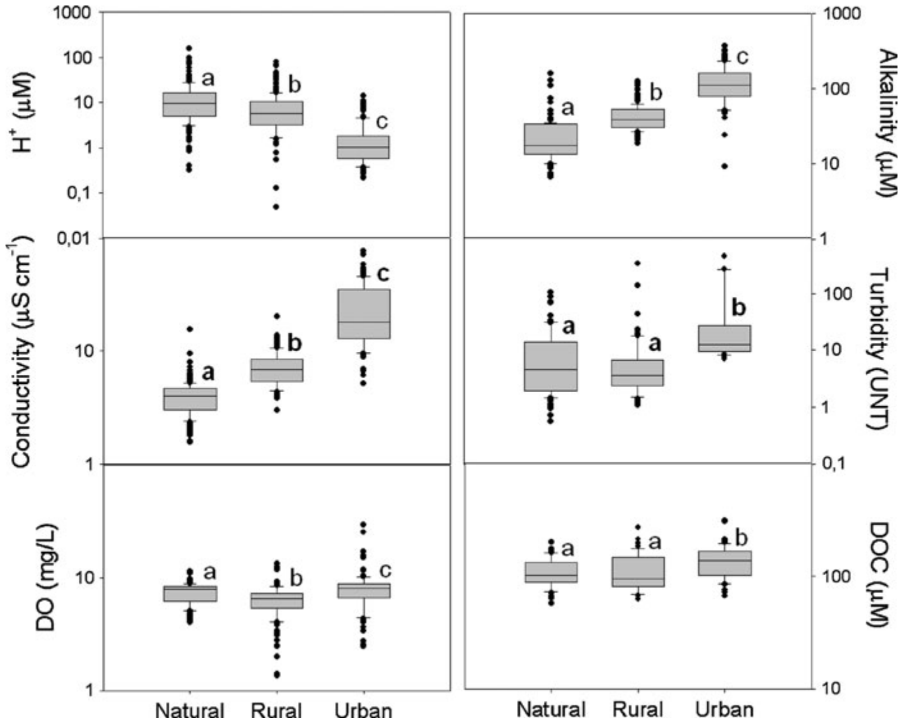

Fig. 5 Median values for H$^+$, alkalinity, conductivity, turbidity, dissolved oxygen (*DO*) and dissolved organic carbon (*DOC*) of the water from streams in areas under different covers (natural, rural and urban) in the Federal District, Brazil (September 2004 to December 2006). *Box plots* display 10th, 25th, 50th, 75th and 90th percentiles, and individual data points outside the 10th and 90th percentiles (*Different letters* indicate differences between the areas; $N = 3$, $\alpha = 0.05$)

Table 2 Mean values for stream water concentrations of streams under three land cover types

Constituent	Natural cover		Rural cover		Urban cover	
	Wet	Dry	Wet	Dry	Wet	Dry
H$^+$	16.07	10.39	9.96	6.86	2.40*	1.09
Conductivity	4.03	3.99	7.38	6.72	25.26	22.93
Alkalinity	28.83*	18.56	49.37*	33.72	126.94	134.21
DO	6.98	7.79*	6.09	6.89*	7.13	7.86*
N-NH$_4{}^+$	4.11	3.03	5.75*	3.76	7.65	6.06
N-NO$_2{}^-$	2.16*	0.86	3.11*	0.96	3.76	3.39
N-NO$_3{}^-$	0.67	0.49	0.98	0.73	3.06	3.11
K$^+$	3.96	2.64	9.13*	6.36	16.08	11.19
Ca^{+2}	3.55*	2.61	7.89*	3.99	34.53	27.88
Mg^{+2}	3.30	3.72	4.86	4.80	12.11	14.36
Na$^+$	19.00*	8.83	25.96*	14.57	69.87	54.50
Cl$^-$	4.22	5.38	10.26	10.34	32.24	31.42
SO$_4^{-2}$	1.06	0.99	1.35	1.34	3.86*	2.68
PO$_4^{-3}$	0.21*	0.03	0.17	0.37	0.13	0.14
TDN	20.29	17.85	21.68*	15.89	35.62	34.20
DOC	125.14*	95.51	121.74*	91.00	146.70*	117.05
Turbidity	19.22	7.78	17.31	3.84	228.37*	17.83

