

Dissolved rainfall inputs and streamwater outputs in an undisturbed watershed on highly weathered soils in the Brazilian cerrado

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Abstract:

The cerrados of Brazil cover 2 million km². Despite the extent of these seasonally dry ecosystems, little watershed research has been focused in this region, particularly relative to the watersheds of the Amazon Basin. The cerrado shares pedogenic characteristics with the Amazon Basin in draining portions of the Brazilian shield and in possessing Oxisols over much of the landscape. The objective of this research was to quantify the stream water geochemical relationships of an undisturbed 1200 ha cerrado watershed for comparison to river geochemistry in the Amazon. Furthermore, this undisturbed watershed was used to evaluate stream discharge versus dissolved ion concentration relationships. This research was conducted in the Córrego Roncador watershed of the Reserva Ecológica do Roncador (RECOR) of the Instituto Brasileiro Geografia e Estatística (IBGE) near Brasília, Brazil. Bulk precipitation and stream water chemistry were analysed between May 1998 and May 2000. The upland soils of this watershed are nutrient poor possessing total stocks of exchangeable elements in the upper 1 m of 81 ± 13 , 77 ± 4 , 25 ± 3 , and 1 ± 1 kg ha⁻¹ of K, Ca, Mg, and P, respectively. Bulk precipitation inputs of dissolved nutrients for this watershed are low and consistent with previous estimates. The nutrient-poor soils of this watershed, however, increase the relative importance of precipitation for nutrient replenishment to vegetation during episodes of ecosystem disturbance. Stream water dissolved loads were extremely dilute with conductivities ranging from 4 to 10 $\mu\text{S cm}^{-1}$ during periods of high- and low-flow, respectively. Despite the low concentrations in this stream, geochemical relationships were similar to other Amazonian streams draining shield geologies. Discharge-concentration relationships for Ca and Mg in these highly weathered soils developed from igneous rocks of the Brazilian shield demonstrated a significant negative relationship indicating a continued predominance of groundwater baseflow contributions these cationic elements. Copyright © 2006 John Wiley & Sons, Ltd.

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INTRODUCTION

The cerrados of Brazil are the second major vegetation formation in the country, after the Amazon forest, occupying 2 million km² or 22% of the national territory (Klink *et al.*, 1995). The nucleus of cerrado vegetation is in central Brazil between 5 and 20° south latitude largely around the capital city of Brasília (Figure 1). Despite the prevalence of this vegetation type, little research on hydrologic or nutrient cycling processes in the cerrado region has been reported in the literature (Haridasan, 2001; Oliveira and Marquis, 2002). The recent effort of the Large-Scale Biosphere–Atmosphere Experiment in Amazonia (LBA project) in Brazil has provided impetus for further expanding research in this region (Pinto *et al.*, 2002; Ferreira *et al.*, 2003).

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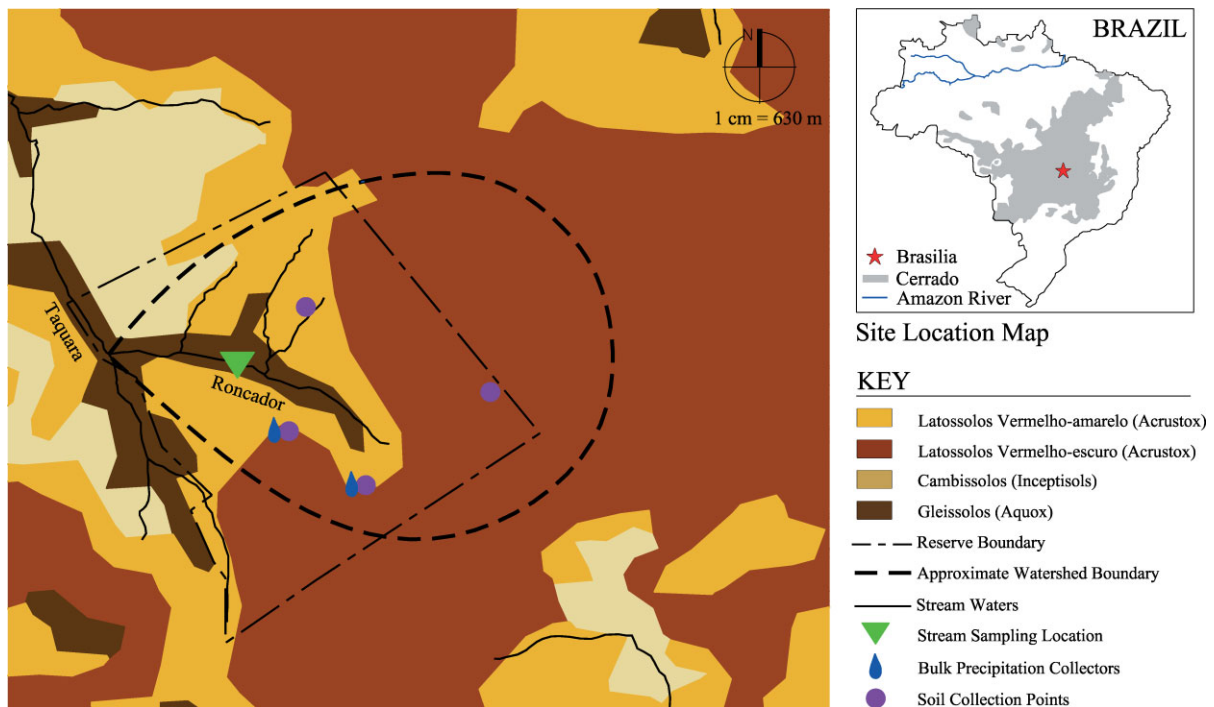


Figure 1. Soil map for the area of the IBGE Ecological Reserve, Brasilia, Brazil. Watershed boundary for the Córrego Roncador is estimated based on drainage patterns and soil types. The northeastern portion of the watershed extending outside the IBGE reserve is within the neighbouring reserve of the Botanical Gardens. Latossolos amarelo-vermelho are red–yellow Oxisols and latossolos vermelho-escuro are dark-red Oxisols

The fire-dominated ecosystems of the cerrados of Brazil share a similarity with the Amazon region in having a preponderance of highly weathered soils. In fact, while the Amazon is reported to have 40% of the basin covered with Oxisols, equivalent to latossolos in the Brazilian soil classification, (Richter and Babbar, 1991) up to 56% of the soil in the cerrado region of central Brazil are Oxisols (Haridasan, 2001). Furthermore, of soils classified as Oxisols in the cerrado, 73% are in the great group Acrustox (i.e. latossolos ácricos), indicating sub-surface soils extremely low in effective cation exchange capacity (ECEC) (i.e. <math><1.5\text{ cmol (+)}/\text{kg clay}</math>). This highly weathered condition of many cerrado Oxisols, even relative to Amazonian Oxisols, results from the region's Precambrian geology (Motta *et al.*, 2002; Marques *et al.*, 2004). Streams in this region drain the metamorphic and igneous rocks of the Brazilian shield. The Brazilian shield was a nearly level plain at the end of the Cretaceous with only a few crests of resistant rocks that in the early and late tertiary, due to tectonic uplift and sea regression, was eroded into today's undulating topography (Motta *et al.*, 2002; Marques *et al.*, 2004).

Presently, there is limited stream water chemical data from the cerrado region and thus examination of a cerrado watershed will provide valuable geochemical insights. The pioneering work of Stallard (1985) and Stallard and Edmond (1983, 1987) reported on the geochemistry of a few large Amazonian rivers draining portions of the Brazilian shield but included no rivers or streams comprised entirely of cerrado vegetation. Similarly, the works of Gibbs (1967), Furch (1984), or Richey and others from the CAMREX project (Mortatti and Probst, 2003; Richey *et al.*, 1990) has reported on the geochemistry of Amazonian rivers from various geologic substrates but none specific to the cerrado. Research from southern Brazil, around the cities of Rio de Janeiro or São Paulo, investigate geologies south of the Brazilian shield and these watersheds are typically impacted by urbanization (Figueiredo and Ovalle, 1998; Krusche *et al.*, 2002). Comparisons of

small Amazonian streams, particularly the Paragominas site in the eastern Amazon that drains soils formed on deep sedimentary deposits and the Nova Vida site in the western Amazon that drains soils formed on the Brazilian shield have demonstrated the importance of regional differences on stream water chemistry and nutrient cycling (Davidson *et al.*, 2004).

Examination of stream water chemistry in a cerrado watershed comprised largely of extremely weathered Acrustox soils could also test the recent hypothesis proposed by Markewitz *et al.* (2001) regarding discharge-concentration relationships of streams on nutrient-poor substrate. Working in a watershed in the eastern Amazon Basin where the highly weathered Haplustox soils were formed on deep sedimentary deposits, Markewitz *et al.* (2001) observed increasing concentrations of cations (i.e. Ca, Mg, and K) with increasing stream discharge. This pattern is counter to that normally observed in watersheds where weathering of cation rich bedrock elevates stream cation concentrations during periods of groundwater-fed baseflow. These authors hypothesized that in extremely weathered soils cationic stream fluxes were no longer controlled by bedrock weathering but rather by contributions to streams from surface soil exchange processes.

The objectives of this work are to: (1) compare the geochemistry of an undisturbed ~1200 ha watershed in the cerrado with previous geochemical assessments for Amazonian rivers and (2) evaluate stream discharge versus dissolved element concentration relationships in this watershed on extremely weathered soils.

STUDY AREA

This work was undertaken in the Reserva Ecológica do Roncador (RECOR) of the Instituto Brasileiro Geografia e Estatística (IBGE) a permanent conservation unit for the cerrado biome. The reserve is situated 35 km south of the centre of Brasília in the Federal District at km 0 of highway BR-251 (15°56'41"S and 47°53'07"W). The RECOR is part of the area for environmental protection (Área de Proteção Ambiental) that comprises a contiguous area of 10 000 ha (RECOR, 2005).

The reserve is located on the Brasília Chapada with a mean altitude of 1100 m and encompasses 1350 ha. The reserve contains a climatological station, which has been operating since 1979 (RECOR, 2005). Annual average rainfall is 1470 mm and is highly seasonal (Figure 2). There are five headwater streams in the reserve that form a sub-basin of the Taquara drainage. The reserve possesses typical vegetation of the central Brazilian plains including cerradão, cerrado (*sensu stricto*), campos, brejos e veredas, and gallery forests (Oliveira-Filho and Ratter, 2002). These phytophysionomic communities form a topographic gradient that has cerrado vegetation dominating on plateaus and gallery forests dominating along stream corridors in valley bottoms (Ribeiro and Walter, 1998).

