

Relative influence of natural watershed properties and human disturbance on stream solute concentrations in the southwestern Brazilian Amazon basin

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[1] We use a synoptic sampling of stream water to quantify the effect of soil type, rock type, deforestation extent determined by Landsat TM imagery, and urban population density on stream solute concentrations for 60 different watersheds in the dry season and 49 in the wet season in the southwestern Brazilian Amazon basin. Catchment areas range between 18 and 12,500 km². Soil exchangeable cation content explains most of the variance in stream concentrations of cations, dissolved silicon (Si), and acid neutralizing capacity (ANC) in both forested and deforested basins based on regression analysis (R^2 range 0.61–0.81), though the mechanism underlying the relationship is unknown. We use the relationship between soil exchangeable cation content and stream solute concentrations in forested catchments to estimate the predisturbance and postdisturbance signal concentrations of stream solutes for deforested watersheds. Signal concentrations of potassium (K), sodium (Na), and chloride (Cl) increase with deforestation extent for streams on gneiss, granite, and sedimentary rock in both the dry and wet seasons after the effect of soil type has been statistically removed. Sulfate (SO₄) signal concentrations increase with deforestation extent in the dry season only. For catchments >40% deforested but with no urban populations, the ratios of disturbed to predisturbance stream concentrations range from 1.2 to 3.1 (K), 0.8 to 2.2 (Na), 0.7 to 2.7 (SO₄), and 2.4 to 14.6 (Cl) in the dry season and 1.2 to 2.2 (K) and 0.6 to 3.4 (Cl) in the wet season. Urban population density strongly affects Cl and SO₄ concentrations in both seasons and Na concentrations in the dry season; the urban signal comprises 40–58% of the dry season Cl signal and 83–89% of the wet season Cl signal for watersheds with >250 persons per km². Streams on mica-schist, mafic rock and carbonate shale have higher concentrations of Ca, Mg, Si, and ANC than watersheds on gneiss, granite, tertiary sediments or sandstone for a given soil exchangeable cation content in both seasons. Simple mass balance calculations suggest that supplemental cattle salts could comprise a significant fraction of the Na and Cl signals in the wet season but would not significantly impact wet season concentrations of Ca, Mg, or K. *INDEX TERMS:* 1045 Geochemistry: Low-temperature geochemistry; 1806 Hydrology: Chemistry of fresh water; 1871 Hydrology: Surface water quality; 1886 Hydrology: Weathering (1625); *KEYWORDS:* stream chemistry, Amazon, deforestation, urbanization, biogeochemistry

1. Introduction

[2] Large-scale clearing of tropical rain forests for agriculture, ranching and timber has intensified globally in the past three decades [Melillo *et al.*, 1996]. In the Brazilian Amazon, the total area deforested increased to over 550,000 km² in 1998, at an annual rate of 17,383 km² or 0.48% of the remaining forest per year. Deforestation occurs as spatially aggregated regional transformations, with 78% of the deforestation in the Amazon basin occurring in 19% of

the Landsat TM satellite images that cover the basin [Instituto Nacional de Pesquisas Espaciais (INPE), 2000]. Despite the implications of these regional land use transformations for soil fertility and agricultural production [Fearnside, 1984], stream ecosystems and water quality [Downing *et al.*, 1999], the processes that govern the biogeochemical response of large watersheds to deforestation are poorly understood, and impacts on stream water chemistry have rarely been documented. Cutting and burning of forest vegetation adds cations to surface soil horizons as ash and decomposing biomass and soil organic matter, causing temporary increases in soil exchangeable cations and pH [Nye and Greenland, 1960; Uhl and Jordan, 1984; de Moraes *et al.*, 1996; Hölscher *et al.*, 1997]. Leaching of this cation pulse from the soil may result in increased stream cation concentrations and fluxes from small tropical watersheds [Williams and Melack, 1997], though it is unknown whether a stream cation signal is detectable in larger watersheds of 10–10,000 km².

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[3] Natural spatial variation in soil type and geology complicate the detection and quantification of the impact of deforestation on regional stream chemistry. The chemical composition of streams draining watersheds with minimal anthropogenic disturbance varies as a function of watershed physiography [Thierfelder, 1998], geology [Meybeck, 1987; Dethier, 1986; Billett et al., 1996] and soil type [Billett and Cresser, 1992]. On the cratons of the Amazon basin, variations in topography and rock type can result in different solute yields under forested conditions [Stallard, 1983; Edmond et al., 1995; Freyssinet and Fara, 2000]. Forested catchments in the humid tropics on soils with high base cation saturation export up to an order of magnitude more cations in stream water than those on cation-poor soils [Bruijnzeel, 1991]. If deforestation occurs preferentially on soils with high cation contents, stream solute concentrations may be higher in deforested watersheds than in forested watersheds due to natural variability and not to the effects of human disturbance. Detection of the effect of deforestation on stream chemistry requires a better understanding of the natural pedologic and geologic controls on pre-disturbance conditions and subsequent catchment response to disturbance.

[4] Studies of the impact of deforestation on stream solute composition have focused on vegetation conversion and subsequent succession as the main processes affecting stream solutes [Bormann and Likens, 1979; Vitousek and Reiners, 1975; Williams and Melack, 1997]. However, deforestation at a regional scale involves not only replacement of forest vegetation with grass and cropland, but also establishment of service centers and urban areas. For the Amazon as a whole, the percent of the population residing in urban areas exceeded 50% in 1980 [Brower and Godfrey, 1997], providing potential sources and transport of solutes to receiving streams. While the influence of urban sources on stream chemistry has been demonstrated in temperate [Novotny and Chesters, 1981; Meybeck, 1998; Prowse, 1987] and subtropical zones [Martinelli et al., 1999; Omoto et al., 2000] and has been suggested to be important in tropical systems [Downing et al., 1999], it has not been documented in tropical rain forest landscapes undergoing rapid, regional land use transformations.

[5] The objective of the present study is to determine the relative influence of soil exchangeable cation content, rock type, deforestation, and urban population density on stream concentrations of base cations, dissolved silicon, chloride and sulfate in both the dry and wet seasons in a humid tropical region undergoing regional land use transformation.

2. Field Area

[6] The Brazilian State of Rondônia lies in the southwestern Amazon basin (8°–13°S, 60°–66°W) on the Brazilian craton, which has a basement of pre-Cambrian gneiss (Figure 1). Plutons dominated by biotite-amphibole granites, quartz syenites and quartz monzonites intrude into the craton throughout the state's center (27% of the sampled catchments' area). Tertiary sediments overlie the craton in the north. In the southeastern part of the state, carbonate shale with interbedded sandstone covers 3.5% of the study

area, and white quartz sandstone with no carbonates cover 20% [Companhia de Pesquisa de Recursos Minerais (CPRM), 1997]. Mica-schist and localized intrusions of gabbro cover 3.7% and 2.8% of the study area, respectively, also in the southeast. The Tertiary sediments form a dissected plain, with elevations between 60 and 160 m. On the craton, topography is gently undulating (average slopes 2–5%) with occasional rocky hills and small massifs up to 600m in elevation [RADAMBRASIL, 1978]. Hillslopes range between 590–1200 m long [Ballantine, 2001], which is typical of humid tropical areas with low relief and dense vegetation cover [Moglen et al., 1998].

[7] Soil types in the state include Oxisols (as described by Natural Resources Conservation Service (NRCS) [1999]), Latossolo distrófico in the Brazilian Soil Classification System, [Camargo et al., 1987]), Entisols (*Solos Aluvias Distróficos*) and Inceptisols (*Cambissolos*) in the north on the Tertiary sediments. Oxisols, Ultisols (*Podzólico distrófico*) and Alfisols (*Solos eutróficos*) occur on the craton, and Entisols (*Areias Quartzosas Distróficas*) on white quartz sands in the southeast (Figure 1) [Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA), 1983].

[8] Rainfall in the study area averages 1930–2690 mm/yr with a distinct wet season lasting from October to April, and average runoff ranges from 563–926 mm/yr, as measured by 9 rain and discharge stations maintained by the Agência Nacional de Energia Elétrica (ANEEL) and CPRM. The streams of the state are dilute, with total cations ranging from 126 to 243 $\mu\text{eq/L}$ for the Jamari and Jiparana rivers [Mortatti et al., 1992], compared to 200–450 $\mu\text{eq/L}$ for other streams on siliceous terrain in the Amazon basin and to 422 $\mu\text{eq/L}$ for the Amazon main stem at Obidos [Stallard, 1983]. Dissolved silicon and bicarbonate comprise between 74–80% of total dissolved solids by mass. Calcium and sodium are the dominant cations, ranging between 26 and 35% (Ca) and 22 and 39% (Na) of total cations on an equivalent basis [Mortatti et al., 1992].