Solutes (μM), Conductivity (in μS cm^{-1}), DO: dissolved oxygen (in mg l^{-1}) and turbidity (in NTU)

* Mean values statistically different (level of 5% significance) between wet and dry season mean values

urban areas (5.1 (11.1) and 10.7 (13.5) μM, respectively), followed by rural (2.2 (2.5) and 2.9 (2.0) μM) and natural streams (1.7 (2.1) and 1.9 (1.0) μM, respectively) (Fig. 6). It was in rural areas where the seasonal influence was more striking with respect to nitrogen compound concentrations. The highest

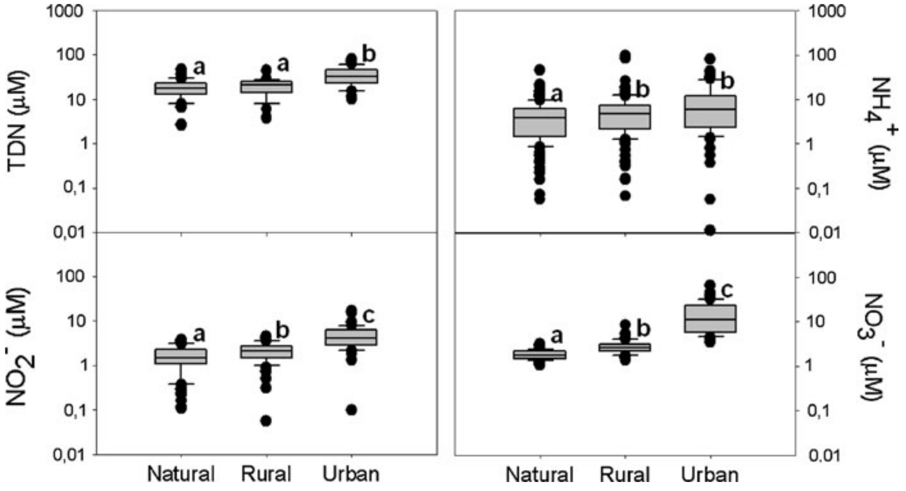

Fig. 6 Median values of total dissolved nitrogen (*TDN*), ammonium (*NH_4^+*), nitrite (*NO_2^-*) and nitrate (*NO_3^-*) of water from streams in areas under different covers (natural, rural and urban) in the Federal District, Brazil (September 2004 to December 2006). *Box plots* display 10th, 25th, 50th, 75th and 90th percentiles, and individual data points outside the 10th and 90th percentiles (*Different letters* indicate differences between the areas; $N = 3$, $\alpha = 0.05$)

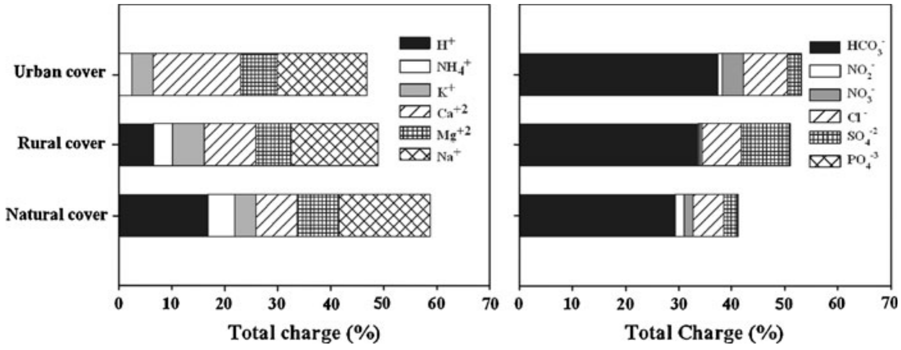

Fig. 7 Median percentage of inorganic nitrogen fractions (N-NH_4^+, N-NO_2^- and N-NO_3^-) and Dissolved Organic Nitrogen in stream water from streams under natural, rural and urban areas. $N = 3$ for each land cover. Federal District, Brazil (September 2004 to December 2006) (*Different letters* indicate differences between the areas; $\alpha = 0.05$)