Cerrados (757 ha) and campos (467 ha) account for most vegetation in IBGE. Cerrados are open savannas (~10 m² ha⁻¹ of tree basal area) that may possess 12–37 Mg ha⁻¹ of standing tree biomass and 25–50 Mg ha⁻¹ of total aboveground biomass (Haridasan, 2001; Resende, 2001). Belowground biomass is important in these ecosystems and may add an additional 25–50 Mg ha⁻¹. Annual litter production may range from 2.1 to 3.2 Mg ha⁻¹ (Haridasan, 2001). Campos include a gradient of intermediate physiognomies with a decreasing density of woody species progressing from campo cerrado to campo sujo to campo limpo with this final phase being relatively 'clean' grassland. Along stream corridors gallery forest predominant. Gallery forests are tall (~30 m), closed canopied (75–95% cover), and productive (6–7 Mg ha⁻¹ year⁻¹ of litterfall) but generally comprise <5% of the landscape (Parron, 2004).

METHODS

Soils

Soil descriptions used in this study come partly from the earlier works of Resende (2001) and Parron (2004). In Resende (2001), soil samples were collected in an upland portion of the watershed under cerrado

vegetation that had been protected from fire for 26 years (Figure 1). These soils were sampled in May 1998 with a 10-cm diameter bucket auger in three holes spaced 500 m apart. Soil layers were sampled as 0–10, 10–20, 20–50, 50–100, 100–200, 200–300, 300–400, and 400–500 cm. In the work of Parron (2004), soils were sampled in gallery forest along a first order stream in the watershed (Figure 1). Soils were sampled with a bucket auger in May 2001 at three random locations along a transect of 200 m that was established parallel to the stream at a distance of 10 m. Soil sampling layers were 0–5, 5–10, 10–20, 20–30, 30–40, 40–50, 50–60, 60–70, 70–80, 80–90, and 90–100 cm.

Two additional locations were sampled, one in campo sujo vegetation and one in periodically burned cerrado vegetation (Figure 1). The campo sujo sampling in May 1998 was approximately 1 km distant from the sampling beneath the unburned cerrado vegetation and was similarly collected from three holes spaced 500 m apart from 0 to 10, 10 to 20, and 20 to 50-cm layers. Sampling beneath the burned cerrado vegetation in August 1998 occurred within a 10 ha plot (500 × 200 m) of the Projeto Fogo (Miranda *et al.*, 1996b). This plot of cerrado vegetation was protected from fire until 1992 but since has been burned every fourth year (1992, 1996, 2000, and 2004) in August (i.e. middle of dry season). Soils were sampled with a bucket auger in three holes spaced at 150, 250, and 350 m along the length of the plot and located at the plot centre (i.e. 100 m from the plot edge). Sampling layers were 0–10, 10–20, 20–50, and 50–100 cm.

Analyses of the upland soils included the pH of soil in water in 1 : 2 mass to volume ratio (Thomas, 1996); soil total C and total N after pulverization with a dry combustion technique using a CE Elantech NA2100 (Lakewood, NJ); extractable P on an Alpkem auto-analyzer (OI Analytical, College Station, TX) using the Murphy-Riley chemistry after exchange with Mehlich I double-acid (H₂SO₄–HCl) in a 1 : 5 m/v ratio (Kuo, 1996); K, Ca, and Mg by atomic absorption in the presence of >10 000 mg/l LaCl₃ using the same extract as for P above (Sumner and Miller, 1996); exchangeable acidity by titration to pH 8.2 using 0.02 M NaOH after extraction with 1 M KCl in a 1 : 10 m/v ratio (Thomas, 1996). In the gallery forest, analysis included water pH, total C and N with a similar CE Elantech Analyzer at the University of São Paulo, Mehlich I extraction followed by analysis on an inductively coupled plasma (ICP) spectrophotometer for P, Ca, Mg, K, and exchangeable Al. Exchangeable Al was treated as being equivalent to exchangeable acidity. For all soils ECEC was estimated from the sum of cations and exchangeable acidity (Sumner and Miller, 1996).

Bulk precipitation

Bulk precipitation was collected from May 1998 through April 2000 in high density polypropylene bottles using 16-cm funnels placed 1.5 m off the ground at two locations in the reserve (Resende, 2001). A third location was established but abandoned after repeated insect infestations. All bulk precipitation funnels were located such that they formed a 45° angle to the nearest trees and fed through looped tubing to restrict evaporation following the methods of Likens and Bormann (1995). Collection bottles were painted and shielded from direct sunlight to limit the growth of algae and in May 1999 glass fibre filters were placed in the base of the funnels in an effort to limit particulate input into the bottles. The maximum time of storage in the field was 14 days. No preservatives were used in the collection vessels.

During collection, total sample volume was measured and a sub-sample transferred to a previously acid-washed (1 M HCl) polypropylene bottle. All funnels, troughs, and bottles were rinsed with deionized water after collection. If algae or insect contamination was apparent, collectors were returned to the laboratory for acid washing. Samples were returned to the University of Brasilia and within 48 h were measured for conductivity, pH, and alkalinity and then filtered through 0.4 µm polycarbonate filters (Nuclepore, Cambridge, MA). Alkalinity determinations were by endpoint titrations with 1 mM HCl to pH 5 (Clesceri *et al.*, 1998).

Bulk precipitation was collected between April 1998 and June 2000 ($n = 78$ samples). Sixty-six of these samples were used for chemical determination of nutrients largely owing to limited sample volume being collected in dry months for some samples. Volume-weighted mean (VWM) annual element concentrations and inputs were estimated for each collector and estimates of precipitation inputs were made for May 1998 to April 1999 and May 1999 to April 2000.

Stream water

Stream water samples were collected from Córrego Roncador, a second order stream in the IBGE reserve (Figure 1). Stream water grab samples were collected in previously acid-washed 250-ml polypropylene bottles between May 1998 and May 2000. Over the course of study, collections were made on ~50% of all days from May 1998 to 1999 (i.e. $n = 168$) while samples were collected weekly from May 1999 to May 2000 (i.e. $n = 56$). Bottles were filled to capacity to minimize headspace and were placed in cold storage ($\sim 4^\circ\text{C}$) within a few hours of collection. Stream gage height was measured on all days of collection and stream discharge was estimated from a gage height versus discharge relationship established for the stream in 1999 following the methods of Rantz (1982). Only ten height measurements during the period (4.5%) exceeded the rating curve. Stream discharge on un-sampled days was estimated using linear extrapolations between sampling dates and instantaneous flows were assumed constant over the day. To estimate elemental fluxes annual discharge was multiplied by VWM annual concentrations.

Samples were returned to the University of Brasilia for analysis of conductivity, pH, and alkalinity, and were then filtered through $0.4\ \mu\text{m}$ polycarbonate filters and stored at 4°C . Alkalinity determinations were estimated by endpoint titrations with 1 mM HCl to pH 5. If possible, samples were analysed the same day of collection, but many were retained cold for up to 1 week until analysis.

Both rainwater and stream water samples were analysed for dissolved organic carbon (DOC) (Shimadzu TOC 5000, Columbia, MD), total N and total P following persulphate digestion (Koroleff, 1983), PO_4 by the Murphy-Riley method (Clesceri *et al.*, 1998), NH_4 by the Berthelot method (Clesceri *et al.*, 1998), Cl, SO_4 , and NO_3 by ion chromatography (Dionex DX 500, Sunnyvale, CA), Ca, Mg, K, Na, Al, Si, and Fe by inductively coupled plasma spectrometer (ICP-MS, ELAN 6000, Perkin-Elmer, Shelton, CT). Standard solutions (Environmental Research Associates, Arvada, CO) were used with all analyses for quality assurance/quality control.

RESULTS

Soil

The upper portion of the Roncador watershed contained a preponderance of dark-red Oxisols (latossolos vermelho-escuro) and yellow-red Oxisols (latossolos vermelho-amarelo) (Figure 1). The colour-based distinctions in the Brazilian soil classification system (e.g. dark-red vs red-yellow) are not strictly equivalent to the chemically based distinctions in Soil Taxonomy (Soil Survey Staff, 1997). Both Oxisols, however, are clearly in the sub-order Ustox owing to the long dry season that cause 90 days or more of soil dryness and to the chemical characteristics in the 5-m profile from the unburned portion of the upper watershed. The red-dark Oxisols are consistent with the low charge definition of the great group Acrustox. These soils possessed extremely low charge capacity having a maximum ECEC of $1.2\ \text{cmolc kg}^{-1}$ clay (i.e. sum of cations calculated on a clay basis in centimoles of charge per kilogram of clay) in the upper 0–10 cm declining to $<0.1\ \text{cmolc kg}^{-1}$ clay by 2 m (Table I). Despite the extremely low charge of these soils, soil C concentrations were not extremely low, exceeding 2.5% in the upper 20 cm. Furthermore, the difference between pHw (i.e. pH measured in deionized water) and pHs (i.e. pH measured in 0.01 M CaCl_2), defined as the ΔpH (data not shown), indicated that there was an excess of negative charge relative to positive charge throughout the soil profile.

Variation in the upper 1 m of soil under the unburned and burned cerrado and Campo Sujo was low for pHw, C, N, exchangeable K and acidity with a coefficient of variation (CV) $<20\%$ in 0–10, 10–20, 20–50, and 50–100-cm layers (Table II). Variation across these upper landscape positions was slightly greater for exchangeable P, Ca, and Mg with coefficients of variation ranging from 19 to 137% (Table II). Much of this variation resulted from higher concentrations in soils beneath the burnt cerrado vegetation.