[9] The undisturbed vegetation includes dense tropical rain forest (*Floresta Densa*, 17% of Rondônia state area) similar to that found in the central Amazon basin and open moist tropical forest (*Floresta Ombrófila Aberta*, 61% of state area), which is often dominated by palms and has a more open canopy than dense tropical rain forest [RADAMBRASIL, 1978]. Savannas are present but limited, covering up to 5–8% of 3 catchments in the southeast as estimated from Landsat TM imagery (unpublished data).

[10] The first modern wave of colonization in Rondônia began in the early 1970s. Approximately 1 million people migrated to the state and settled along the principal highway BR-364 between 1970 and 1990 (Figure 1). By 1998, 53,275 km², or 22% of the State's area had been deforested, representing 9.6% of the deforested area of the Amazon Basin [INPE, 2000]. Land use has been dominated by replacement of forest with grassland for cattle ranching [Pedlowski et al., 1997]. Up to 50% of the cleared area is in some stage of regrowth [Pedlowski et al., 1997; Rignot et al., 1997], though recent Landsat TM surveys indicate low rates of pasture abandonment and 18% of cleared areas in secondary succession [Roberts et al., 2002]. Of the 1.2 million people living in Rondônia in 1996, 62% resided in urban settlements of between 767 and 238,314 persons [Instituto Brasileiro de Geografia e Estatísticas (IBGE),

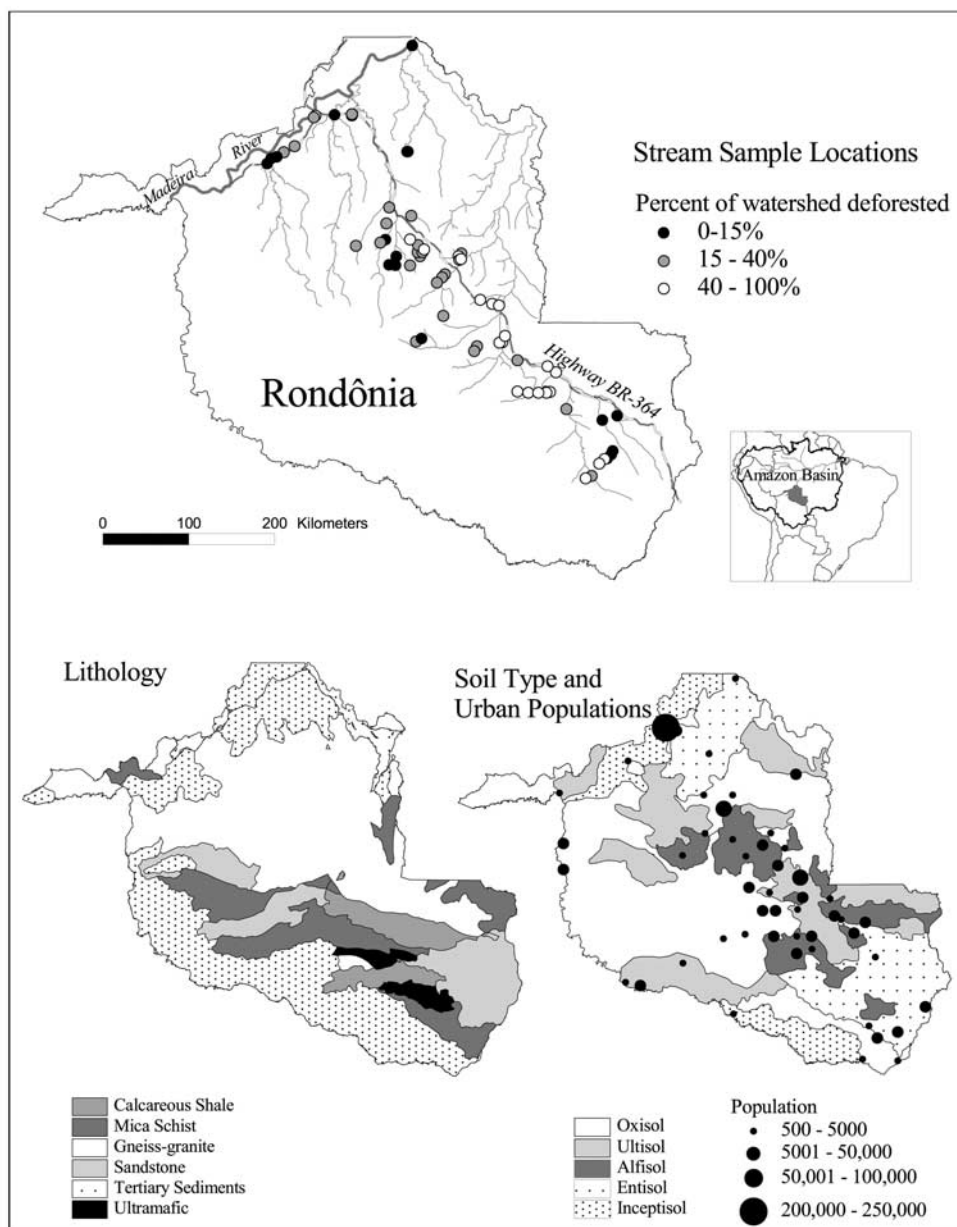


Figure 1. State of Rondônia with sample locations, lithology, soil orders and urban areas. Stream network includes sampled area only. The original soils map has been coarsened to emphasize regional patterns in soil type.

1996]. Fertilizer use is rare [Jones *et al.*, 1995] though ranchers supply cattle with salts containing Na, Cl, Mg, Ca, S, and P (H. Schmitz, Fundação Fauna e Flora Tropicais Rondônia, personal communication, 1998).

3. Methods

3.1. Stream Samples

[11] Stream water samples were collected at 60 different sites in the dry season (August 1998) and at 49 different sites in the wet season (late January–early February 1999, Figures 1 and 2). Each stream was sampled only once along its course, so each watershed represents an independent sample. The pH and conductivity were measured on the

unfiltered samples using an Orion 250A pH meter and an Orion 115 conductivity meter. The samples were then filtered in the field with Gelman GFF 0.7 μm filters, kept at 4°C and then frozen prior to transport from the state for analysis. Cations were analyzed by flame atomic absorption spectrometry (Varian model AA6), dissolved silica by the colorimetric acid-molybdate method, acid-neutralizing capacity (ANC) by Gran-titration [Stumm and Morgan, 1981], and chloride, nitrate and sulfate by ion chromatography (Dionex model DX500). Eighty-seven percent of dry season samples and 76% of wet season samples had <10% error in cation-anion balance, and samples in both seasons had high correlation between total cations and total anions ($r^2 = 0.98$ dry season, 0.94 wet season). A more detailed

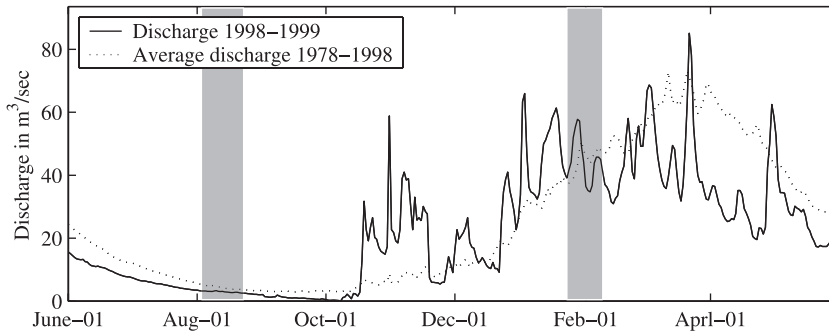


Figure 2. Discharge hydrograph for the Rio Branco in central Rondônia with a basin area of 1221 km². Shaded areas show the synoptic sampling periods.

description of quality assurance analysis is included elsewhere [Biggs, 2000].

3.2. Watershed Properties

[12] Watershed boundaries were digitized into a geographic information system using 1:100,000 scale topographic maps and the coordinates of collection points recorded in the field with a global positioning system. Land use was determined from a mosaic of eight Landsat Thematic Mapper (TM) images from 1996 classified using spectral mixture analysis (SMA) as described by Roberts *et al.* [1998]. Spectral end-members for soil, shade, non-photosynthetic vegetation, and green vegetation were selected from the image to generate end-member fraction images. Training areas were then selected to develop a decision classification tree that used end-member fraction values to assign pixels to one of five categories: pasture, regenerating forest, mature forest, urban/bare and water. Natural grasslands were classified manually via image interpretation. Due to the difficulty of spectrally separating pasture from regenerating vegetation, the designation “deforested” for this study includes both pasture and regenerating vegetation. This definition represents a complex mosaic of clearings of different ages and regenerating forest in various stages of regrowth as recognized by SMA and includes no information about the successional status of vegetation in the watershed.