concentrations of these compounds (TDN, NH_4^+ and NO_2^-) were measured during the rainy season (Table 2).

The DIN/DON ratios (0.21, 0.26 and 0.29) did not differ significantly among the land cover types (natural, rural and urban, respectively). The relative contributions of dissolved inorganic nitrogen forms (N-NO_2^-, N-NO_3^- and N-NH_4^+) differed among the streams in the different land covers, with N-NH_4^+ being predominant in the three land covers (Fig. 7). Natural and rural areas showed no differences in the percentages of inorganic nitrogen forms. Relative contributions of N-NH_4^+ and N-NO_3^- in urban streams, on the other hand, differed from the other areas ($p = 0.000$) with higher percentages of N-NO_3^- and lower N-NH_4^+, while N-NO_2^- contribution remained unchanged. Dissolved Organic Nitrogen also did not presented significant differences when the three land cover types were compared (Fig. 7).

The concentrations of calcium, magnesium, potassium and sodium in stream water samples differed significantly ($p = 0.000$) among the land covers. As for the other elements, higher median concentrations were found in urban streams ($Ca^{+2} = 19.7$ (26.4) µM, $Mg^{+2} = 9.9$ (12.3) µM, $K^+ = 10.2$ (9.2) µM and $Na^+ = 48.3$ (52.1) µM, Fig. 8), followed by rural areas ($Ca^{+2} = 5.2$ (4.6) µM,