In the riparian zones of the watershed, soils are classified as either cambissolos or gleissolos. Cambissolos are generally equivalent to inceptisols in Soil Taxonomy but there is no direct correlation for gleissolos. In the

Table I. Chemical characteristics for soil in an upper landscape position of the Córrego Roncador watershed under dense cerrado vegetation that has not burned for 26 years

Depth (cm)	pHw ^a	C (%)	N (%)	P _{ext} ^b ($\mu\text{g g}^{-1}$)	Exchangeable			ECEC ^c
					K	Ca	Mg	
(cmolc kg ⁻¹)								
0–10	4.33 (0.09)	3.18 (0.06)	0.17 (0.01)	0.2 (0.1)	0.090 (0.013)	0.072 (0.004)	0.075 (0.007)	1.281 (0.143)
10–20	4.61 (0.02)	2.45 (0.18)	0.11 (0.01)	0.2 (0.1)	0.059 (0.009)	0.062 (0.006)	0.055 (0.005)	0.821 (0.128)
20–50	5.01 (0.05)	1.69 (0.07)	0.07 (0.01)	0.1 (0.1)	0.029 (0.01)	0.051 (0.007)	0.029 (0.009)	0.355 (0.052)
50–100	5.23 (0.09)	1.11 (0.06)	0.04 (0.00)	0.2 (0.2)	0.013 (0.001)	0.052 (0.003)	0.016 (0.002)	0.130 (0.002)
100–200	5.44 (0.07)	0.84 (0.06)	0.03 (0.00)	0.1 (0.0)	0.009 (0.004)	0.055 (0.005)	0.013 (0.004)	0.089 (0.005)
200–300	5.60 (0.05)	0.69 (0.01)	0.02 (0.00)	0.1 (0.0)	0.007 (0.001)	0.054 (0.001)	0.010 (0.002)	0.071 (0.003)
300–400	5.74 (0.08)	0.52 (0.03)	0.01 (0.00)	0.1 (0.0)	0.006 (0.001)	0.044 (0.006)	0.008 (0.001)	0.063 (0.008)
400–500	5.91 (0.11)	0.39 (0.03)	0.01 (0.00)	0.3 (0.4)	0.009 (0.004)	0.053 (0.010)	0.011 (0.003)	0.073 (0.018)

Soils were collected in three pits in 1998 in the IBGE Ecological Reserve, Brasilia, Brazil. Values are mean with 1 SD in parentheses.

^a pHw is soil pH in water in 1:2 mass to volume ratio.

^b Extractable P and exchangeable cations are derived from the Mehlich I extract in 1:5 mass to volume ratio.

^c ECEC is effective cation exchange capacity by the sum of cations method.

Table II. Coefficient of variation (CV) for soil chemical characteristics of Oxisols sampled in three upper landscape positions of the Córrego Roncador watershed

Depth	pHw ^a	C	N	Mehlich I extractable				ECEC ^b
				P	K	Ca	Mg	
(%)								
0–10	5	19	17	84	14	45	64	22
10–20	4	11	11	48	15	27	21	17
20–50	3	9	3	46	6	49	19	34
50–100 ^c	3	9	7	137	4	72	27	54

Sampling occurred in May 1998 within cerrado vegetation that had not burned for 26 years and within the campo limpo grassland, and in August 1998 within cerrado vegetation that had received controlled burns in 1992 and 1996. Each vegetation type was sampled in three auger holes spaced 100 to 500 m apart. CVs are estimated from the average value among the three vegetation types.

^a pHw is soil pH in water in 1:2 mass to volume ratio.

^b ECEC is effective cation exchange capacity by the sum of cations method.

^c CVs at this depth include only soils under the unburned and burned cerrado vegetation.

Brazilian soil classification, gleissolos are defined by the presence of a gleyed horizon defined by low chroma colours (EMBRAPA, 1999). In Soil Taxonomy the classification of gleyed horizons would be associated with the Aquept, Aquult, or Aquox sub-orders and then would depend on the development of the B horizon and the textural contrast between A and B horizon with depth. Field observations indicate that riparian zone soils are most consistent with the Aquox sub-order.

Table III. Chemical characteristics for soil along a stream in the Córrego Roncador watershed under gallery forest vegetation

Depth (cm)	pHw ^a	C (%)	N (%)	P _{ext} ^b ($\mu\text{g g}^{-1}$)	Exchangeable			ECEC ^c
					K	Ca	Mg	
(cmolc kg ⁻¹)								
0–10	4.55 (0.27)	8.41 (1.69)	0.54 (0.09)	4.4 (0.9)	0.156 (0.036)	0.204 (0.033)	0.080 (0.032)	3.07 (0.96)
10–20	4.50 (0.10)	5.23 (1.07)	0.32 (0.04)	2.4 (1.5)	0.136 (0.044)	0.144 (0.024)	0.069 (0.013)	2.10 (0.73)
20–50	4.59 (0.11)	3.09 (0.84)	0.19 (0.03)	0.6 (0.4)	0.053 (0.023)	0.117 (0.010)	0.051 (0.017)	1.39 (0.44)
50–100	4.62 (0.08)	1.95 (0.27)	0.12 (0.02)	0.2 (0.1)	0.040 (0.010)	0.102 (0.008)	0.034 (0.008)	0.39 (0.11)

Soils were collected in the IBGE Ecological Reserve, Brasilia, Brazil in May 2001 from 0–5, 5–10, 10–20, 20–30, 30–40, 40–50, 50–60, 60–70, 70–80, 80–90, and 90–100-cm layers and are reported as mass-weighted averages.

^a pHw is soil pH in water 1:2 mass to volume ratio.

^b Extractable P and exchangeable cations are derived from the Mehlich I extract in 1:5 mass to volume ratio.

^c ECEC is effective cation exchange capacity by the sum of cations method.

The riparian soils (Table III) along the first order stream demonstrated that these soils were still charge poor (i.e. ECEC <3.0 cmolc kg⁻¹) but they exceed the charge capacity of the upland soils. In these lower portions of the landscape, soils are likely affected by translocated inputs from upper portions of the watershed as well as deposition inputs from flood events, although sediments being input would already be in a weathered condition. The largest difference in the riparian zone soils relative to the upland soils was the high C and N concentration, >8% C and ~0.5% N, in the 0–10-cm soil layer. In addition, these soils differed in being seasonally saturated and had reduced conditions on a periodic basis. Low chroma colours (Munsell colour chart chromas <2) were regularly observed below 30 cm in soils along the stream corridor.

Bulk precipitation

Precipitation in the IBGE reserve was strongly seasonal with a dry season extending from May to September (Figure 2). From May 1998 through April 1999, rainfall inputs were 102 cm while those from May 1999 through April 2000 were 151 cm. Precipitation inputs were acidic with VWM pH over the 2 years of ~5.0

Table IV. Macro-element dissolved ionic concentrations for bulk precipitation and streamwaters in the IBGE Ecological Reserve Brasilia, Brazil

Type	Year	Cond ($\mu\text{S cm}^{-1}$)	pH	ALK	NO ₃ -N	NH ₄ -N	K	Ca	Mg	Na	Cl	SO ₄
Ppt	1998/1999	11.4 (5.2)	4.92 (0.1)	18.4 (6.3)	9.2 (2.0)	9.8 (9.8)	14.9 (6.7)	21.5 (1.6)	5.9 (2.7)	5.6 (1.3)	56.2 (35.4)	3.8 (1.2)
	1999/2000	6.1 (3.0)	5.20 (0.1)	13.3 (3.0)	7.6 (2.1)	11.7 (11.0)	3.4 (2.3)	10.8 (6.3)	2.7 (1.8)	4.6 (1.8)	10.7 (4.5)	4.1 (1.2)
Stream	1998/1999	6.1	5.54	37.3	0.8	0.4	2.0	29.4	10.0	9.2	8.9	0.4
	1999/2000	5.6	6.03	40.3	1.1	0.5	2.2	24.5	8.5	9.3	8.1	0.7

Precipitation values are volume-weighted means while streamwaters are discharge-weighted means. Standard deviations in parentheses ($\pm 1\text{SD}$) represent spatial variation for within year rainfall. Samples were collected from May 1998 to May 2000.

Cond, conductivity; ALK, alkalinity.

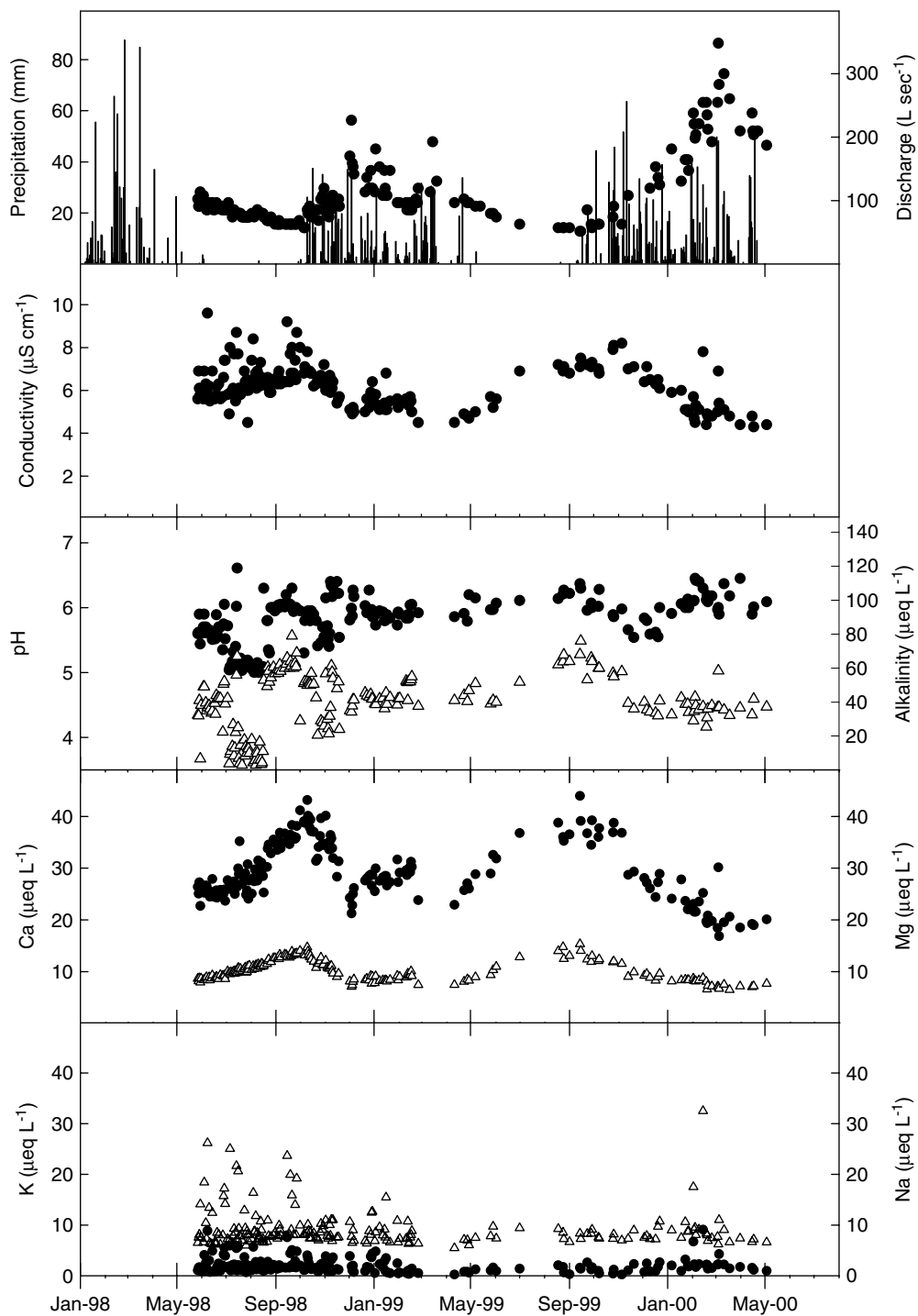


Figure 2. Precipitation inputs, stream water discharge, and stream water chemical concentrations for the Córrego Roncador in the IBGE Ecological Reserve, Brasília, Brazil. In the first panel, bars relate to precipitation inputs on the left-hand axis and discharge is on the right-hand axis. In all other panels, dark circles relate to the left-hand axis and clear triangles to the right-hand axis