[13] Soil exchangeable cation contents (S) were calculated for each watershed from digitized soil maps and soil profile analyses from the Sigteron project [Cochrane, 1998]. The methodology used in the Sigteron project delineates soil-terrain units that contain “a distinctive, often repetitive, pattern of landform, lithology, surface form, slope, parent material, and soil.” [Food and Agriculture Organization (FAO), 1993] Each soil-terrain unit is assigned multiple soil types and the percentage cover of each soil type within the unit. The soil exchangeable cation content S for a given watershed and cation is calculated as a weighted average of the soil exchangeable cation contents for each soil type:

$$S = \sum_{v=1}^w \sum_{k=1}^m \lambda_{vk} X_k \frac{A_v}{A_{tot}} \quad (1)$$

where w is the number of terrain units in the watershed, m is the number of soil types in terrain unit v , λ_{vk} is the fraction of terrain unit v covered by soil type k , X_k is the average

kilomoles of exchangeable cation per hectare in the upper 1.3 m of soil for soil type k , A_v is the area of the catchment covered by terrain unit v , and A_{tot} is the total catchment area. Exchangeable cation content for soil type k is calculated as

$$X_k = \frac{\sum_{j=1}^r \sum_{i=1}^n \alpha \rho_{ij} M_{ij} d}{n} \quad (2)$$

where ρ_{ij} is the bulk density of soil in profile i in-depth interval j in kg/m³, M_{ij} is the exchangeable cation concentration of soil profile i at depth interval j in kmol/kg, d is the depth of interval j in meters, α is 10,000 m²/ha, n is the number of soil profiles of type k at depth interval j , and r is the number of depth intervals. Four depth intervals of 0–20 cm, 20–50 cm, 50–80 cm, and 80–130 cm were chosen based on the most common depth intervals sampled in the Sigteron project. The predisturbance soil exchangeable cation content, S_{for} , was calculated using soil profiles located in forested areas only (2152 of 2932 profiles), which included reserves, areas with selective logging activity, and extractive reserves. We included forested pits only because we use the exchangeable cation content to estimate predisturbance solute concentrations. Including profiles in deforested areas would overpredict predisturbance soil exchangeable cation contents and also overpredict predisturbance stream solute concentrations.

[14] Bulk density (ρ_{ij}) was measured for only 413 of the 10680 soil samples, and was calculated for the rest of the soil profiles from a linear regression on soil texture and organic carbon. Previous studies find that regression model performance improves when models are calibrated for different soil types and horizons [Bernoux *et al.*, 1998]. To test the influence of different bulk density regressions on the calculated X_k and S , regression models of bulk density were parameterized both for all samples and in regressions that stratified samples by soil depth and soil type. The calculated X_k and S differ by <10% among the different regressions used to predict bulk density, so the bulk density regression model parameterized using all 413 soil samples is used to calculate X_k and S .

[15] The percent of each watershed covered by each of 24 different lithologies was calculated using a 1:1,000,000 geologic map from CPRM [1997]. The 24 different rock types were aggregated into groups of pre-Cambrian gneiss, biotite-amphibole granitic intrusions, carbonate shale, arenitic sandstone with no carbonates, Tertiary sediments,

mica-schist, and mafic rocks. These groups were further aggregated into acid lithology (gneiss, granite, sandstone, Tertiary sediments) and basic lithology (mica-schist, mafic rocks, and carbonate shale).

[16] Urban population density was calculated as the number of persons living in urban areas in the catchment divided by watershed area to yield urban population/km². The urban population included all persons living in areas designated as urban by the IBGE in the 1996 census, which includes settlements defined as urban by local municipal law, and in the 1996 census included settlements ranging between 24 and 238,314 persons.

3.3. Partitioning Stream Chemistry Into Background and Signal Concentrations

[17] Stream chemistry may be partitioned conceptually into a predisturbance background concentration and a signal concentration due to human disturbance:

$$C_t = C_f + C_d \quad (3)$$

where C_t is the observed concentration of a solute in the stream, C_f is the predisturbance, forested background concentration and C_d is the signal concentration of the solute due to deforestation and urbanization, all in $\mu\text{mol/L}$. C_f is predicted from a regression of the soil exchangeable cation content (S_{for}) versus stream solute concentration for forested catchments only, called the background or BKG model:

$$C_f = \beta_{so} + \beta_s S_{for} + \epsilon_s \quad (4)$$

where β_{so} , β_s , and ϵ_s are the intercept, slope and error terms of the regression. The C_f includes solutes that originate both from atmospheric deposition and from catchment sources, and the two are not statistically separated in equation (4). Forested catchments include those with <15% of the total catchment area deforested by 1996 ($n = 14$ dry season, $n = 12$ wet season). Where Landsat TM images were available for 1998, the deforestation extent was recalculated for the forested watersheds, and watersheds with significant land cover changes were excluded from the BKG regressions.

[18] Substituting equation (4) into equation (3), the deforestation signal concentration is

$$C_d = C_t - (\beta_{so} + \beta_s S_{for} + \epsilon_s) \quad (5)$$

The relation between deforestation percent and the stream signal concentration is quantified by the signal (SIG) regression:

$$C_d = \beta_d D + \beta_{RS} S_{for} + \epsilon_d \quad (6)$$

where D is the percent of the catchment cleared up to and including 1996 as measured by the classified Landsat TM imagery, β_d is the deforestation regression slope, β_{RS} is the residual soil parameter, and ϵ_d is the regression error. We include S_{for} and β_{RS} in the SIG regression to test the assumption that the regression parameters of equation (4) are constant over the study area.

[19] Least squares estimation of the regression parameters in equations (4) and (6) assumes that the independ-

ent variable does not have error [Draper and Smith, 1998]. The S_{for} calculated from equations (1) and (2) has error and violates this assumption. Within a given soil type, the standard deviations of X_i and S_{for} exceed their means for all cations, indicating that a functional relationship may be a more robust estimation of the β_s [Draper and Smith, 1998]. To test the influence of estimating β_s and C_f using a geometric mean functional relationship versus a least squares linear regression, the predicted background concentrations of all solutes were calculated using the β_s determined with both estimation techniques. Background concentrations (C_f) estimated using a geometric mean functional relationship differ from the least squares estimates by <2.5 μM for Ca, 1 μM for Mg, 4 μM for K, 7 μM for Si, and 9 μM for ANC for all soil exchangeable cation contents in the dry season, and by <2 μM for Ca, 7 μM for Mg, 6 μM for K, 34 μM for Si, and 16 μM for ANC in the wet season. These errors in background concentration introduced by assuming fixed S_{for} are small relative to both the errors in the regression and to the magnitude of the signal concentrations. The least squares estimate of β_s is used here because it allows for estimation of the standard error and confidence intervals of β_s .

[20] The residuals of all signal regressions equation (6) were heteroscedastic, which may result in inaccurate estimates of the standard error and p value of the regression parameters. The standard error and p values of β in equation (6) were estimated using a bootstrap resampling with 1000 repetitions, which assumes no particular distribution of residuals [Chernick, 1999]. The mean and standard deviation of the 1000 realizations of the regression parameters were used to test the significance level of the parameters by a t test.

[21] The variance explained by soil exchangeable cation contents includes the variance explained by S_{for} in both the BKG regression and SIG regression and is calculated as

$$R^2_{soil} = 1 - SSE_{SIG}/TSS_{raw} \quad (7)$$

where SSE_{SIG} is the sum of squared errors of the SIG regression equation (6) with S_{for} as the only independent variable, and TSS_{raw} is the total sum of squares of the raw concentrations.