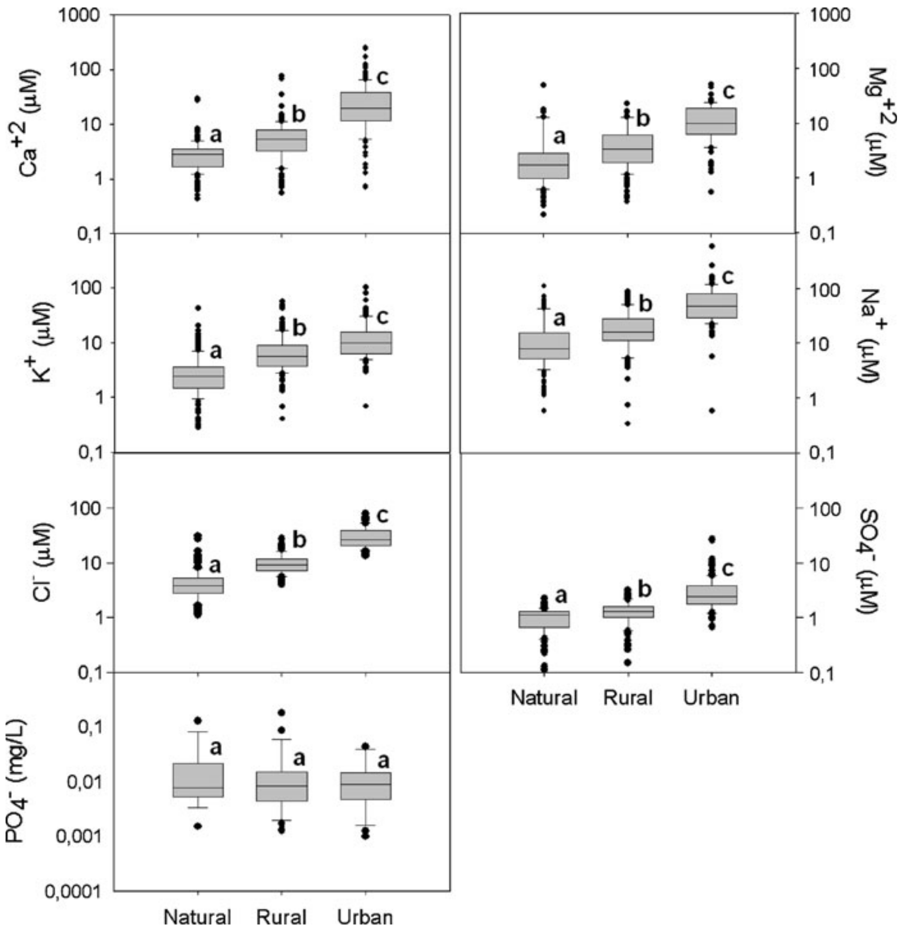

Fig. 8 Median values of Ca^{+2}, Mg^{+2}, K^+, Na^+, Cl^-, SO_4^{-2} and PO_4^{-3} of water from streams in areas under different covers (natural, rural and urban) in the Federal District (September 2004 to December 2006). *Box plots* display 10th, 25th, 50th, 75th and 90th percentiles, and individual data points outside the 10th and 90th percentiles (*Different letters* indicate differences between the areas; $N = 3$, $\alpha = 0.05$)

$Mg^{+2} = 3.3$ (4.1) µM, $K^+ = 5.6$ (5.3) µM and $Na^+ = 16.1$ (17.1) µM) and natural areas ($Ca^{+2} = 2.7$ (1.7) µM; $Mg^{+2} = 1.7$ (1.8) µM, $K^+ = 2.6$ (2.1) µM and $Na^+ = 7.8$ (10.1) µM). The highest ion concentrations in urban areas when comparing the three urban sampling points were observed in November (rainy season) ($Ca^{+2} = 251$ µM, $Mg^{+2} = 50$ µM and $K^+ = 104$ µM), while the peak of Na^+ (590 µM) was in January (rainy season). The concentrations of anions (Cl^- and SO_4^{-2}) showed the same pattern observed for cations (differences between land cover types, $p = 0.000$), with highest median values in urban streams ($Cl^- = 26.5$ (17.8) µM; $SO_4^{-2} = 2.4$ (2.1) µM) followed by rural ($Cl^- = 9.3$ (4.6) µM; $SO_4^{-2} = 1.4$ (0.6) µM) and natural ($Cl^- = 4.0$ (2.5) µM; $SO_4^{-2} = 1.0$ (0.6) µM) areas, respectively (Fig. 8).

The overall cation–anion charge balance also changed from natural to rural to urban streams. In natural streams there was an anion deficit while rural streams were nearly balanced and urban streams had a slight cation deficit (Table 3). There was a reduction in the relative share of H^+ ions from natural streams (16.8%) through the rural streams (6.5%) to urban streams where there was virtually no contribution of H^+ ions to charge balance (Fig. 9, Table 4). On the other hand, the relative share of Ca^{+2} increased from natural streams (7.8%) to rural (9.8%) and urban (16.5%). Among the anions, HCO_3^- was predominant in all the streams studied, with the relative contribution increasing from natural to urban (Fig. 9). In general, it appears that the natural systems are being changed from dilute, low pH, $NaHCO_3$ dominated solutions to streams with higher solute load and pH that are dominated by $CaCO_3$.