(Table IV). The total dissolved loads of ionic elements in bulk precipitation inputs were uniformly low, having VWM annual conductivities of 11 and 6 $\mu\text{S cm}^{-1}$ in the 2 years. Conductivity was negatively correlated with precipitation volume ($r = -0.649$ for Pearson linear correlation coefficient on the log transformed values). This dilution effect was evidenced by both higher early season rain (i.e. September or October) conductivities and concentrations and by higher VWM annual concentrations of all macro-ionic elements other than $\text{NH}_4\text{-N}$ in the lower rainfall year of 1998/1999 compared with 1999/2000 (Table IV). Concentrations of total dissolved P followed a similar dilution pattern to the ionic components in 1999/2000 but were low in both years. Conversely, total DOC concentrations were greater in 1999/2000 (Table V). Total dissolved N (TDN) had a similar pattern to DOC. The geochemically important elements Al, Si, and Fe were all low in precipitation (i.e. $<1.1 \mu\text{M}$) with dissolved Si and Fe showing strong dilution effects in 1999/2000 while dissolved Al concentrations increased (Table V).

Despite the lower element concentrations in 1999/2000, total bulk precipitation inputs on a mass basis for many elements were similar or sometimes higher than 1998/1999 inputs because of the greater volume of precipitation (Table VI). Most of the macro-elements (N, K, Ca, Mg, Na, and SO_4) had average inputs for the 2 years in the range of 1–5 kg ha^{-1} . Inputs of Cl and DOC were somewhat higher. The coefficients of variation between the two years for DOC, N, Ca, Mg, Na, and S were $<40\%$ while those for P (103%) and K (70%) were higher. For P, the total dissolved inputs were low ($\sim 0.1 \text{ kg ha}^{-1}$) so the high variation did not meaningfully change the total annual input. Inputs of Al, Si, and Fe were uniformly low (i.e. $<0.2 \text{ kg ha}^{-1}$).

Stream water discharge and concentrations

Discharge for the Córrego Roncador ranged from a baseflow of approximately 55 l s^{-1} in both years to a high of 240 or 350 l s^{-1} in 1998/1999 and 1999/2000, respectively (Figure 2). The load of dissolved ionic elements in the stream water was consistently low, with conductivities of $<10 \mu\text{S cm}^{-1}$ throughout both years and minimum values of 4 $\mu\text{S cm}^{-1}$ during high flow portions of the year (Figure 2). All the other macro-element ionic components (Ca, Mg, K, Na, Cl, SO_4 , $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$, and alkalinity) also had seasonal variations in concentration, although the patterns for $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ were weak (Figures 2 and 3). Alkalinity, Ca, Mg, Na, and Cl all ranged approximately threefold in concentration over the year, similar to the range in conductivity. Sulphate and K had a greater relative difference between high and low values (Figures 2 and 3). DOC, TDN, TDP, Al, and Fe all had some periods of extremely low concentrations and thus ranged over orders of magnitude (Figure 3). For example, DOC ranged from a low of 10 μM to a few samples exceeding 4000 μM . Silicon was an exception in that although there was a seasonal concentration pattern, all values ranged between 60 and 120 μM (Figure 3).

The charge balance of these waters was dominated by Ca and HCO_3 with each contributing approximately 50% of cationic or anionic charge, respectively. Sodium and Cl played secondary roles contributing an additional 10–25% of cationic or anionic charge, respectively, with the importance of Na contributions increasing in the rainy season.

Table V. Dissolved organic C (DOC), total dissolved N, P, Al, Si, and Fe in bulk precipitation and streamwaters in the IBGE Ecological Reserve, Brasília, Brazil

Component	Year	DOC	TDN	TDP	Al	Si	Fe
Ppt	1998/1999	214 (3)	30.4 (16.2)	0.22 (0.26)	0.15 (0.01)	1.13 (0.42)	0.47 (0.04)
	1999/2000	266 (205)	29.5 (18.5)	0.02 (0.03)	0.56 (0.57)	0.14 (0.04)	0.07 (0.01)
Stream	1998/1999	676	9.8	0.01	0.76	90.5	0.35
	1999/2000	196	8.1	0.01	1.84	87.4	0.30

Precipitation values are volume-weighted means while streamwaters are discharge-weighted means. Standard deviations in parentheses (1SD) represent spatial variation for within year rainfall. Samples were collected from May 1998 to May 2000. All units are μM .

Table VI. Dissolved ionic fluxes for bulk precipitation and streamwaters in the IBGE Ecological Reserve, Brasilia, Brazil

Type	DOC ^a	TDN ^b	NO ₃ -N	NH ₄ -N	TDP ^b	K	Ca	Mg	Na	Cl	SO ₄	Si
Ppt 1999/2000	48	6.2	1.6	2.5	0.01	2.0	3.3	0.5	1.6	5.7	3.0	0.1
Stream 1998/2000 2-year avg	15 ± 1.0	0.4 ± 0.0	<0.1 ± 0.0	<0.1 ± 0.0	<0.1 ± 0.0	0.3 ± 0.1	1.6 ± 0.1	0.3 ± 0.0	0.6 ± 0.1	0.9 ± 0.1	0.1 ± 0.0	7.4 ± 1.0

Samples were collected from May 1998 to May 2000. Stream values (mean ± 1SD) are average annual fluxes ($n = 2$). All units are kg ha^{-1} .

^a DOC: Dissolved organic carbon.

^b TDN/TDP: Total dissolved nitrogen or phosphorus determined on a filtered and digested sample.

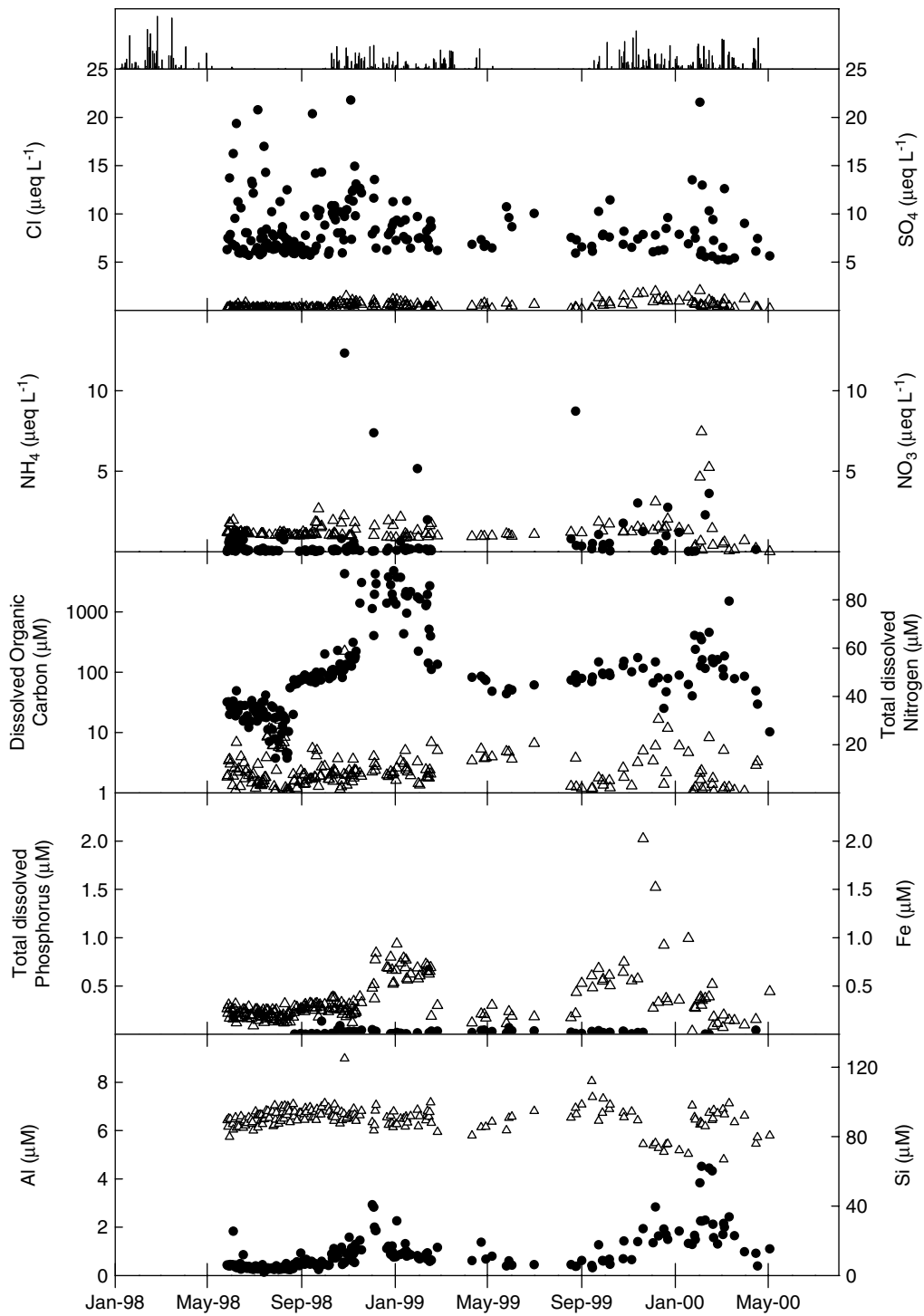


Figure 3. Relative precipitation inputs and stream water chemical concentrations for the Córrego Roncador in the IBGE Ecological Reserve, Brasília, Brazil. In the first panel, unscaled bars relate to relative precipitation inputs. In all other panels, dark circles relate to the left-hand axis and clear triangles to the right-hand axis

Although there was a pronounced seasonality in the stream water concentrations of almost all elements there were no strong correlations with stream discharge. There was a significant negative correlation between discharge and conductivity representing an overall decline in dissolved solids concentration with high flow (Figure 4). This relationship was largely driven by a strong negative relationship between stream discharge and Ca (Figure 4). The discharge-Mg relationship was similar to Ca. Silicon concentrations were also negatively related to stream discharge (Figure 4). Sulphate was the only anion that varied significantly with discharge; in fact it had a positive relationship to discharge as it did to total aluminium and DOC concentrations (Figure 4). All the other elements either had very weak (i.e. coefficient of determination <0.1) or non-significant relationships with discharge.