4. Results

4.1. Watersheds Properties

[22] The sampled watersheds range from 18 to 12,500 km² and include the major soil and rock types found in Rondônia (Figure 1) from forested catchments with high cation contents (S_{for}) to heavily deforested catchments on cation-poor soils (Table 1). Watersheds >40% deforested have higher S_{for} , ECEC, CEC, and pH than forested watersheds. Because S_{for} includes soil profiles under forested vegetation only, this suggests that deforestation has occurred preferentially on soils with higher predisturbance cation contents (Table 1). Eight dry season and six wet season watersheds have an urban population density >5 persons per km². Deforestation percent (D) correlates weakly but significantly ($p < 0.05$) with soil exchangeable cation content (S_{Tz}), urban population density, and water-

Table 1. Watershed Attributes as Mean (Range) for Three Deforestation Classes, Dry Season Watersheds

	Deforestation Extent		
	0–15%	15–40%	>40%
Number of watersheds	15	24	20
Soil properties, kmol/ha			
S_{Na}	2.3 (1.7–3.4)	2.6 (1.9–3.8)	2.8 (1.9–3.6)
S_{Ca}	129 (36–510)	206 (36–443)	319 (40–520)
S_{Mg}	41 (12–137)	59 (14–118)	85 (21–131)
S_{K}	14 (5–39)	19 (7.5–34)	24 (9.3–34)
S_{TZ}	186 (55–690)	287 (59–594)	431 (73–689)
S_{ECEC}	412 (230–820)	509 (320–740)	600 (380–780)
S_{CEC}	773 (530–1220)	910 (730–1140)	1000 (740–1180)
S_{pH} (pH units)	4.8 (4.5–5.6)	4.9 (4.4–5.5)	5.2 (4.5–5.7)
Number of watersheds			
Gneiss-granite	7	17	9
Sandstone or Tertiary sediments	5	3	1
Basic lithology (>33% area)	1	4	10
Urban population, persons/km ²	0.3 (0–4)	0.3 (0–5.6)	29 (0–499)
Area, km ²	2620 (80–12540)	454 (10–2580)	201 (11–1090)

shed area [Biggs, 2000] Note that all watershed property and stream chemistry data are available electronically.¹

4.2. Watershed Properties and Stream Chemistry: Acid Lithology Only

[23] Stream concentrations of base cations, dissolved Si, and ANC correlate with soil exchangeable cation contents in streams draining both forested and deforested catchments (Figure 3). Stream Na correlates more strongly with S_K than with S_{Na} , which may be due to the large number of zero values for exchangeable Na in the soil profile analyses, limiting the precision of Na soil measurements. These relationships are used to calibrate the BKG model (equation (4)). The intercepts of the linear regressions, β_{so} , are not significantly different from zero for any solute in either season but are used to calculate the background (C_f) and signal (C_d) concentrations (Table 2). The background concentrations of SO_4 and Cl are the mean of the SO_4 and Cl concentrations in streams draining forested catchments. Similar relationships between S_{for} and stream solute concentrations hold in the wet season, and only a statistical summary of results is presented for the wet season (Table 2).

[24] To reduce the confounding effect of rock type on stream solute concentrations, the parameters of the SIG regressions equation (6) are estimated using watersheds on gneiss-granite, Tertiary sediment or arenitic sandstone only. The residual soil regression parameter β_{RS} exceeds zero for Ca, Mg, and ANC, suggesting that the BKG model does not account for all predisturbance variability in stream solutes. Soil exchangeable cation content alone explains between 0.70 and 0.83 of the variance in stream Ca, Mg, Si, and ANC concentrations, and between 0.60 and 0.69 of the variance in stream K and Na concentrations for catchments with an urban population density <5 persons/km² (Table 3 and Figure 3). Dry season signal concentrations of Na, Cl, SO_4 and K have statistically significant deforestation

parameters (Table 3 and Figure 4). In the wet season, Cl has a significant deforestation parameter, and K and Na have significant deforestation parameters when the intercept of equation (6) is not constrained to zero. Signal Ca, Mg, ANC, and Si concentrations do not have significant regression parameters in either season ($p > 0.05$).

[25] For the two most highly urbanized watersheds (288 and 499 persons/km²) chloride concentrations are 37 and 73 μ M higher than the SIG regression predictions for deforested, nonurbanized catchments in the dry season, and 13 and 32 μ M higher in the wet season. This urban signal concentration comprises 61–73% of the dry season chloride signal and 73–81% of the wet season chloride signal for those two watersheds. For SO_4 , the urban signal concentration is 71–85% of the total deforestation signal concentration in the dry season, and 100% of the total signal in the wet season. Stream Ca, Mg, K, Si, and ANC do not have significant urban regression parameters in either season. Area does not have a significant regression parameter for any solute, either alone or with any other combination of variables.

[26] The ratio of observed stream concentrations (C_f) to predisturbance concentrations (C_f) decrease in the order Cl > K > Na > SO_4 for catchments >40% deforested (Table 4). Urban watersheds have more than double the signal concentrations of chloride in both seasons.

4.3. Effect of Geology on Stream Solute Concentrations

[27] Streams on basic rock types have higher Ca, Mg, Si, and ANC concentrations than streams on acid lithology for a given soil exchangeable cation content in both seasons (Table 5). The relationship between soil cation content and stream solute concentrations is linear for both lithologies, with different slopes and intercepts for each lithology (Figure 5). Stream K concentrations are slightly higher for watersheds on mica-schist, but not for watersheds on mafic rocks and carbonate shale.

[28] Rock type confounds the detection and quantification of the effect of deforestation on stream solute concentrations for watersheds on basic lithology. Most solutes, including Ca, Mg, Si, and ANC, have statistically significant deforestation regression parameters when catchments with basic lithology are included in equation (6), but this is

¹ Supporting data tables are available via Web browser or via Anonymous FTP from <ftp://agu.org>, directory “append” (Username = “anonymous”, Password = “guest”); subdirectories in the ftp site are arranged by paper number. Information on searching and submitting electronic supplements is found at http://www.agu.org/pubs/esupp_about.html.

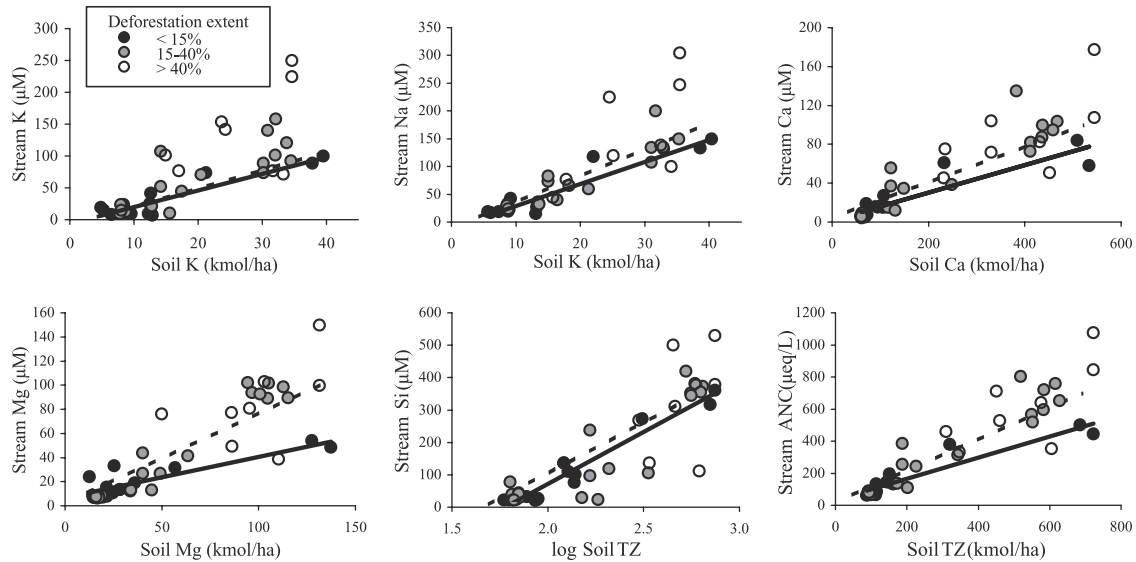


Figure 3. Watershed soil exchangeable cation contents (S_i) versus stream solute concentrations (μM) grouped by deforestation extent for nonurbanized watersheds on gneiss-granite, arenitic sandstone, and tertiary sediments during the dry season. The solid lines indicate the relationship between soil exchangeable cation content and stream solute concentration using forested watersheds only (BKG), and the dashed lines indicate the relationship using all watersheds (BKG + SIG model).

likely an artifact due to the higher background concentrations on basic lithology and does not demonstrate an effect of deforestation on stream Ca, Mg, Si or ANC.

4.4. Solute Sources

[29] Determination of which anions accompany each cation in solution can indicate whether cation concentrations are influenced by human disturbance. “Mobile” or strong acid anions such as sulfate and nitrate have been used to assess the contribution of anthropogenic sulfuric and nitric acid deposition to cation leaching and catchment acidification [Kirchner, 1992] and multiple regression equations can be used to separate the effect of each anion on cation concentrations [Christ *et al.*, 1999]. We use Cl as a tracer of human disturbance and ANC to indicate mineral

weathering and exchange of cations with hydrogen ions in the soil column. Stream ANC does not have a statistically significant deforestation parameter (Table 3), and we assume here that it has natural sources only. The relative influence of human and natural sources on a cation concentration may be assessed with a multiple linear regression:

$$C_i = \beta_{Cl}[Cl] + \beta_{ANC}[ANC] + \varepsilon \quad (8)$$

where C_i is the concentration of a given cation, β_{Cl} is the regression parameter associated with Cl concentrations, β_{ANC} is the regression parameter associated with ANC concentrations, and ε is the error term. Nitrate and sulfate comprise a small proportion of total anions on an equivalent basis (average 7%), and do not have significant regression parameters when included in equation (8).