Of the five collections during storm events only the one performed in the Barreiro do Mato stream

Table 3 Median average cationic and anionic charge contributions for streams ($n = 3$) under different land cover (natural, rural and urban) between September-2004 and December-2006 in the Federal District, Brazil

Solute	Natural area	Rural area	Urban area
H^+	14.00	9.00	0.00
NH_4^+	4.28	5.00	8.57
K^+	3.32	8.18	14.10
Ca^{+2}	6.49	13.50	57.50
Mg^{+2}	6.58	9.05	23.87
Na^+	14.35	22.61	59.13
HCO_3^-	24.48	46.27	130.39
NO_2^-	1.43	0.43	2.86
NO_3^-	1.43	0.65	13.56
Cl^-	4.80	10.16	29.14
SO_4^{-2}	2.08	12.50	8.96
PO_4^{-3}	0.21	0.21	0.21
Σcations	49.03	67.35	163.17
Σanions	34.42	70.21	185.12
Balance	18	−2	−6

Ion balance (%) = (Σcations − Σanions)/(Σcations + Σanions) × 100

Values above 5% are considered unbalanced

Table 4 Cations and anions share (as percentage) for streams located in areas under natural, rural and urban land coverage in Federal District, Brazil (2004–2006)

Solute	Natural cover	Rural cover	Urban cover
H^+	16.78 (a)	6.54 (b)	0.00 (c)
NH_4^+	5.13 (a)	3.63 (a)	2.46 (b)
K^+	3.98 (a)	5.95 (b)	4.05 (a)
Ca^{+2}	7.78 (a)	9.81 (a)	16.51 (b)
Mg^{+2}	7.88 (a)	6.58 (a)	6.85 (a)
Na^+	17.20 (a)	16.44 (a)	16.98 (a)
HCO_3^-	29.33 (a)	33.64 (b)	37.44 (c)
NO_2^-	1.71 (a)	0.31 (a)	0.82 (a)
NO_3^-	1.71 (a)	0.47 (a)	3.89 (b)
Cl^-	5.75 (a)	7.39 (ab)	8.37 (b)
SO_4^{-2}	2.49 (a)	9.09 (b)	2.57 (a)
PO_4^{-3}	0.25 (a)	0.15 (a)	0.06 (a)

The values were calculated using the median among the three streams to each cover land type. *Different letters* indicate differences between the areas; $N = 3$, $\alpha = 0.05$

showed samples with a slight increase in the solute concentrations. During these collections the maximum precipitation found was 5.7 mm. This amount of rainfall corresponds to approximately 45% of the cumulative frequency of daily precipitation that occur in the Federal District. The range of events with higher precipitations (30–160 mm) represents only 10% of the cumulative daily frequency. During sampling under storm flow events stream water level ranged from 67 to 92 cm for Barreiro do Mato stream while for Taquara and Pitoco streams the variations were 65–95 and 35–38 cm, respectively.

The stream level measurements under base flow conditions in the Pitoco and Taquara streams during the rainy season ranged from approximately 40 to 65 cm, respectively, while during the dry period stage height declined to 15 and 45 cm, respectively (Figs. 2 and 3). For Barreiro do Mato stream the values