DISCUSSION

The soils in the upland portions of our cerrado watershed were clearly of low charge and nutrient poor. In comparison with other dystrophic Oxisols (latossolo distrifico) within the cerrado identified in the Brazilian soils database (Cooper *et al.*, 2005), the soils in the Roncador watershed possessed extremely low concentrations of Ca and Mg in the upper 1 m (Table VII). Conversely, the soil concentrations of C were slightly high (i.e. >75 th percentile), while N and K were within the interquartile range (Table VII). Utilizing the measured bulk densities of 0.66, 0.68, 0.68, and 0.74 g cm⁻³ for the 0–10, 10–20, 20–50, and 50–100-cm layer, respectively (Resende, 2001), the estimated total stock of exchangeable elements in the upper 1 m of these soils contained as little as 77 ± 4 , 25 ± 3 , 81 ± 13 , and 1 ± 1 kg ha⁻¹ of Ca, Mg, K, and P. These estimates of exchangeable nutrient contents for our cerrado profile were consistent with those made for soils in the same region by Lilienfein *et al.* (2003) but low compared with Marques *et al.* (2004).

The soils along the stream corridors (i.e. gleissolos), which covered $<10\%$ of the Roncador watershed, were generally enriched in C and had nutrient concentrations greater than upland soils. Relative to other gleissolos throughout Brazil identified in the Brazilian soils database, which were not formed on limestone, these profiles were high in C and N (>75 th percentile) through the upper 1 m but low in exchangeable Ca and Mg (<25 th percentile) (Table VII). Owing to high C contents, these soils had low bulk densities of 0.41 g cm⁻³ in the 0–10 cm layer and 0.45 g cm⁻³ in the 10–20 cm layer (Parron, 2004). Densities increased slightly to 0.55 and 0.70 g cm⁻³ for the 20–50 and 50–100-cm layers, respectively. On the basis of these bulk densities, the soils contained 139, 31, 145, and 5 kg ha⁻¹ of Ca, Mg, K, and P, respectively, in the upper 1 m; higher than upslope soils but still relatively nutrient poor.

The bulk precipitation inputs estimated for this site in the central cerrado were generally consistent with the few other available deposition input estimates for the region (Table VIII). There were no clear trends in the data of Table VIII relative to the deposition input estimates made using bulk versus wet-only deposition collectors. Bulk collectors are assumed to capture some portion of dry deposition and thus should have higher deposition estimates than wet-only deposition alone. Furthermore, the total atmospheric deposition load from wet and dry deposition is expected to exceed the load estimated from bulk collectors alone (Lindberg *et al.*, 1986). In the cerrado, Lilienfein and Wickle (2004) estimated dry deposition inputs nearly equal to bulk deposition inputs listed for their study in Table VIII.

Bulk deposition collectors that are left in the field for some number of days, such as was done in this project, may suffer from loss of elements through volatilization, or oxidation as well as transformation from one form of an element to another (Galloway, 1978; Titus and Mahendrappa, 1996). Transformation between organic and inorganic phases of N and P are of most concern. Controlled comparative studies that have manipulated the collection interval from event based up to 3 weeks have typically demonstrated macronutrient differences $<20\%$ (Galloway, 1978; Madsen, 1982; Pena *et al.*, 1985; Sisterson *et al.*, 1985). Minimizing evaporative losses and particulate inputs were demonstrated to be beneficial in maintaining chemical stability. In the current study, during the second year of rainfall collection, when filters were placed in the base of the funnels to limit particulate inputs, the annual charge balance (i.e. $\Sigma\text{cations}/\Sigma\text{anions}$) was superior to year

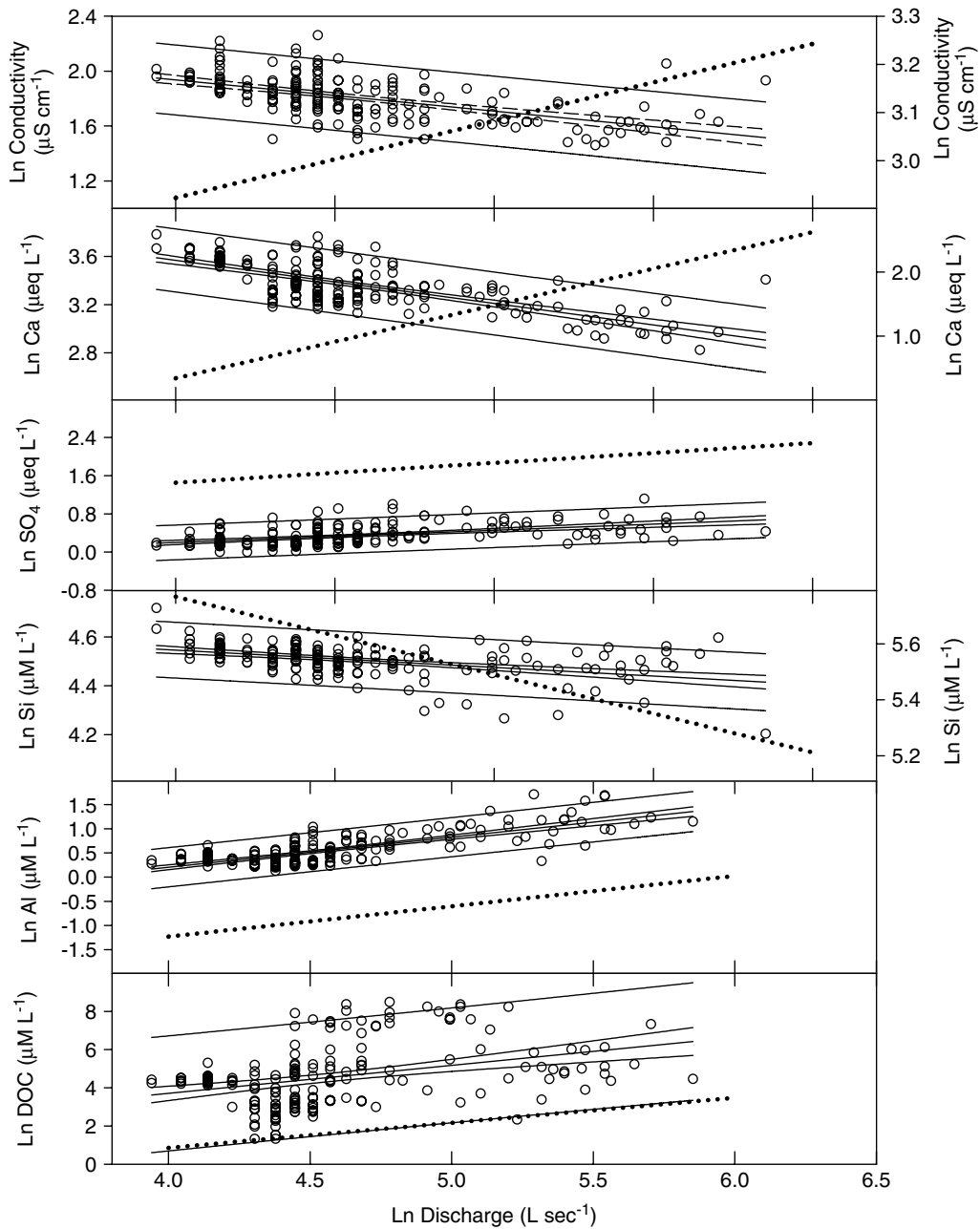


Figure 4. Data points represent discharge-concentration relationships for the stream waters of the Córrego Roncador in the IBGE Ecological Reserve, Brasília, Brazil. Samples were collected from May 1998 to April 2000. The innermost solid line is the least-squares regression fit to the data. The inner set of solid lines around the regression is the 95% confidence interval and the outer set of lines is the 95% prediction interval. The dotted line is the regression fit to similar discharge-concentration data from May 1996 to April 2000 for Igarape 54 within Fazenda Vitoria, Paragominas, Brazil. If a right-hand axis is present it refers to the Igarape 54 data. In Igarape 54, five of the highest discharge values demonstrated contrary relationships for some elements and were treated as outliers for the current analysis. Natural logarithm transformations were used to control for heteroscedasticity in the data

Table VII. Summary statistics for sub-sets of soil profiles in the Brazilian soils database. Soil descriptions identified as dystrophic Oxisols within the cerrado region of Brazil or gleissolos not formed in limestone from throughout Brazil were analysed for comparison to soils in this study

Source	Soil description	Depth	Component	pHw ^a	C	N	K	Ca	Mg
This study	Acru tox	0–20 ^b		4.40	2.77	0.14	0.07	0.07	0.06
		50–100		5.2	1.11	0.04	0.01	0.05	0.02
Brazilian soil database ^c	Dystrophic Oxisols	0–20	N profiles	239	237	236	239	183	183
			Minimum	3.8	0.32	0.03	0.02	0.07	0.02
			25th percentile	4.8	1.09	0.09	0.06	0.32	0.09
			Median	5.1	1.55	0.12	0.09	0.76	0.28
			75th percentile	5.5	2.18	0.17	0.16	1.70	0.60
		Maximum	7.9	11.92	1.00	0.92	10.00	4.32	
		50–100	N profiles	186	185	182	186	113	112
			Minimum	4.2	0.06	0.01	0.01	0.06	0.00
			25th percentile	5.0	0.30	0.04	0.01	0.18	0.05
			Median	5.3	0.49	0.05	0.02	0.30	0.10
75th percentile	5.7		0.70	0.07	0.05	0.52	0.20		
Maximum	7.0	1.70	0.30	0.61	5.00	2.40			
This study	Aquox	0–20		4.3	6.5	0.41	0.13	0.14	0.07
		50–100		4.6	1.95	0.12	0.04	0.10	0.03
Brazilian soil database	Gleissolos ^d	0–20	N profiles	55	53	36	55	43	44
			Minimum	3.3	0.70	0.08	0.01	0.03	0.01
			25th percentile	3.9	1.90	0.18	0.08	0.18	0.13
			Median	4.1	2.74	0.26	0.14	0.50	0.31
			75th percentile	4.6	3.90	0.41	0.25	2.10	0.89
		Maximum	5.5	19.40	2.02	0.72	11.50	2.60	
		50–100	N profiles	35	34	22	35	34	34
			Minimum	3.7	0.10	0.01	0.01	0.02	0.01
			25th percentile	4.2	0.20	0.03	0.03	0.12	0.03
			Median	4.5	0.30	0.04	0.05	0.25	0.18
75th percentile	5.0		0.50	0.10	0.10	0.80	0.48		
Maximum	5.4	2.40	0.67	2.90	5.50	2.58			

Sampling layers are inconsistent in the database and thus the 0–20-cm surface horizon includes layers ranging from 10 to 20 cm, although all sampling started at 0 cm. In the sub-surface, all sampling layers fully contained within the 50–100-cm depths are included. Values were averaged as reported although analytical methods vary among the profiles. Units are percent for C and N, and cmolc kg⁻¹ for K, Ca, and Mg. N profiles is the number of profiles averaged from the database.