Table 2. Regression Results for Forested Stream Solute Concentrations Versus Watershed Averaged Soil Properties (BKG model)^a

Stream Solute	Soil Regressor Variable	Regression Slope (β_s)		R^2		SEE	
		Dry Season (n = 14)	Wet Season (n = 11)	Dry Season	Wet Season	Dry Season	Wet Season
Ca	S_{Ca}	0.14 (0.02) ^b	0.11 (0.01) ^b	0.82	0.86	11	6.5
Mg	S_{Mg}	0.34 (0.05) ^b	0.23 (0.03) ^c	0.76	0.85	7.9	3.5
K	S_{K}	2.6 (0.3) ^b	1.5 (0.4) ^d	0.84	0.57	13	13
Si	S_{TZ}	0.48 (0.05) ^b	0.48 (0.13) ^d	0.86	0.55	46	72
Na	S_{Na}	61 (18) ^d	32 (14) ^e	0.53	0.36	36	23
Na	S_{K}	4.0 (0.5) ^b	2.7 (0.3) ^b	0.89	0.87	18	10
ANC	S_{TZ}	0.61 (0.06) ^b	0.39 (0.09) ^d	0.89	0.69	53	49

^a S_i was calculated using soil profiles in forest vegetation only. SEE is the standard error of estimate of the regression. Forested streams are those with <15% deforestation in 1996. None of the intercepts of the linear models (β_{soil}) was significantly different from zero to $p < 0.05$.

^b $p < 0.0001$.

^c $p < 0.001$.

^d $p < 0.01$.

^e Not significant at 0.05 level.

Table 3. Parameter Values and Standard Deviations for Signal Concentration Models (6) Using Nonurbanized Watersheds on Acid Lithology, Symbolized by Solid Circles in Figure 4^a

	Deforestation Parameter β_d	Residual soil Parameter β_{RS}	R^2		
			BKG Model	Soil Only	Soil Plus Deforestation
K					
Dry season	1.02 (0.37) ^b	ns	0.50	0.60	0.68
Wet season ^c	0.31 (0.19) ^d	0.70 (0.31) ^d	0.43	0.69	0.74
Na					
Dry season	0.76 (0.29) ^b	ns	0.58	0.68	0.72
Wet season ^c	0.35 (0.21) ^d	ns	0.67	0.69	0.71
Ca					
Dry season	ns	0.046 (0.02) ^d	0.64	0.79	0.80
Wet season	ns	0.060 (0.02) ^b	0.50	0.78	0.79
Mg					
Dry season	ns	0.34 (0.12) ^b	0.09	0.70	0.72
Wet season	ns	0.35 (0.15) ^b	0.0	0.74	0.77
Si					
Dry season	ns	ns	0.75	0.80	0.81
Wet season	ns	ns	0.83	0.83	0.85
ANC					
Dry season	ns	0.26 (0.11) ^b	0.59	0.81	0.82
Wet season	ns	0.21 (0.15) ^d	0.46	0.81	0.82
Cl					
Dry season	0.69 (0.16) ^c	ns	0	0	0.59
Wet season	0.12 (0.03) ^c	ns	0	0	0.39
SO₄					
Dry season	0.067 (0.017) ^c	ns	0	0	0.75
Wet season	ns	ns	0	0	0.29

^a Here ns indicates $p > 0.05$.

^b $p < 0.01$.

^c Intercept is not equal to zero.

^d $p < 0.05$.

^e $p < 0.0001$.

[30] Stream ANC and Cl concentrations explain 0.88–0.98 of the variance in stream cation concentrations (Table 6). The chloride regression parameters (β_{Cl}) are statistically significant for stream K in both seasons, and for stream Na in the dry season. Stream Ca and Mg concentrations have significant regression parameters for ANC only, and do not have statistically significant chloride regression parameters in either season.

5. Discussion

[31] Numerous processes determine stream solute composition, especially in disturbed areas. Uptake and release of solutes occur along various hydrologic pathways by both abiotic and biotic mechanisms that vary spatially and temporally. Releases of solutes following vegetation removal, burning, and establishment of pasture and cattle add a set of even more variable processes. Additional changes in land use and land cover, such as abandonment and vegetation regeneration, may reduce solute concentrations in receiving streams [Vitousek and Reiners, 1975; Bormann and Likens, 1979]. Changes in hydrologic regime following deforestation could also alter stream solute concentrations. The primary goal of the current study is to detect the effect of deforestation and urbanization on stream solutes, averaging over heterogeneities of watershed properties and processes in space and time. In the discussion we perform some simple calculations to assess the relative influence of some of

these mechanisms on observed background and signal concentrations.

5.1. Soil Exchangeable Cation Content and Stream Solute Concentrations

[32] Soil exchangeable cation contents (S_{for}) explain the majority of the variance in stream concentrations of all solutes except Cl and SO₄ in both forested and deforested basins. Relationships between soil characteristics and stream solute concentrations have been observed in a variety of climates. The fraction of soil exchange sites occupied by Ca correlates with stream Ca concentrations [Billett and Cresser, 1992] and streams draining basins with higher proportions of exposed rock, rocky soils and less weathered soils yield higher concentrations of cations per unit of dissolved silicon [Bluth and Kump, 1994]. The relationship between soil exchangeable cation contents and stream cation concentrations in the Rondônia streams does not, however, demonstrate that stream solutes originate on exchange sites in the upper 1.3 m of the soil. In fact, the correlation between stream Si and stream ANC in both seasons in Rondônia streams (Figure 6) suggests that weathering of silicate minerals provides cations to Rondônia streams, particularly Ca and Mg.

[33] Assuming that weathering of primary minerals is the dominant source of stream solutes in Rondônia, the concentration of cations in the soil likely reflects other

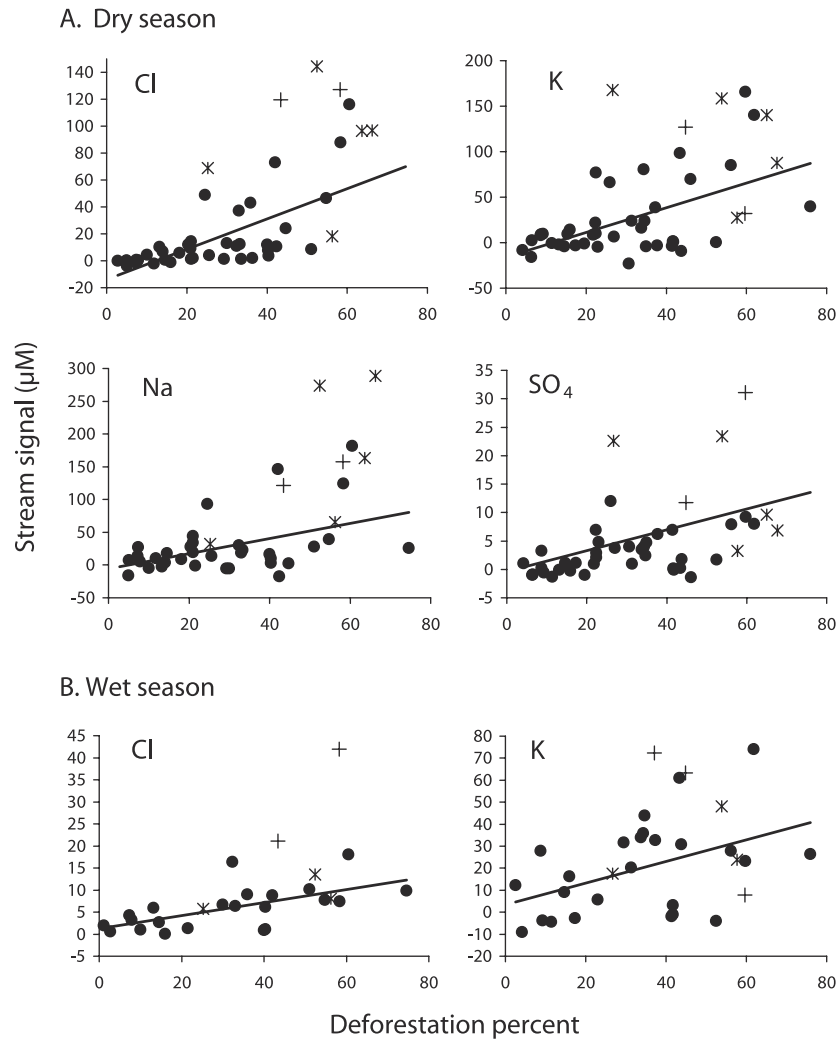


Figure 4. Signal concentrations versus deforestation percent (D) in (a) dry and (b) wet seasons. Best fit lines were determined with nonurbanized watersheds on gneiss-granite, tertiary sediments, or arenitic sandstone. Solid circles indicate watersheds on acid lithology with urban population density <5 persons/km². Pluses indicate acid lithology, urban population density >5 persons/km², and asterisks indicate $>33\%$ of watershed area on basic lithology and urban population density >5 persons/km². Nonurbanized watersheds on basic lithology are not shown.

catchment properties that regulate stream chemistry and the weathering rate of primary minerals. Soils developed on mafic rocks and mica-schist have consistently higher pH and cation concentrations than soils on acid igneous and metamorphic rock, so the soil exchangeable cation content may serve as an indirect index of rock and saprolite weathering rate [Holmes *et al.*, 2000]. Streams on a given rock type have differing solute concentrations (Figures 3 and 5), suggesting that depth to weatherable bedrock may also impact stream solute concentrations in addition to the differences caused by bedrock mineralogy. Stream solute concentrations and fluxes decrease as soil thickness increases, because thick soils reduce the volume of annual runoff in contact with fresh bedrock [Stallard, 1985]. Further information on the relationship between soil depth, soil exchangeable cation concentrations and bedrock and soil mineralogy would help elucidate the mech-

anisms relating soil exchangeable cation contents and stream solute concentrations.