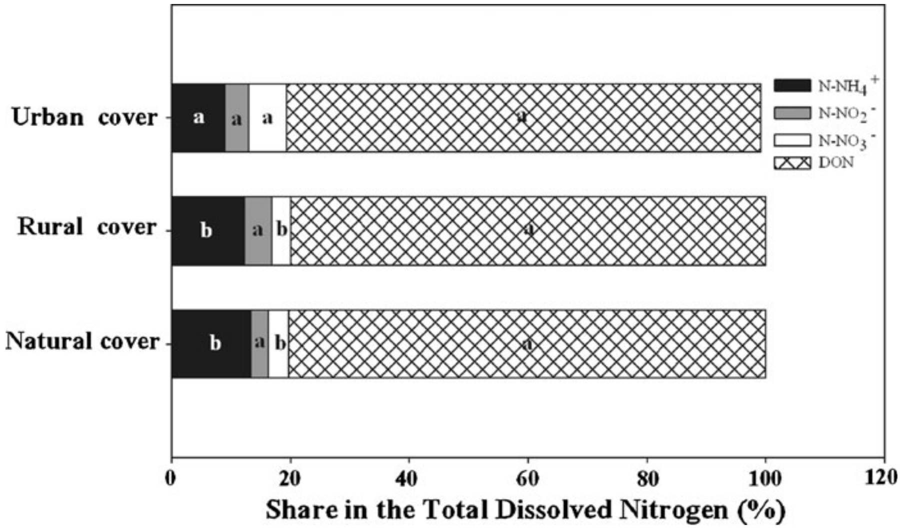

Fig. 9 Average cationic and anionic charge contributions for streams ($n = 3$) under different land cover (natural, rural and urban) between September-2004 and December-2006 in the Federal District, Brazil

ranged from 22 cm in the dry season to 70 cm in the wet season (Fig. 4). All these streams were also quite responsive to individual storm events as indicated by the periodic spikes in stage height (Fig. 2, 3, and 4).

Discussion

Low ion concentrations previously observed in Cerrado region streams under natural cover are a result of the highly weathered soils and their associated low nutrient concentrations (Markewitz et al. 2006). Given these low background concentrations, it was hypothesized that increases in dissolved solute loads under anthropogenic land covers would be readily observed. It was further hypothesized that the increases in the solute concentrations in streams draining urban areas would be greater than in rural locations due to greater point source inputs of effluents. Both these hypotheses were supported by the data with a few exceptions: PO_4^{-3}, concentration did not differ among land uses and dissolved oxygen declined in rural areas but increased in urban areas.

The increase in solute concentrations in streams of the areas under urban and rural cover in relation to natural results were related to changes in land cover as soils were dystrophic and had similar texture (clay). Increases in solute concentrations with land use change have been observed previously for the conversion of forest to pasture in the Amazon (Forti et al. 2000; Neill et al. 2006; Figueiredo et al. 2010). In the present study, increases in electrical conductivity and major ion concentrations in stream water samples demonstrates that conversion of natural vegetation impacts Cerrado streams as well. Despite these significant increases in concentrations in Cerrado streams, the comparison with streams draining similar soils in the Amazon, indicates values 3–40 times lower in the Cerrado, especially for K^+, Ca^{+2}, and Mg^{+2} (Forti et al. 2000; Neill et al. 2006; Markewitz et al. 2004). The nutrient cycling in the terra-firme Amazonian forests is less conservative than in Cerrado ecosystems (Bustamante et al. 2004), and the higher concentrations may be due to the higher nutrient fluxes and stocks in the Amazon forest than in the Cerrado.

The absence of an increase in stream PO_4^{-3} is surprising, particularly in rural areas where fertilization with P (inputs up to 150 kg P_2O_5 ha/year) is regularly practiced (Miranda et al. 2000; Sousa et al. 2002). On the other hand, Cerrado soils are rich in Fe and Al-oxides and typically have high P adsorption capacities (Fox and Kamprath 1970). This can be one reason for the small amount of P reaching the rural and urban streams. Another reason that can explain the absence of increased concentrations of P in streams with land cover change is the instream processing, either through deposition with sesquioxides or particulate organic matter or uptake by plants and algae. In Rondonia (Brazil), the comparison between small pasture streams and small forests streams, indicated greater uptake velocities and rates for PO_4^{-3} (Neill et al. 2006).

The dissolved oxygen (DO) pattern was also somewhat anomalous with the highest dissolved oxygen concentrations observed in urban streams. These higher DO concentrations may be due to factors such as: (a) higher cross section of these streams, with consequent increased surface of interaction with the atmosphere, and (b) higher algae activity due to higher light incidence (result of the absence of gallery forests in the urban land covers) that provide additional DO generation. The high solute and DOC concentrations found in urban streams apparently were not sufficient to create eutrophic environments and to decrease DO levels (Daniel et al. 2002). The DO levels observed in streams under natural areas are typical of streams that show rapid flows, turbulent mixing, and relatively low heterotrophic activity (Thomas et al. 2004). Rural areas, on the other hand, showed the lowest median concentrations of DO 6.5 (Interquartile Range: 1.8) mg/L that might be caused by an increase in ion loads resulting from the passage of stream water for portions of riparian cover and thus stream shading. Additionally, two of the rural streams had no well-defined channels, which also could contribute to a reduction in stream velocity, thus reducing turbulent flow and re-oxygenation.

