Biogeochemistry **68:** 227–257, 2004.

Natural controls and human impacts on stream nutrient concentrations in a deforested region of the Brazilian Amazon basin

T.W. BIGGS[1,*], T. DUNNE[2] and L.A. MARTINELLI[3]
[1]*Department of Geography, University of California, Santa Barbara, CA 93106, USA;* [2]*Donald Bren School of Environmental Science and Management, and Department of Geological Sciences, University of California, Santa Barbara, CA 93106, USA;* [3]*Centro de Energia Nuclear na Agricultura, Avenida Centenário 303, Piracicaba-SP, 13416-000, Brazil; *Author for correspondence (e-mail: tbiggs@bren.ucsb.edu; phone: +1-805-893-8816; fax: +1-805-893-7612*

Received 5 August 2002; accepted in revised form 19 August 2003

Key words: Biogeochemistry, Deforestation, Nitrogen, Phosphorus, Tropical, Urban

Abstract. This study documents regional patterns in stream nitrogen and phosphorus concentrations in the Brazilian state of Rondônia in the southwestern Amazon basin, and interprets the patterns as functions of watershed soil properties, deforestation extent, and urban population density. The survey includes 77 different locations sampled in the dry and wet seasons, with a watershed size range from 1.8 to 33,000 km^2 over a total area of approximately 140,000 km^2. A sequential regression technique is used to separate the effects of natural watersheds properties and anthropogenic disturbance on nutrients and chloride. Natural variation in soil texture explains most of the variance in stream nitrate concentrations, while deforestation extent and urban population density explain most of the variance in stream chloride (Cl) and total dissolved nitrogen (TDN) concentrations. Stream TDN, total dissolved phosphorus (TDP), particulate phosphorus (PP) and Cl concentrations all increase non-linearly with deforestation extent in the dry season after controlling for natural variability due to soil type. Stream nutrient and Cl disturbances are observed only in watersheds more than 66–75% deforested (watershed area range 2–300 km^2), suggesting stream nutrient concentrations are resistant to perturbation from vegetation conversion below a 66–75% threshold. In heavily deforested watersheds, stream Cl shows the largest changes in concentration (12 ± 6 times forested background), followed by TDP (2.3 ± 1.5), PP (1.9 ± 0.8) and TDN (1.7 ± 0.5). Wet season signals in Cl and TDP are diluted relative to the dry season, and no land use signal is observed in wet season TDN, PN, or PP. Stream TDN and TDP concentrations in non-urban watersheds both correlate with stream Cl, suggesting that sources other than vegetation and soil organic matter contribute to enhanced nutrient concentrations. Small, urbanized watersheds (5–20 km^2) have up to 40 times the chloride and 10 times the TDN concentrations of forested catchments in the dry season. Several large watersheds ($\sim$1000–3000 km^2) with urban populations show higher Cl, TDN and TDP levels than any small pasture watershed, suggesting that human impacts on nutrient concentrations in large river systems may be dominated by urban areas. Anthropogenic disturbance of dry-season stream Cl and TDN is detectable in large streams draining deforested and urbanized watersheds up to 33,000 km^2. We conclude that regional deforestation and urbanization result in changes in stream Cl, N and P concentrations at wide range of scales, from small pasture streams to large river systems.

Introduction

Cattle ranching, agriculture and logging in the Amazon basin have resulted in the clearing of 550,000 km^2 of tropical rainforest by 1998, totaling 15% of the basin

(INPE 2000). Despite the scale and rate of these transformations of the rainforest ecosystem, their impact on regional biogeochemical cycles, water chemistry and water quality are not well understood or quantified. Changes in nitrogen and phosphorus concentrations are of particular concern, since they often limit the productivity of aquatic ecosystems and have been identified as contributors to enhanced eutrophication and water quality deterioration (Novotny and Chesters 1981; Carpenter et al. 1998; Downing et al. 1999). Streams draining pastures in small watersheds ($\sim 10\,km^2$) in the Amazon basin exhibit marked differences in stream nutrient concentrations and dissolved N:P ratios compared with forested streams (Neill et al. 2001). How results from small streams on a given soil type generalize to other soil types, how spatially variable the response is, and how results from small watersheds scale to larger watersheds are unknown.

Land use change impacts stream nutrient chemistry partly through its effects on nutrient cycling in vegetation and soil organic matter. Cutting and burning of forest vegetation adds nutrients to soils directly via combusted biomass and indirectly by enhancing the rates of decomposition of organic matter and reducing plant nutrient uptake (Nye and Greenland 1960, Uhl and Jordan 1984, Guggenberger et al. 1996). These enhanced inputs may increase the concentration and fluxes of nitrogen and phosphorus in streams draining disturbed catchments (Bormann and Likens 1979; Vitousek et al. 1979; Malmer 1996; Williams and Melack 1997). Subsequent vegetation growth may retard or reverse this process via uptake by vegetation and storage in soil organic matter (Vitousek and Reiners 1975). Nutrient cycling rates may also change following deforestation. Nitrogen mineralization and nitrification rates in pasture soils are lower than in forest soils (Neill et al. 1995), which results in lower nitrate concentrations in streams draining small deforested catchments (Neill et al. 2001).