^a pHw—All pH values utilized were measured as soil pH in water.

^b Values are mass-weighted means from 0 to 10 and 10 to 20 cm (Tables I and III) utilizing measured bulk densities from the sites.

^c The Brazilian soil database is available at <http://www.esalq.usp.br/gerd/> (verified December 1, 2005).

^d Gleissolos—In the Brazilian soil classification, gleissolos are defined by the presence of a gleyed horizon defined by low chroma colours. In Soil Taxonomy there is no equivalent soil order. The classification of gleyed horizons in Soil Taxonomy is associated with the Aquept, Aquult, or Aquox sub-orders. After identification of gleying, classification would depend on the development of the B horizon and the textural contrast between A and B horizon with depth.

1 (0.92 and 0.66, year 2 and 1 respectively). Deposition inputs for the 2 years were relatively consistent, however, with only K and Cl differing substantially with three and fourfold differences between years, respectively.

The precipitation inputs of nutrients to this watershed, given the extremely nutrient poor nature of these clay rich Oxisols, comprised a large portion of the available nutrient pool cycling through the ecosystem. For example, 3.8 kg-Ca ha⁻¹ of precipitation input comprised 5% of the exchangeable Ca pool of upslope soils in the upper 1 m and thus under a steady-state condition could replace the entire pool in 20 years. The same estimate for Mg indicated a replacement time of 40 years. In the case of P, both rainfall inputs (i.e.

Table VIII. Annual atmospheric element inputs (kg ha^{-1}) for the cerrado of Brazil and the Amazon Basin. Locations are in Brazil unless otherwise indicated

Region	Reference	Location	Latitude/ longitude	Sampling protocol	Period of sampling	Avg or actual rainfall	DOC ^a	TN ^b	TDN ^c	NH ₄ N	NO ₃ N	TP ^b	TDP ^c	PO ₄	K	Ca	Mg	Na	Cl	SO ₄
Cerrado	Current study	Brasilia	15°56'41"S 47°53'07"W	B, 14d	1998/1999 1999/2000 1978	102 151 130	30.6 56.3 —	— — —	4.3 6.2 —	1.4 2.5 —	1.3 1.6 —	— — 2.9	0.1 0.0 —	— — —	6.0 2.0 2.6	4.4 3.3 5.6	0.7 0.5 0.9	1.3 1.6 —	20.1 5.7 —	1.9 3.0 36.0
	Coutinho (1979) (In Pivello and Coutinho, 1992)	Sao Paulo	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Amazon	Lima (1985) (in Lilientein and Wickle, 2004)	Uberlandia	19°5'S 48°7'W	B, 7–14d	1997/99	155	55.0	6.4	—	3.1	2.4	—	—	—	5.3	2.8	1.2	5.1	7.4	3.9
	Brinkmann (1985b) Jordan (1982)	Manaus San Carlos, Venezuela	1°56'N 67°03'W	— B, 7d	1968/1972 1975/1979	290	—	5.0	—	1.4	0.1	0.4	—	—	—	0.3 11.6	0.2 10.1	— 3.0	— —	— —
Amazon	Steinhardt and Fassbender (1979)	San Eusebio, Venezuela	8°37'N 71°21'W	B, 7d	1973/1974	158	—	9.9	—	—	—	1.1	—	—	2.6	5.6	5.2	3.3	59.4	35.4
	Franken and Leopoldo (1984)	Manaus	—	—	1976/1977	207	—	—	—	4.7	—	—	—	0.32	2.1	—	—	10.4	21.2	—
Amazon	Stallard and Edmond (1981) (In Lesack and Melack, 1991) ^d	Central Amazon Basin	—	W, 34 events	1976/77	—	—	—	—	0.6	1.1	—	—	—	—	—	—	—	—	1.0
	Galloway <i>et al.</i> (1982) (In Lesack and Melack, 1991) ^d	San Carlos, Venezuela	1°54'N 67°03'W	B, one weekly event	1980/1981	391	—	—	—	1.3	1.4	—	—	—	—	—	—	—	—	—
Amazon	Franken and Leopoldo (1984)	Bacia Modelo	—	—	1980/1981	209	—	—	—	—	—	—	—	0.71	4.8	—	—	8.2	14.1	61.5
	Russell (1983) (In Bruijnzeel, 1990)	Jari	—	B, 1d	1981/1982	—	—	—	—	—	—	0.1	—	—	10.2	15.8	6.5	—	—	—
Amazon	Lewis <i>et al.</i> (1987)	Caura River, Venezuela	—	B, 3–4 d	1982/1984	450	—	2.3	—	—	—	0.1	—	—	1.0	1.3	0.3	8.2	11.7	8.5
	Lesack and Melack (1991) ^e	Manaus	3°15'S 60°34'W	W, event	1983/1985	287	—	—	—	1.5	1.2	—	—	—	0.14	0.7	0.9	0.4	1.4	2.1
Amazon	Andreae and Andreae (1988)	Central Amazon	—	W, event	—	240	—	—	—	1.4	0.7	—	—	—	—	—	—	—	—	0.4

(continued overleaf)

Table VIII. (Continued)

Region	Reference	Location	Latitude/ longitude	Sampling protocol	Period of sampling	Avg or actual rainfall	DOC ^a	TN ^b	TDN ^c	NH ₄ N	NO ₃ N	TP ^b	TDP ^e	PO ₄	K	Ca	Mg	Na	Cl	SO ₄
	Mortatti and Probst (2003)	Amazon avg. (N = 8)	—	—	1989	226	—	—	—	—	—	—	—	—	3.4	4.3	0.4	3.4	3.8	18.1
	Mortatti and Probst (2003)	Obidos	—	—	1989	220	—	—	—	—	—	—	—	—	3.6	4.4	0.5	3.6	4.2	18.4
	Williams <i>et al.</i> (1997)	Manaus	3°15'S 60°34'W	W, event	1989/1990	275	—	—	—	1.1	1.6	—	0.00	0.08	0.9	1.3	0.3	1.5	4.4	2.6
	Filoso <i>et al.</i> (1999)	Lower Rio Negro	—	B, 30 events	1991	208	—	—	8.3	0.6	0.8	—	0.31	0.31	0.7	2.5	0.4	2.4	1.6	3.1
	Klinge <i>et al.</i> (2004)	Belem	1°11'5"S	—	1992/1993	248	—	8.0	—	—	—	3.0	—	—	4.0	9.0	2.0	26.0	—	18.0
	Holscher <i>et al.</i> (1998)	Igarape Acu	47°34'15"W	B, 1 week per month	1992/1993	250	—	2.6	—	—	—	0.8	—	—	2.1	5.5	2.8	19.7	37.2	12.0
	Forti <i>et al.</i> (2000)	Serra do Navio	00°55'54"N 51°59'16"W	B, 7d	1993/1994	228	—	—	—	0.7	1.0	—	—	—	10.3	36.7	4.3	10.7	14.8	6.8
	Schroth <i>et al.</i> (2001)	Manaus	3°8'S	W, 10 events	1996/1997	262	—	—	5.5	1.8	1.4	—	0.07	0.02	2.6	0.8	0.3	—	—	—
	Markewitz <i>et al.</i> (2004)	Paragominas	2°59'S 47° 31'W	B, 14d	1996/1998	180	123.0	—	4.0	1.5	0.2	—	0.03	—	5.0	3.2	1.2	4.7	10.7	2.4
	Ungemach (1972); Nye and Greenland (1960) (In Lewis, 1981)	Amazon Basin	—	—	—	—	—	10.0	—	3.2	2.5	0.27	—	—	—	3.6	3.0	—	11.2	16.8

Sampling protocols indicate the use of wet (W) or bulk (B) deposition collectors and the periodicity of sampling.

^a DOC: dissolved organic carbon.

^b TN and TP: Total nitrogen or phosphorus determined on an unfiltered and digested sample.

^c TDN and TDP: Total dissolved nitrogen or phosphorus determined on a filtered and digested sample.

^d Reported values were calculated in (Lesack and Melack, 1991) and thus were not available in the original reference.

^e Elements other than N and S were estimated by the authors using the reported rainfall input for the study year and the volume-weighted mean concentrations.

$<0.1 \text{ kg ha}^{-1} \text{ year}^{-1}$) and soil available pools ($<1 \text{ kg ha}^{-1}$) were extremely low such that small changes in either the input flux or the pool greatly affect the replacement time estimate.

Similar replacement time calculations made by Marques *et al.* (2004) for soil Ca in the cerrado, using similar rainfall inputs, resulted in estimates 10–100-fold higher (220–2200 years) because of using Oxisols with higher Ca contents. For the Amazonian location of Markewitz *et al.* (2004) the upper 1 m of soil under undisturbed forest contained $\sim 550 \text{ kg ha}^{-1}$ of exchangeable Ca and thus the 3.2 kg ha^{-1} of bulk precipitation inputs estimated there from May 1996 to May 1998 represent only 0.6% of the soil pool, or a replacement time of 170 years. For Mg, replacement time was estimated at ~ 250 years. This disparity in the ratio of atmospheric element input to soil element availability simply highlights the importance of atmospheric inputs in nutrient deficient soils. In the presence of disturbance, such as land clearing or fire, that may facilitate nutrient element loss, forest ecosystems can regenerate aboveground vegetation biomass based on the drawdown of exchangeable soil pools, at least for cations, given sufficient stocks. Our cerrado watershed would appear to be more dependent on atmospheric nutrient inputs for ecosystem recovery because of extremely low nutrients stocks.