Dissolved organic carbon (DOC) concentrations were also found to be greatest in urban streams, probably due to the entry of untreated domestic sewage in these areas where there is still limited sanitation infrastructure. Ometto et al. (2000) and Daniel et al. (2002) studied the Piracicaba river basin in the São Paulo state and also found higher DOC concentrations with higher urbanization, although in the Piracicaba basin DOC values were between 2 and

30 times higher than those found in this study. Although the increased DOC levels were still insufficient to cause further biological oxygen demand (BOD) in the urban streams, other effects on streams can occur. A previous study in the Mestre D'Armas stream (Distrito Federal) has observed a change in the structure of the benthic communities, with the dominance of filter feeding organisms and predators, and a reduction of collectors and scrapers, which are more sensitive to pollution (Fernandes 2007).

Despite the consistent land cover response, seasonal responses were inconsistent with a hypothesized dilution effect in the wet season due to higher flows. Across all the studied streams, consistent responses were observed for DOC (higher in wet season) and DO (lower in wet season). However, natural and rural streams had increased Ca^{+2}, Na^{+}, alkalinity, and NO_2^{-} in the wet season while urban areas presented increased H^{+}, SO_4^{-2} and turbidity at the same time (Table 2). The higher DO concentrations observed during the dry season may result from changes in physical conditions, like transparency and temperature. In fact, the lowest stream water temperatures are usually recorded in the dry season (16.9–19.8°C in dry season against 18.9–22.2°C during wet season in the present study, while that the lowest air temperatures in the Cerrado biome are recorded also in the dry season) likely due to a predominance of groundwater contributions during this season. The increased concentration of many other elements in the wet season, including DOC, however, might better reflect leaching of surface organic matter and runoff. Increased soil compaction and the associated decreases in rainwater infiltration are commonly reported with conversion to pasture or agricultural lands uses and may be playing a role here as well (Germer et al. 2010; Moraes et al. 2006). Biggs et al. (2006) found that deforestation and pasture establishment increased solute and nutrient export to streams largely due to increasing Hortonian overland flow. Furthermore, the loss of riparian forests in rural and urban areas might also contribute to increased surface inputs during the wet season (Pedron et al. 2004; Spera et al. 2006).

Associated with changes in land cover, effluent inputs, and potential for increased surface runoff, it was hypothesized that forms of N would shift from predominantly organic to inorganic forms, which was observed. The highest total dissolved nitrogen (TDN) median concentrations were observed in urban streams 33.0 (24.1) µM being as much as 85% higher than another streams, which likely results from sewage discharge present in these areas. In the Piracicaba river basin (São Paulo State) a similar pattern was also found, with higher concentrations of TDN in streams draining urban areas as a result of sewage inputs (Krusche et al. 2003). In the Mestre D'Armas and Atoleiro watershed residences near the streams (40 m approximately) were observed to be releasing sewage directly into the streams through pipes, as well as through surface discharge.

The streams under rural and urban cover had higher concentrations of DIN forms (NH_4^{+}, NO_2^{-} and NO_3^{-}) in relation to natural areas. Silva (2008) analyzed the flow components (bulk precipitation, runoff, soil solution (−50 cm depth) and groundwater) in the riparian zones of the Pitoco, Taquara, Estanislau and Barreiro do Mato streams, and observed that the flow components from rural areas showed an increase in NH_4^{+}, NO_2^{-} and NO_3^{-} concentrations, in relation to natural areas. These increases occurred mainly for the groundwater component, especially for NH_4^{+} and NO_3^{-}. Nitrate, which is particularly mobile in case of disturbance, is leached by rainwater infiltration (Vitousek et al. 1979 and Vitousek 1980) while NH_4^{+} entering the aerobic hyporheic zone is commonly oxidized to NO_3^{-} by nitrification (Williams et al. 1997). So, the decrease of N-NH_4^{+} proportion of DIN, associated with an increase in N-NO_3^{-} proportion on urban streams suggests a predominance of microbial processes, but this is a mechanism that acts in line with the absorption by vegetation.