Land-use activities besides conversion of forest vegetation to grassland may also affect stream nutrient concentrations. Following the cutting and burning of forest vegetation, farmers in the Amazon establish a mix of annual crops, perennial crops, and pasture (Pedlowski et al. 1997). This early ‘slash and burn’ agriculture is typified by low inputs of fertilizer, and over time, pastures often replace the crops due to falling crop productivity and weed invasion (Nye and Greenland 1960). Ranching dominates land use in the Brazilian Amazon, and the number of cattle in the Brazilian state of Rondônia reached 3 million by 1994 (Pedlowski et al. 1997). Though low intensity grazing tends to have lower impacts on stream chemistry than fertilized agriculture in humid temperate watersheds (Sonzogni et al. 1980; Clark 1998) high stocking densities can contribute to high concentrations of N and P in streams (Beaulac and Reckhow 1982; Carpenter et al. 1998; McFarland and Hauck 1999).

Deforestation of large areas (>100–$1000\,km^2$) also involves the establishment of urban service centers. A majority of the human population of Rondônia lives in urban areas, and the Brazilian Amazon is increasingly becoming recognized as an ‘urbanizing frontier.’ (Browder and Godfrey 1997). Urban areas are associated with increased concentrations and fluxes of nitrogen and phosphorus in streams (Vollenweider 1971; Sonzogni et al. 1980; Howarth et al. 1996; Carpenter et al.

1998). In the economically more developed southeastern states of Brazil, urbanized watersheds have substantially elevated concentrations of nitrogen and phosphorus, and point sources dominate over non-point sources of enhanced stream nutrient concentrations (Martinelli et al. 1999; Ometo et al. 2000). In the Amazon basin, watersheds with urban populations have higher concentrations of Cl and SO_4 than non-urbanized watersheds of similar deforestation extents (Biggs et al. 2002), though how urbanization affects nutrient concentrations in streams of varying sizes has not been reported.

The detection of human influence on biogeochemical processes is complicated by natural variability in nutrient cycling and stream chemistry in undisturbed watersheds (Sonzogni et al. 1980). Stream concentrations of cations vary with soil cation status (Biggs et al. 2002), and stream carbon, nitrogen, and phosphorus levels vary with soil nutrient content (Pote et al. 1999), C:N ratios (Aitkenhead and McDowell 2000), geology (Dillon and Kirchner 1975) and geomorphology (Kirchner 1974; Hill 1978; Creed and Band 1998), confounding the separation of natural and human effects on nutrient concentrations. Soil texture in the Amazon basin varies on both local and regional scales (Sombroek 1966), which can impact the stocks and cycling rates of nitrogen (Vitousek and Matson 1988) and phosphorus (Vitousek and Sanford 1986), though watershed-scale controls on stream concentrations of nitrogen and phosphorus in undisturbed humid tropical catchments have not been documented (Vitousek and Sanford 1986; Bruijnzeel 1991).

The questions we address in this paper are: (1) What natural watershed properties control the stream concentrations of nitrate, dissolved and particulate nitrogen and phosphorus in forested catchments; (2) Is there a detectable human influence on stream nutrient concentrations, after natural variability has been controlled for; (3) For how large a watershed is a land-use signal detectable; and (4) What might cause changes in stream nutrient concentrations? We employ a 'snapshot' survey method (Grayson et al. 1997) and quantify watershed-averaged soil properties, deforestation extent, and urban population density in a geographic information system (GIS) to determine the relationship between stream nutrient concentrations and watershed characteristics.

Field area

The Brazilian state of Rondônia (Figure 1) lies in the southwestern Amazon basin on the Brazilian craton (8–13°S, 60–66°W), with a basement of gneiss and granite (Bettencourt et al. 1999). Tertiary sediments overlie the craton in the north and mica-schist and mafic gabbros occur in the southeastern intracratonic graben (CPRM 1997). Soil types include Oxisols, Entisols and Inceptisols in the north on the Tertiary sediments, Ultisols and Alfisols in the state's central cratonic region, and psamments on white quartz sands in the southeast. For maps of soil type and lithology, see Biggs et al. (2002).

Rainfall averages 1930–2690 mm/year with a distinct wet season lasting from October to April. Average runoff ranges from 563–926 mm/year, as measured by