Consistent with the nutrient-poor soils of this watershed, the dissolved element concentrations of this cerrado stream were clearly low. Total VWM annual cation content (i.e. $\text{TZ}^+ = \text{Na} + \text{K} + \text{Mg} + \text{Ca}$) of $87 \mu\text{eq l}^{-1}$ was among the lowest values observed for lowland Amazonian rivers that ranged from 40 to $600 \mu\text{eq l}^{-1}$ (Edmond *et al.*, 1995; Stallard and Edmond, 1983) and far below many other rivers, especially those that drain the Andes mountains (e.g. $\text{TZ}^+ > 4000 \mu\text{eq l}^{-1}$) (Edmond *et al.*, 1995; Ballester *et al.*, 2003; Mortatti and Probst, 2003; Stallard, 1985; Stallard and Edmond, 1983; Stallard and Edmond, 1987). The stream water of this cerrado drainage, in fact, approximated concentrations of the black water Rio Negro, a stream draining quartz sand-dominated soils in the tertiary deposits of the Amazon trough. For example, concentrations of Ca, Mg, and K in the Rio Negro were 18, 10, and $11 \mu\text{eq l}^{-1}$ (Mortatti and Probst, 2003) compared with 27, 9, and $2 \mu\text{eq l}^{-1}$ for the Córrego Roncador. The dilute nature of this cerrado stream relative to others draining shield bedrock was likely influenced by the smaller size of this watershed compared to the mesoscale watersheds (i.e. 10^4 – 10^6 ha) often reported on in the Amazon. This difference may result from the inclusion of other bedrock lithologies in larger watersheds (Stallard, 1985) or the longer reaction time for in-stream processes (Drever, 1997; Norton, 1974). Relative to data from smaller watershed studies (i.e. $<10^4$ ha) in the Amazon (Table IX) these waters are still generally more dilute (e.g. conductivities $<6 \mu\text{S}$) but have relatively high concentration for specific elements (e.g. Ca, Mg, and DOC).

As a result of the low nutrient concentrations in the Córrego Roncador, the total elemental fluxes out of the watershed were also quite low (Table VI). Estimated hydrologic flux for the stream based on the stage height discharge relationship indicated that 26 and 32 cm of outflow occurred for the 1998/1999 and 1999/2000 water years, respectively. These outflows represented 22 and 26% of precipitation inputs for the 2 years. We know of no other similar hydrologic watershed budgets for the cerrado but using eddy covariance and energy budget estimates, Miranda *et al.* (1997) estimated water use in these seasonally dry ecosystems at 50% of precipitation inputs. In studies from the Amazon Basin where rainfall ranged from 208 to 385 cm, runoff accounted for 18–63% of water inputs (Bruijnzeel, 1990). We did not continuously record stream discharge during this study so the maximum size of storm flow events is unknown but must cause some underestimate in total stream discharge. Storm flow, only accounted for 5% of water yield in the small watershed studied by Williams and Melack (1997) and Lesack (1993) but on average accounted for 20% of the dissolved solute fluxes of the macronutrients.

Using the dissolved element inputs in rainfall estimated in 1999/2000 relative to the dissolved element outputs in streamwater averaged over the two years of this study, Si was the only element in this cerrado watershed for which outputs exceeded inputs (Table VI). For the other elements, inputs generally exceeded outputs by 2–15-fold. In the case of inorganic N and P, these ratios were much higher as stream water outputs were virtually zero.

Table IX. Stream water chemical concentrations^a for small watersheds (<10⁴ ha) in the cerrado of Brazil and the Amazon Basin

Reference	Location	Latitude/ longitude	Sampling Protocol ^b	Period	Area (ha)	Avg. or actual Ppt. (cm)	Runoff (cm)	Dis (l s ⁻¹)	Land cover	Cond (μ S cm ⁻¹)	pH	ALK (μ eq l ⁻¹)	DOC	TDN	TDP	NO ₃ -N	NH ₄ -N	K	Ca	Mg	Na	Cl	SO ₄	Al	Si	Fe	(μ M)		(μ eq l ⁻¹)	(μ M)					
																											676.2	9.8		0.01	0.8	0.4	2.0	29.4	10.0
This study	Brasilia	15° 56'41"/S 47° 53'07"/W	Daily	1998/ 1999	1200	102	26	55–240	C	6.1	5.5	37.3	676.2	9.8	0.01	0.8	0.4	2.0	29.4	10.0	9.2	8.9	0.4	0.8	91	0.3									
			Weekly	1999/ 2000	—	151	32	55–350	—	5.6	6.0	40.3	196.5	8.1	0.01	1.1	0.5	2.2	24.5	8.5	9.3	8.1	0.7	1.8	87	0.3									
Brinkmann (1985a, b)	Manaus			1968/ 1972	—	228	—	—	F	5.1	—	—	—	—	—	0.1	5.0	35.5	tr	10.7	51.3	20.0	—	—	67	7.5									
Furch (1984)	Central Amazon	10 forest streams	2 dates	1974/ 1975	—	—	—	—	F	10.0	4.5	—	—	—	—	—	—	3.8	1.9	3.0	9.4	62.1	—	—	3.3	75	1.8								
Franken and Leopoldo (1984)	Reserva Ducke/ Barro		Weekly	1976/ 1977	1300	207	400	0.1–120	F	—	—	—	—	—	—	—	2.8	2.6	—	—	—	9.6	29.7	79.0	—	—									
	Barro			1981/ 1982	—	251	869	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—									
Nortcliff and Thornes (1978)	Reserva Ducke/ Barro		Daily	1977	—	—	—	—	F	—	—	—	—	—	—	—	—	1.5	0.4	2.4	8.3	—	—	—	—	—									
Neal <i>et al.</i> (1992)	Reserva Ducke/ Barro	02° 57'S 59° 27'W		1987	—	247	148	—	F	—	—	—	—	—	—	2.6	0.9	1.1	4.3	1.2	9.6	12.2	4.4	—	—	—									
Lesack (1993)	Manaus/ Braço		Weekly BF	1984/ 1985	23.4	287	169	0.5–62	F	4.6	—	—	15.3	0.08	11.5	0.7	0.6	1.5	1.4	6.3	13.0	3.9	—	—	—	—									
Williams and Mellack (1997); William <i>et al.</i> (1997)	Manaus/ Lower Braço Upper Braço Mota Brook		Weekly BF	1989/ 1990	23.4	276	208	5–47	20%F	8.4	5.0	4.3	158.0	19.7	0.49	11.7	1.0	3.9	8.0	4.4	15.6	14.7	3.6	1.5	80	0.7									
			Weekly BF	—	<23.4	—	—	—	—	10.2	4.6	—5.6	83.0	19.4	0.40	11.9	1.7	2.5	6.4	3.8	2.4	14.7	3.6	2.2	70	0.9									
			Biweekly BF	—	18	—	—	—	F	9.3	4.7	—10.2	73.0	11.6	0.29	8.2	0.3	1.3	5.6	1.2	10.6	11.9	3.4	1.9	90	0.5									

(continued overleaf)

Table IX. (Continued)

Reference	Location	Latitude/ longitude	Sampling Protocol ^b	Period	Area (ha)	Avg. or actual Ppt. (cm)	Runoff (cm)	Dis ($l s^{-1}$)	Land cover	Cond (μS cm^{-1})	pH	ALK (μeq l^{-1})	DOC	TDN	TDP	NO ₃ N	NH ₄ N	K	Ca	Mg	Na	Cl	SO ₄	Al	Si	Fe	Ppt.			
																											(μM)	($\mu eq l^{-1}$)		
Forti <i>et al.</i> (2000)	Serra do Navio, Anapa	00° 55'54"N 51° 59'16"W	Weekly	1993/ 1994	<164	228	—	—	F	—	6.2	85.5	—	—	—	6.5	2.3	15.4	140.0	80.4	83.5	75.4	13.2	—	—	—	—	—	—	
Neill <i>et al.</i> (2001)	Ariquemes	10° 30'S 62° 30'W	Periodic- BF	1994/ 1998	164 1740	228 220	135	—	65%F	—	6.7	45.2	—	—	—	10.7	7.9	49.6	141.0	85.2	76.1	71.9	199.2	—	—	—	—	—	—	
Markewitz <i>et al.</i> (2004)	Parago- minas	2° 59'S 47° 31'W	Daily weekly	1996/ 1998	<10 ⁴	132	30	800–3000	20%F	29.6	4.9	55.7	108.3	19.8	0.06	7.9	2.4	21.7	39.4	42.0	150.9	202.0	15.0	—	—	—	—	—	—	
Eisenbeer <i>et al.</i> (In McClain and Eisenbeer, 2001)	La Cuenca	—	—	—	—	—	—	—	—	—	5.8	—	—	—	—	—	—	20.2	79.0	21.4	—	—	—	—	—	—	—	—	—	—

Cond, conductivity; ALK, alkalinity; DOC, dissolved organic carbon; TDN and TDP, total dissolved nitrogen or phosphorus determined on a filtered and digested sample.

^a Values are typically reported as volume-weighted mean concentrations of weekly collections over a year but some are arithmetic means of periodic sample collections. Similarly, values typically represent baseflow (BF) concentrations.

^b Sampling protocol refers to the frequency of sampling as either daily, weekly, or periodic. In some cases samples were always collected during baseflow (BF).

Nutrients and other elements can certainly accumulate in ecosystems during short periods of time (i.e. 1–10s of years) but over long timescales (i.e. 100s of years) it is hypothesized that inputs will equal outputs (Vitousek and Reiners, 1975). This input–output balance, however, does not necessitate that dissolved inputs in precipitation must equal dissolved outputs in streamwater. For example, we did not measure stream sediment loads that would likely increase nutrient outputs. Other mechanisms are also present that facilitate nutrient movement outside the watershed-ecosystem boundary. In the cerrado region, fire is clearly a predominant pathway of nutrient redistribution and loss (Kauffman *et al.*, 1994; Miranda *et al.*, 2002) and although our watershed was undisturbed through human habitation, fire has periodically entered portions of the watershed (Miranda *et al.*, 1996a).