5.2. Effect of Rock Type on Stream Solute Concentrations

[34] Streams draining watersheds on basic rock types have higher concentrations of Ca, Mg, Si, and ANC in both seasons than watersheds on acid lithology for a given soil exchangeable cation content (Figure 5, Si only), with dry season Mg being the most affected (Table 5). The sensitivity of Mg to rock type likely reflects the high Mg concentrations of mafic rocks. The ratios of solute concentrations in streams on basic lithology to streams on acid lithology (Table 5) are consistent with previous comparisons of the weathering rates of different rock types. Meybeck [1987] estimated that gabbro, carbonate shale, and carbonate rocks

Table 4. Concentration Partitions for Catchments >40% Deforested, Acid Lithology Only as Mean (Standard Deviation)^a

	Nonurban Watersheds		Urban Population >200 persons/km ²	
	Dry (N = 10)	Wet (N = 8)	Dry (N = 2)	Wet (N = 2)
		<i>Na</i>		
Total concentration (C_t)	153 (92)	77 (43)	185 (16)	76 (36)
Predisturbance (C_f)	96 (32)	60 (39)	55 (42)	30 (21)
Deforestation signal (C_d)	56 (75)	17 (39)	38 (8)	16 (4)
Urban signal	–	–	91 (17)	31 (16)
Ratio of Total:Soil ($C_t:C_f$)	1.5 (0.7)	1.3 (0.6)	4.5 (3.1)	2.9 (0.8)
		<i>K</i>		
Total concentration (C_t)	133 (69)	69 (25)	–	–
Predisturbance (C_f)	62 (22)	52 (15)	–	–
Deforestation signal (C_d)	71 (62)	17 (22)	–	–
Ratio of Total:Soil ($C_t:C_f$)	2.2 (0.9)	1.7 (0.5)	–	–
		<i>SO₄</i>		
Total concentration (C_t)	6.9 (4.3)	2.4 (0.8)	24 (14)	2.9 (0.7)
Predisturbance (C_f)	4.2	2.0	4.2	2.0
Deforestation signal (C_d)	2.7 (4.3)	0.4 (0.8)	3.4 (0.7)	0
Urban signal	–	–	21 (13)	0.9 (0.7)
Ratio of Total:Soil ($C_t:C_f$)	1.7 (1.0)	1.2 (0.4)	5.8 (3.3)	1.4 (0.3)
		<i>Cl</i>		
Total concentration (C_t)	57 (41)	13 (6.0)	129 (5.4)	31 (12)
Predisturbance (C_f)	6.8	4.4	6.8	4.4
Deforestation signal (C_d)	50 (41)	8.6 (6.7)	35 (7)	6.0 (1.3)
Urban signal	–	–	87 (2)	25 (11)
Ratio $C_t:C_f$	8.5 (6.1)	2.0 (1.4)	19 (1)	7.1 (2.7)

^a C_{ti} is the observed concentration in the stream, C_{fi} is the predicted background concentration based on the BKG regression, and C_{di} is the signal concentration (3).

weather at 1.3, 2.5, and 12 times the rate of granite-gneiss, respectively. Deforestation obscures the effect of rock type on K concentrations, indicating the importance of biologic cycling and disturbance for determining K release from ecosystems in addition to mineral weathering.

5.3. Deforestation Signals

[35] Vegetation disturbance increases the concentration and fluxes of solutes from small watersheds in a variety of climatic, geologic and soil conditions. At Hubbard Brook, New Hampshire, clear-cutting of forest and suppression of vegetation regrowth increased stream concentrations by factors of 1.7 for Na, 4.6–5.8 Ca, 3.9 Mg, 9.5–11 K, 1.4 dissolved Si, and 1.4 Cl. In the humid tropics, *Williams and Melack* [1997] documented ratios of postdisturbance to

predisturbance concentrations of 3.8 for Na, 6.8 for Ca, 3.8 for Mg, 1.3 for Cl, 1.4 for SO₄ and 10.5 for K in a catchment in the central Amazon basin one year following cutting and burning of 80% of the catchment vegetation. The changes in stream cation and ANC following deforestation of small watersheds in these past studies exceed the changes measured in Rondônia, where we observed no statistically significant changes in stream Ca, Mg and ANC, and disturbed to predisturbance ratios of 1.5 and 1.3 (Na) and 2.2 and 1.7 (K) in the dry and wet seasons, respectively. By contrast, changes in chloride in the Rondônia streams exceed changes measured in the small watersheds, suggesting that other processes besides vegetation conversion influence stream Cl response to deforestation.

[36] The lower cation and ANC response in the Rondônia streams may be due to a number of factors, including secondary succession, physiography, sampling strategy, and clearing age. Uptake of nutrients during secondary succession reduces the concentration of solutes in streams [*Bormann and Likens*, 1979; *Vitousek and Reiners*, 1975]. While previous studies report that 47% of deforested areas in the Amazon basin are in some stage of regrowth [*Rignot et al.*, 1997], more recent estimates using Landsat TM imagery and airborne videography suggest that regrowth rates in Rondônia are relatively low (18%) and that most cleared areas remain in pasture after clearing (D. A. Roberts, unpublished data, 2001). Given these land use characteristics, regrowth may have some influence on stream cation concentrations but is not likely to be the main mechanism attenuating land use signals in streams.

Table 5. Ratio of Solute Concentrations in Streams on Basic Lithology to Solute Concentrations in Streams on Acid Lithology for a Given Soil Exchangeable Cation Content^a

	Dry Season	Wet Season
Ca	1.9–2.7	0.8–2.5
Mg	2.7–4.3	1.2–2.4
Si	1.8–2.3	1.8–2.0
ANC	1.8–2.9	0.8–3.2

^a The stream concentrations on each lithology were calculated using regressions of stream solute concentrations versus soil exchangeable cation content parameterized using watersheds on acid lithology only and using watersheds with >33% of the drainage area on basic lithology.

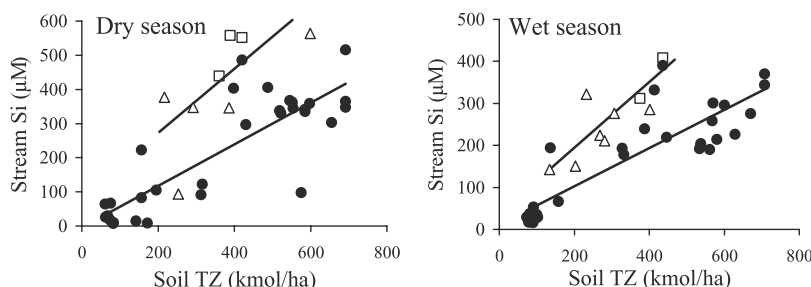


Figure 5. Relationship between soil exchangeable cation content and stream dissolved silicon concentrations for streams on acid lithology (solid circles), for streams with >33% of the watershed area on mica-schist (open squares) and for streams >33% on mafic rock and carbonate shale and <20% on mica-schist (open triangles).

[37] Physiographic characteristics in Rondônia may also reduce the impact of surface disturbance on stream chemistry. The long hillslopes (~590–1200 m) and deep soils of the sampled catchments increase water residence times and the path length of solutes transported through the soil compared with the temperate zone studies, which occurred on catchments with relatively thin soils on steeper, shorter slopes. Elements mobilized by vegetation combustion and organic matter mineralization may be retained on exchange sites within the soil/saprolite during transport in the long hillslopes, buffering streams from the effects of land use change on solute concentrations. Increases in soil pH raise soil cation exchange capacity, further increasing the ability of the soil to retain cations input after surface disturbance [Nye and Greenland, 1960].