The urban areas presented the largest proportion of NO_3^{-} ($p = 0.000$) in relation to other DIN forms (Fig. 7), and these proportions may be a result of nitrification processes that are favored by higher dissolved oxygen concentrations observed in these streams, as well as NH_4^{+} adsorption in the stream bed (Jordan et al. 1997), that generate higher proportions of NO_3^{-} in these areas. Mulholland et al. (2008) observed that urban streams presented higher denitrification rates caused probably by high NO_3^{-} concentration. Kemp and Dodds (2002) observed that the rates of nitrification were more positively influenced by the combined addition of NH_4^{+} and dissolved oxygen than by the single addition of these factors. The higher dissolved oxygen concentrations in urban streams in the present study may also be shifting the balance within the fractions of DIN to NO_3^- generation. In the streams under natural and rural cover the DIN forms were dominated by NH_4^+. Some studies suggest that stream water NO_3^- concentrations can be reduced through the removal via biotic uptake within the water column (McClain et al. 1994), via denitrification occurring along exchange flowpaths re-entering the hyporheic zone (Grimm and Fisher 1984; Triska et al. 1989; Duff and Triska 1990) or through absorption by the vegetation (Forti et al. 2000; Forti et al. 1995).

Effects of seasonality on concentrations of N were most evident in rural streams, with higher concentrations for total dissolved nitrogen, NH_4^+ and NO_2^- in the wet season. These results can be explained by higher amounts of runoff and soil solution that reach the stream during this period (Silva 2008), as well as higher decomposition rates, bulk deposition and throughfall in this period due to a larger amount of water circulating in the system (Xuluc-Tolosa et al. 2003; Forti et al. 2000). On the other hand, a study on the decomposition of leaf litter in the riparian zone of the Pitoco stream indicated that release rate of nitrogen from litter was lower than those of other nutrients (Parron 2004). In the natural streams, NO_2^- concentration also increased in the wet season. The higher amounts of nitrite present in these well oxygenated streams are probably due to the fact that it is the intermediate compound of the nitrification process.

The results of collections performed under storm flow were unexpected as significant increases in the solute concentrations were not observed. This response could be related to the low intensity of the rain events. The volume of rainfall may have been insufficient to saturate the soil and thus drive the solutes to the stream.

Conclusions

The results indicate that changing land cover has an effect on the hydrochemistry of small streams in the Cerrado. Higher nutrient concentrations in streams draining through rural and urban cover was observed with the highest concentration in urban streams. The streams in all areas had seasonal differences and in most cases concentrations in the wet season were higher than those in the dry season despite increasing wet season discharge. Also, although higher nutrient concentrations were observed in rural and urban streams in relation to those in areas under natural cover, changes were less significant than those observed in urban streams of southeastern Brazil and in agricultural areas in the Amazon. Finally, the relative contribution of forms of inorganic nitrogen changed from natural to rural and urban streams. These changes may be particularly important because nitrogen is one of the most limiting nutrients in the Cerrado ecosystems, with possible effects on the composition and functioning of aquatic communities. Conservation and restoration of small streams should be a central focus of management strategies in the Cerrado to ensure N and nutrient processing in watersheds, especially through the conservation of riparian forests, which in turn will improve the quality of water delivered to downstream ecosystems. Moreover it is also important to collect and treat domestic wastewater to prevent the entry of large loads of solutes in streams.

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