Despite the low dissolved concentration and total fluxes in Córrego Roncador the geochemistry and charge balance relationships of this cerrado stream were similar to other Amazon Basin river waters including those draining portions of the Brazilian shield (Edmond *et al.*, 1995; Furch, 1984; Mortatti and Probst, 2003; Stallard and Edmond, 1983). The ternary diagrams of Figure 5 demonstrate the proportional abundances of various elements in the stream waters and compare the cerrado stream data to similar data for Amazonian streams (Mortatti and Probst, 2003). The preponderance of Si in the cerrado stream waters (Figure 5) was consistent with water chemistry from streams in the Amazon and Orinoco Basins from lowland shield geologies (Stallard, 1985) as well as with the observed desilication of the soil and parent material within the input–output budget for this watershed. The relative abundance of Si compared with HCO_3 or $\text{Cl} + \text{SO}_4$ in this stream was slightly high compared with the other Amazonian streams (Figure 5(a)) sampled during CAMREX (Mortatti and Probst, 2003). These more nutrient-poor soils of the cerrado are typically expected to possess greater contents of gibbsite relative to kaolinite, as kaolinite is lost through long periods of desilication (Reatto *et al.*, 1999; Reatto *et al.*, 2000). Streamwater Al and Si contents of Córrego Roncador, however, indicated that kaolinite was still the predominate mineral phase (Figure 6). The source of Si in this cerrado watershed formed in the surface exposed rocks of Brazilian shield, however, may well differ from that of the Amazon watershed formed in the deep tertiary sediments of the Amazon trough (Putzer, 1984). The balance of cations (Figure 5(b)) and anions (Figure 5(c)) in the stream waters was consistent with desilication in that Ca and HCO_3 are predominant. These elements are typically assumed to be derived from carbonic acid weathering of aluminosilicate rocks (Drever, 1997). These results are generally similar with the other Amazonian streams with the exception of the Rio Negro.

In the Amazonian watershed of Markewitz *et al.* (2001), the authors observed a similar correspondence between Ca and HCO_3 but found an atypical result in that the concentration of these elements decreased with increasing stream flow (Figure 4). The authors hypothesized that a similar pattern might exist in all highly weathered soils that no longer have primary minerals in the parent material to provide weatherable Ca or Mg. In the Amazonian watershed, Al and Si concentrations indicated a similar mineral phase equilibrium with kaolinite (Figure 6) although discharge-weighted mean annual concentration of Si ($120 \mu\text{M}$) exceeded those in the Córrego Roncador ($89 \mu\text{M}$). The hypothesis, however, was not supported by the concentration–discharge relationships observed in this cerrado watershed (Figure 4). This watershed demonstrated the more typical pattern of decreasing conductivity, Ca, and Si concentration with increasing stream discharge (Drever, 1997). The difference in the geomorphological formation of this cerrado watershed and its soil from igneous shield rocks, relative to formation in tertiary sediments of the Amazon, may well affect the continued presence of weatherable minerals in this ecosystem (Marques *et al.*, 2004). Aluminium, which like Si can be released during mineral weathering, demonstrated a contrary pattern to Si and concentrations increased with discharge. This likely resulted from the incorporation of organically bound Al in the measure of total Al, since increases in total dissolved Al were consistent with increasing stream concentrations of DOC (Figure 4). Similar patterns for Al and DOC were observed in the Amazon watershed (Markewitz *et al.*, 2004).

These discharge–concentration relationships for the Córrego Roncador demonstrated a greater concentration of Si, Ca, and Mg during periods of baseflow when water chemistry was largely reflecting groundwater inputs. We did not measure groundwater concentrations of Ca or Mg in this watershed. Earlier work of Resende (2001) on soil solution concentrations at 25 and 100-cm depths in upland soils of this watershed reported Ca

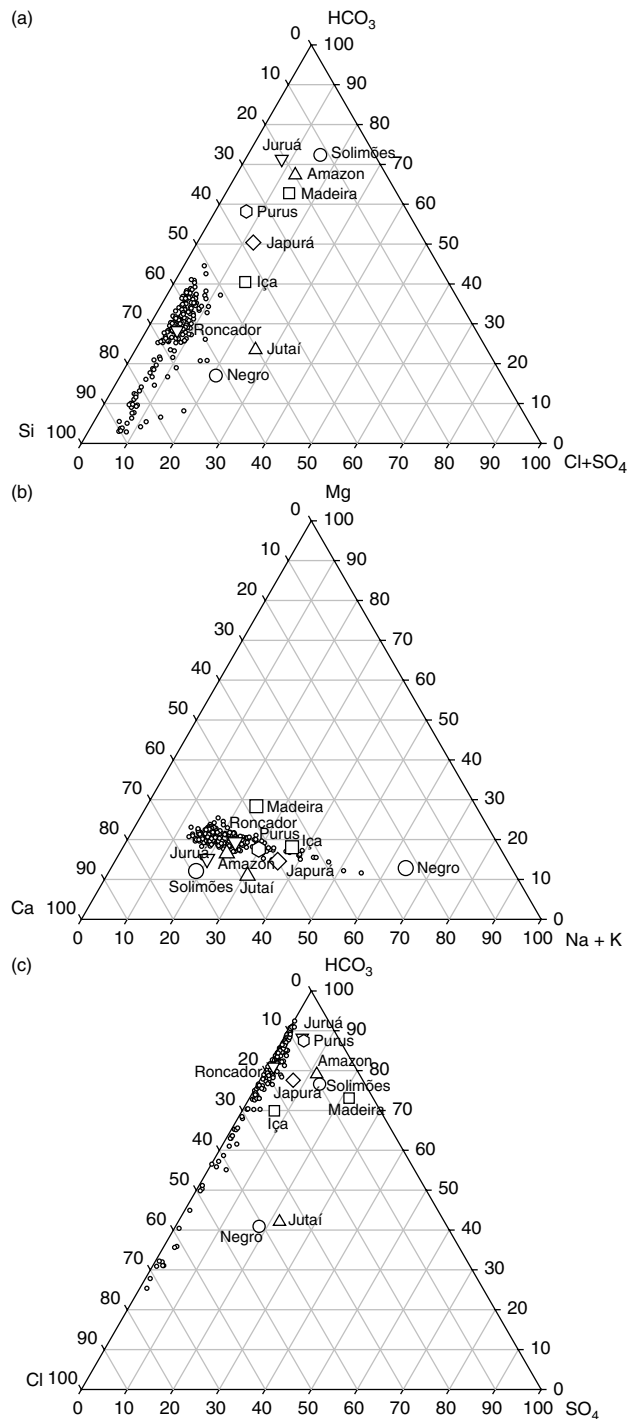


Figure 5. Ternary diagrams for stream waters of the Córrego Roncador in the IBGE Ecological Reserve, Brasília, Brazil. Samples were collected in the IBGE from May 1998 to April 2000. Data are plotted as normalized proportions of the indicated elements. For normalization, silicon is in $\mu\text{M l}^{-1}$ all other components are in $\mu\text{eq l}^{-1}$. The closer a data point to a specific corner of the triangle the more highly represented is that element (a) is the contributing substrate proportionality as proposed by Stallard (1985), (b) is the cation proportionality, and (c) is the anion proportionality. Large symbols are mean concentrations for Amazon basin rivers from Mortatti and Probst (2003), small circles are individual grab samples from the IBGE with the VWM represented in the cloud of points

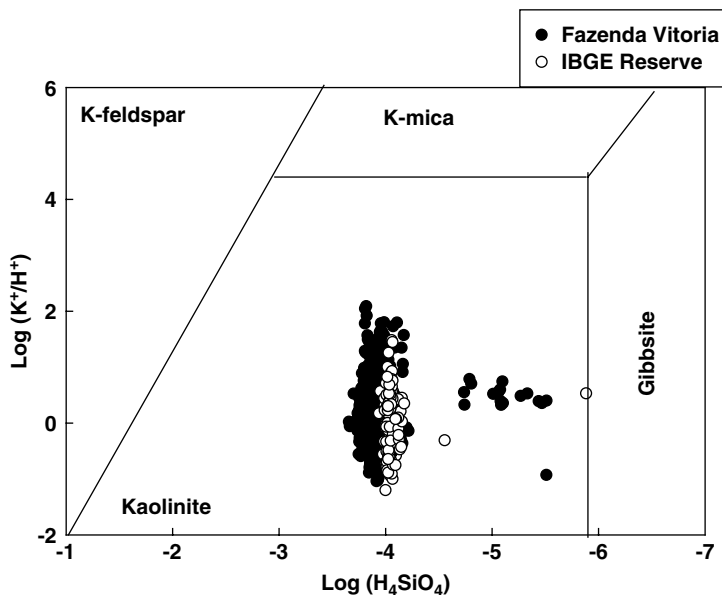


Figure 6. Mineral stability diagram for kaolinite, gibbsite, and K-mica after Meng and Maynard (2001) for stream waters of the Córrego Roncador in the IBGE Ecological Reserve, Brasília, Brazil and of Igarape 54 within Fazenda Vitoria, Paragominas, Brazil. Samples were collected in the IBGE from May 1998 to April 2000 and in the Fazenda Vitoria from May 1996 to April 2000

concentrations of 33 and 14 $\mu\text{eq l}^{-1}$ and Mg concentrations of 16 and 8 $\mu\text{eq l}^{-1}$ at the two depths, respectively. These values were similar to stream water concentrations, although the observed declines in concentration with depth would be expected to continue as water passed through these deep soils on route to the stream. Similar soil solution lysimetry analyses from 50-cm depth within riparian soils was also reported on in this watershed by Parron (2004). Parron (2004) found Ca and Mg concentrations of 27 and 7 $\mu\text{eq l}^{-1}$. These values were strikingly similar to the 2-year average concentrations for Córrego Roncador and suggests that riparian zone soils may well be a predominant source of cations to the stream.

CONCLUSIONS

The stream water concentrations of dissolved elements in this cerrado drainage were extremely dilute and thus consistent with the Brazilian shield geology and nutrient-poor conditions of the soil. Dissolved concentrations in this cerrado stream were lower than the concentrations in many mesoscale Amazonian streams draining portions of the basin but relatively similar to such streams draining the Brazilian shield and to previous smaller watershed studies in the Amazon Basin. The low stream water concentrations in this cerrado watershed led to low dissolved element fluxes that were well below the dissolved element inputs in rain. Silicon was the one exception, with stream outputs exceeding inputs, clearly demonstrating a continued desilication despite the pedological history of the watershed. The geochemical and charge balance relationships for this stream were generally consistent with geochemical interpretations for Amazonian streams. The discharge-concentration relationships, in particular, demonstrated decreasing Ca and Mg concentrations with increasing baseflow, a pattern typical for groundwater contributions from weathering of aluminosilicate parent material. The differing pedologic and geomorphologic history of this cerrado watershed relative to watersheds in the Amazon trough, where bedrock is much deeper below the surface, may well be critical to retaining these negative discharge-concentration relationship. In this cerrado watershed, the correspondence between soil solution concentrations

of Ca and Mg in the riparian zone with stream waters suggested that these zones might play an important role in controlling stream water cation concentrations.

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