[38] The synoptic sampling strategy may also underestimate stream solute responses to deforestation due to undersampling of storm events. In small watersheds, concentrations of stream solutes, especially K, often increase during storm events in undisturbed [Elsenbeer *et al.*, 1995] and disturbed catchments [Williams and Melack, 1997]. Dry season samples do not capture these higher flows and the potentially high solute concentrations associated with them. Wet season samples represent a mixture of wet season base flow and storm flows, depending on the location of the sample relative to the location, spatial extent, intensity and duration of storm events in the watershed. The fraction of total discharge occurring as storm flow is likely to be lower in large catchments sampled during stable hydrologic conditions (Figure 2) compared with small, intensively sampled

catchments [Williams and Melack, 1997] that demonstrate larger impacts of land use activities on solute concentrations. To the extent that the synoptic sampling does not sample storm flows with high solute concentrations, the synoptic sampling method may underestimate the effect of disturbance on stream composition and annual solute fluxes.

[39] Finally, the lack of a strong land use signal for Ca and Mg and relatively low signal for K may be due to the duration of the impact of deforestation on soil water and stream solute concentrations. High concentrations of Ca in seepage water last only four months following deforestation in the eastern Amazon basin [Hölscher *et al.*, 1997], and soil water from deforested areas in the northern Amazon basin have elevated concentrations of K and Mg for 2 years that return to predisturbance levels 5 years after burning [Uhl and Jordan, 1984]. At the small catchment scale, stream Ca concentrations decrease after 3 years following clear-cutting of a small watershed in the eastern United States [Likens *et al.*, 1998], and stream K concentrations fall within 5 years but exceed the predisturbance concentrations for 15 years [Likens *et al.*, 1994]. The average age of clearings in the Rondônia watersheds ranges between 5 and 17 years as measured from a series of Landsat TM images (D. A. Roberts, unpublished data, 2001), which exceeds the duration of the solute pulses measured in soil and stream waters of previous studies. It is possible that deforestation impacts Ca and Mg concentrations, but that the pulse of solutes is short-lived and difficult to detect in watersheds where the average pasture age exceeds the length of the pulse. In that case, the fraction of newly

Table 6. Regression Coefficients of Stream Cation Concentrations Versus Stream Cl and Stream ANC for Streams Draining Acid Lithology and Nonurbanized Catchments Only (Equation (8))^a

	Dry Season			Wet Season		
	β_{Cl}	β_{ANC}	R^2	β_{Cl}	β_{ANC}	R^2
K	0.83 (0.18) ^b	0.14 (0.02) ^b	0.92	1.9 (0.6) ^c	0.11 (0.02) ^b	0.88
Na	0.56 (0.22) ^d	0.21 (0.02) ^b	0.92	ns	0.20 (0.03) ^b	0.81
Ca	ns	0.15 (0.01) ^b	0.98	ns	0.17 (0.01) ^b	0.94
Mg	ns	0.15 (0.01) ^b	0.95	ns	0.15 (0.01) ^b	0.96

^aHere ns indicates $p > 0.05$.

^b $p < 0.0001$.

^c $p < 0.01$.

^d $p < 0.05$.

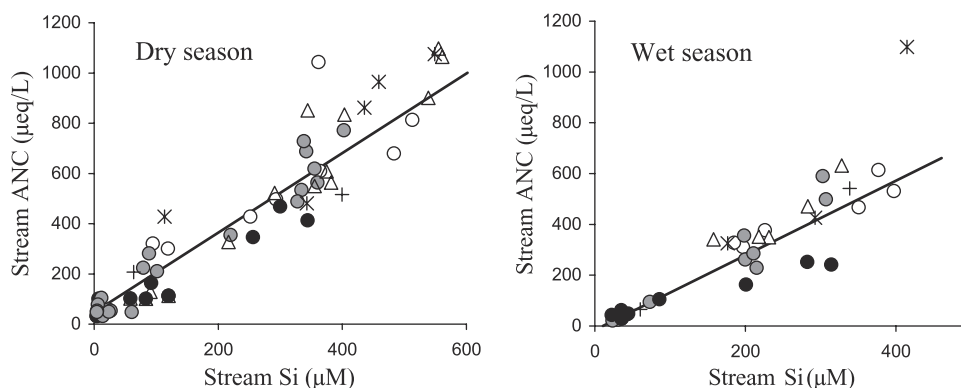


Figure 6. Stream Si versus ANC. Symbols are as in Figures 4 and 5.

cleared and/or burned area in a watershed may more accurately predict stream signals due to deforestation than the aggregate measure used here that includes clearings of all ages.

[40] The presence of K, Na, and SO_4 stream signals and the lack of Ca and Mg signals are consistent with geochemical models of the mobility of elements added to soil as combusted biomass. Ludwig *et al.* [1999] combined the geochemical model PHREECQ with experimental data and found that only 4.7–14.3% of the Ca and 24.7–54.5% of the Mg added to an Amazon Acrisol as wood ash were released into soil water, the remainder being retained on cation exchange sites. The low mobility of Ca and Mg contrasts with the relatively high mobility of K (55–72% of the added K was in dissolved form), Na (70–80% dissolved) and SO_4 (72–85% dissolved). These differences in solubility may explain the different behavior of stream solutes following deforestation, where the most soluble (K, Na, and SO_4) have detectable stream responses to vegetation disturbance, and the least soluble (Ca and Mg) do not. This does not prove that the K, Na, and SO_4 are derived only from ash, or that solubility variation alone explains differences in solute behavior following deforestation, but suggests that differences in solubility may be one mechanism explaining the differences in solute responses to deforestation, and that differences in solubility are consistent with observed solute responses for large (10–10,000 km^2) watersheds.

[41] Deforestation alters not only the mobility of elements in the landscape, but also the hydrologic conditions that determine stream solute concentrations and fluxes. Removal of forest vegetation causes decreases in evapotranspiration, increased groundwater recharge and subsequent increases in annual runoff [Williams and Melack, 1997; Bosch and Hewlett, 1982]. Though it was not possible to measure pre-disturbance and post-disturbance discharge for the sampled catchments, deforestation in Rondônia most likely increases discharge in both dry and wet seasons, which would reduce stream solute concentrations due to dilution. Changes in discharge are probably not responsible for the observed increases in stream solute concentrations, and the Na, K, SO_4 and Cl signals observed here result from enhanced mobilization and transport of solutes to streams.

[42] The considerable scatter about the least squares regression lines in Figures 4a and 4b suggests that streams vary widely in their response to deforestation at the scale of

18–12,500 km^2 . Such variability is expected in a regional survey where aggregate and static measures of watershed properties are used to interpret stream solute concentrations. The deforestation extent measured by Landsat TM imagery used here does not account for other variables that may be important for determining solute composition, including the dynamics of land use history, pasture age and successional status [Vitousek and Reiners, 1975]. We also have not included the location of deforested areas in relation to drainage networks, the presence or absence of riparian zones, and soil properties other than S_i such as soil texture that might influence solute release rates [Smith *et al.*, 1997]. The lack of correlation of stream Ca, Mg, and ANC concentrations with deforestation extent does not conclusively demonstrate that deforestation has no influence on the concentrations of these solutes. Rather, the influence of deforestation on Ca, Mg and ANC is not detectable due to the strong natural controls on pre-disturbance concentrations and to the potential variability of stream solute response to deforestation.

5.4. Urban Signals

[43] Deforestation at a regional scale is not only a process of vegetation conversion for agriculture, but also involves aggregation of human populations in settlements. This is expressed in stream Na, Cl and SO_4 concentrations, which have strong signals in urbanized catchments. The impact of urban areas is expected to increase with time as urbanization progresses and urban populations increase. Streams draining urbanized watersheds in the more industrialized Brazilian state of Sao Paulo have 75% higher chloride concentrations and 91% higher SO_4 concentrations than nonurbanized watersheds [Martinelli *et al.*, 1999]. Urban areas have been identified as strong contributors to stream Cl concentrations, with sources including a wide range of domestic and industrial processes [Prowse, 1987].

5.5. Solute Sources

[44] Simple mass balance calculations can give a preliminary assessment of the potential contributions of burned and decaying biomass, and cattle salts to stream signal concentrations in nonurbanized catchments. The volume-weighted mean deforestation signal concentration of solute i (VWM_i) may be calculated by assuming that solutes from burned and

Table 7. Estimates of Forest Biomass and Cattle Salt Element Inputs, the Expected Volume-Weighted Signal Concentration Expected from the Export of 50% of that Biomass and Cattle Salt in Rondônia Streams, and Comparison with Observed Signals from Nonurbanized Watersheds

	Biomass, Mg/ha	Na, kmol/ha	Ca, kmol/ha	Mg, kmol/ha	K, kmol/ha	Si, kmol/ha	Cl, kmol/ha	SO ₄ , kmol/ha
Aboveground biomass (B_i)								
Central Amazon basin ^a	314	4.92	66.4	31.7	12.2	21.9	–	–
Infertile soils, central Amazon basin ^b	above 406	–	10.8	8.7	11.2	–	–	–
Infertile soils, central Amazon basin ^b	below 32.3	–	1.4	1.1	0.8	–	–	–
Fertile soils, Venezuela ^c	402	–	84.5	17.5	77.4	–	–	–
Rondônia, Brazil ^d	290–495	–	–	–	–	–	–	–
Rondônia, Brazil ^e	285	–	–	–	–	–	–	–
Brazil ^f	–	–	–	–	–	–	3.3	–
Rondônia, Brazil ^g	355–399	–	–	–	–	–	–	1.8–2.1
Soil exchangeable pool ^h	–	1.7–3.6	36–520	12–131	5–34	–	–	–
Input from cattle salts per year ⁱ	–	0.01–0.15	0.006–0.09	0.001–0.021	–	–	0.01–0.15	0.001–0.01
Fraction of biomass element lost to atmosphere during burning (v_i) ^j	–	0.17–0.23	0.09–0.24	0.17–0.43	0.16–0.31	0	0.83 ⁱ	0.67–0.68
Concentration of biomass elements in runoff for 50% deforestation averaged over 10 years, ^k μM	–	29–43	63–748	38–277	59–685	169	4–25	5.3–19
Concentration of biomass elements in runoff for 50% deforestation averaged over 50 years, ^k μM	–	5.8–8.6	13–150	7.6–55.5	12–137	34	0.8–5	1.1–3.7
Concentration of cattle salts in annual runoff ⁱ	–	0.8–12	0.5–7.3	0.1–1.6	–	–	0.8–12	0.06–0.9
Total signal concentration from 10 year averaged biomass export and cattle salts	–	30–55	64–755	38–279	59–596	169	5–37	5.3–18.5
Observed wet season signal concentration (C_{di}) ^h	Mean \pm SD	17 \pm 39	–	–	17 \pm 22	–	9 \pm 7	–
Observed background concentration (C_{fi})	–	60 \pm 39	75 \pm 37	64 \pm 26	52 \pm 15	278 \pm 96	4.4	2.0

^a Lucas *et al.* [1993].^b Klinge [1976] as cited by Vitousek and Sanford [1986].^c Hase and Fölster [1982].^d Alves *et al.* [1997].^e Brown *et al.* [1995].^f McKenzie *et al.* [1996].^g Guild *et al.* [1998].^h This study, Table 4.ⁱ H. Schmitz (personal communication, 1999). Calculated for 50% of watershed as pasture and stocking densities between 0.1 and 1.5 cattle/ha.^j Mackensen *et al.* [1996].^k Equation (9), this study.^l Lobert *et al.* [1999].

decaying biomass are released into streams at a constant rate over a time period t :

$$\text{VWM}_i = \frac{10^3 DB_i (1 - v_i)}{qt} \quad (9)$$

where VWM_i is in μM , D is the percent of the catchment deforested, B_i is the biomass content of element i in kmol/ha, v_i is the fraction of element i lost to the atmosphere via particle transport and volatilization during burning, q is annual specific discharge in mm/year, and t is in years. Though the element content of biomass has not been measured for Rondônia's open tropical rain forests, total biomass has been measured in Rondônia and does not differ significantly from the biomass of rain forests for which elemental data are available (Table 7). The range of elemental composition of Rondônia's open rain forests is therefore assumed to be similar to other forests in the

Amazon basin. Belowground biomass on moderately fertile to infertile soils varies between 3.4% and 14% of total biomass (Table 7). An upper bound on the VWM_i can be estimated on the assumption that belowground biomass decomposes and represents 15% of total biomass, and a lower bound can be specified if there is no export of elements contained in belowground biomass to streams. The net amount of each cation transferred to the atmosphere due to volatilization and particle transport (v_i) varies from a low of zero if cations are deposited locally within the watershed to a high of field-scale measured values for cation export in ash if those particles are exported beyond watershed boundaries. Specific discharge (q) is 650 mm/year, the average for 1998 and 1999 for 7 discharge stations in the state.

[45] In addition to combusted biomass, additional cations, chloride and sulfur added via supplemental minerals and salts given to cattle may influence stream chemistry. Table 7

shows the range of cation and chloride inputs expected from the supply of cattle salts at 0.9 kg salt/month per head (H. Schmitz, personal communication, 1998), at stocking densities reported for the Amazon basin between 0.1 and 1.5 head per hectare [Loker *et al.*, 1997; Weinhold, 1999]. The calculations assume no net retention of salt ions in cattle biomass or on soil exchange sites, and that all ranchers give cattle supplemental salts.

[46] Sodium and chloride have the largest potential contribution from cattle salts relative to the 10-year average biomass contribution, with 2–30% (Na) and 4–75% (Cl) of their VWM potential signal concentrations attributable to cattle salts, depending on cattle stocking density and the magnitude of the biomass signal. Although high concentrations of K may occur in cattle wastes [Withers *et al.*, 1998], no additional K is added in the supplemental salts reported here. Cattle-derived K originates in ingested biomass, which may alter the form and rate of transport but not the ultimate source of K to streams.

[47] The wet season land use signal concentrations of Na, K, SO₄ and Cl for nonurbanized watersheds fall within the range of the 10-year VWM_{*i*} concentrations from the export of biomass and cattle salts (Table 7). Averaged over 50 years, the biomass input could still provide most of the observed K signal, but the observed Na and Cl signals require inputs from other sources, here assumed to be cattle salts. The low SO₄ signals measured in streams correspond with the low concentration of sulfur in biomass, a high loss of sulfur during biomass burning, and low inputs from cattle salts.

[48] The calculated VWM_{*i*} overestimates the actual amount of elements available for export to streams, since the calculation assumes that soils and regenerating biomass do not absorb or assimilate any elements mobilized by deforestation. It may also underestimate the amounts of available elements, since regenerating vegetation may make previously inorganically held elements biologically active and available for release in the next burning cycle [Nye and Greenland, 1960]. Finally, deforested catchments likely have higher runoff rates than forested catchments due to the reduction of evapotranspiration following removal of forest vegetation. This would cause runoff volumes to be higher in deforested basins and disturbance effects on stream concentrations to be lower. Despite these uncertainties, the observed land use signal concentrations fall within and below the range of concentrations of Na, Cl, K, and SO₄ expected from exporting biomass element content and cattle salts over a decadal timescale. This does not prove that biomass and cattle salts are the only sources of the signal, but does demonstrate the likelihood and provides a framework for testing the effect of remaining uncertainties on calculated signal concentrations. Soil cation reservoirs could contribute even more cations to soil and stream waters following disturbance, but their influence is not calculated here.

6. Conclusion

[49] Natural variations in soil and rock type exert strong controls on all stream solute concentrations except Cl and SO₄. Soil exchangeable cation content is the best predictor of the concentrations of all stream solutes except chloride and sulfate, which depend on deforestation extent and urban population density. The mechanism relating soil

cation content to stream solute concentrations is not known, but may be related to the effect of soil depth on bedrock weathering rates. Deforestation happens preferentially on soils with high cation contents, so streams draining deforested watersheds have higher Ca, Mg, Si, and ANC concentrations than streams draining forested watersheds due to natural variations in soil properties and rock type and not to human disturbance. Rock type influences stream Ca, Mg, Si, and ANC concentrations and further complicates the detection of human impacts on their concentrations.

[50] The natural controls on stream chemistry may be statistically removed to demonstrate that K, Na, and Cl concentrations in both seasons and SO₄ in the dry season depend on deforestation extent for nonurbanized watersheds, though the response is highly variable. Stream K and Na concentrations are associated with stream Cl concentrations, indicating anthropogenic contributions to stream Na concentrations in the dry season and to stream K in both seasons. Stream Ca, Mg and ANC may be influenced by deforestation, but the effect is either too small or too variable to be detected given natural variability due to soil and rock type. The weak stream signal may be caused by retention on cation exchange sites or by the duration of solute pulses following deforestation that may not be detectable averaged over a catchment with variable pasture ages. Watershed level indices of pasture age and regrowth rates may help explain the substantial variation in watershed level responses to regional deforestation.

[51] Land use activities besides vegetation conversion are important for determining the ultimate impact of regional deforestation on stream solute concentrations. Cattle salt inputs likely impact Na and Cl concentrations, particularly during the dry season, and urban areas significantly influence stream Cl and SO₄ concentrations in urbanized watersheds. Further research could examine how these other processes deliver solutes to streams, and for what watershed sizes each becomes important in determining human impact on stream chemistry.

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