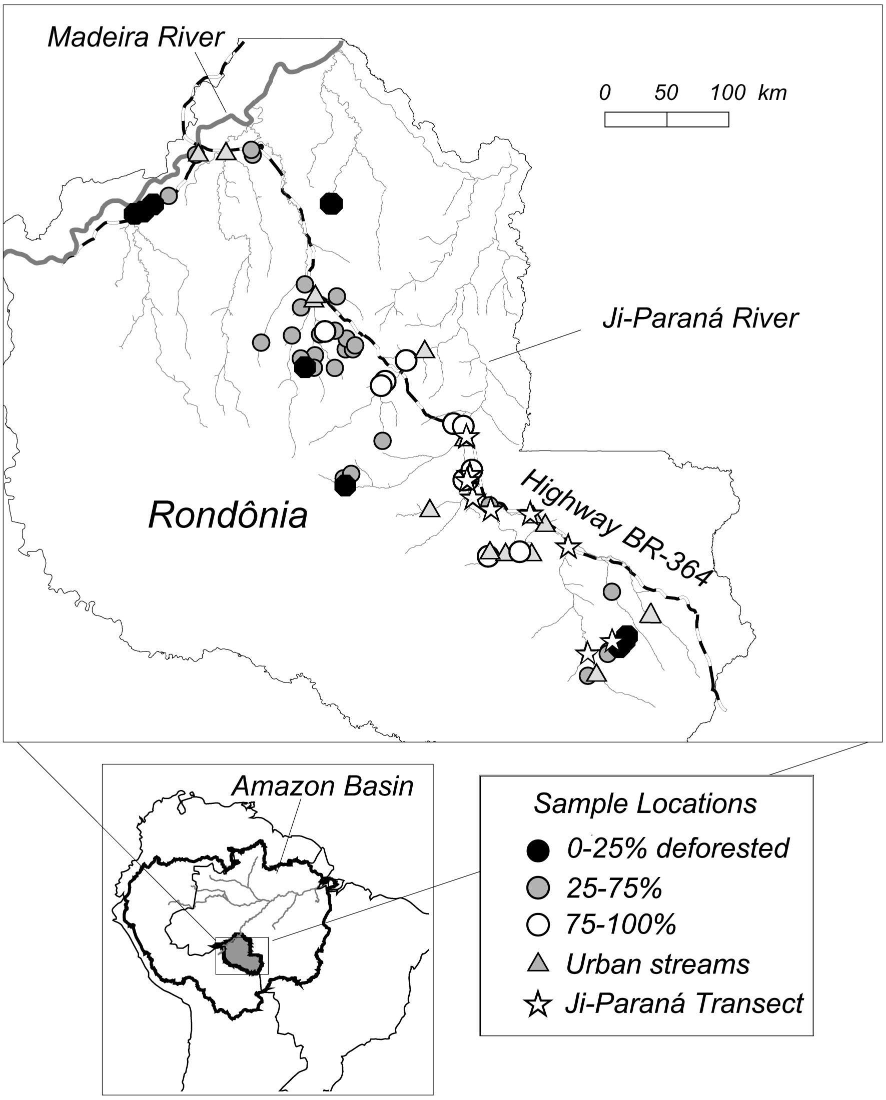

Figure 1. Field site in the Brazilian State of Rondônia, with stream sampling locations by deforestation extent.

nine discharge stations maintained by the Agência Nacional de Energia Elétrica and CPRM. The streams drain to the Madeira River, a white-water tributary of the Amazon main-stem (Figure 1). Streams in Rondônia are clear and black water streams, with low dissolved and particulate loads (Mortatti et al. 1992). The largest river in the state is the Ji-parana River, which drains an area of 64,000 km^2 where it meets the Madeira River.

The undisturbed forest includes dense tropical rainforest (*floresta densa*, 17% of Rondônia state area), 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 rainforest (RADAMBRASIL 1978). Savannas cover 5–8% of the southeast of the state as estimated from Landsat TM imagery (Roberts et al. 2002).

The first wave of colonization in Rondônia began in the early 1970s. Approximately 1 million people migrated to the state and settled along the principal highway between 1970 and 1990. By 1998, 53,275 km^2, or 22% of the total state 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 on Tertiary sediments is in some stage of regrowth (Rignot et al. 1997), though on the craton up to 85% of cleared areas remain as pasture (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 (IBGE 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).

Methods

Stream nutrient concentrations model

Stream nutrient concentrations represent the sum of a pre-disturbance background concentration and a signal concentration due to disturbance (Biggs et al. 2002):

$$C_t = C_f + C_d \tag{1}$$

where C_t is the observed concentration in the stream at a given location, C_f is the background or pre-disturbance concentration, and C_d is the concentration due to disturbance, which may be either positive or negative. The background concentrations C_f are modeled as linear functions of soil properties:

$$C_f = \beta_o + \beta_s S_{for} + \varepsilon_s \tag{2}$$

where β_o is the regression intercept, β_s is the soil regression parameter, S_{for} is a watershed-averaged soil property, such as soil N or P content in kmol/ha, or soil sand percent, in the upper 20 cm of the soil profile, and ε_s is the error term. S_{for} was calculated using only soil profiles located in forested areas, since including soil profiles in deforested areas would bias the estimate of pre-disturbance stream nutrient concentrations. For all catchments, forested and deforested, the signal concentration due to disturbance is calculated as the difference between the observed concentration and the background concentration predicted by (2)

$$C_d = C_t - (\beta_o + \beta_s S_{for} + \varepsilon_s) \tag{3}$$

The signal concentration is modeled as a non-linear function of deforestation extent, both with and without a soil-interaction term:

$$C_d = \beta_d D^{\delta} + \varepsilon_d \tag{4a}$$

$$C_d = \beta_t (SD)^{\eta} + \varepsilon_d \tag{4b}$$

where β_d is the deforestation regression parameter, D is the deforestation extent as a fraction of watershed area, δ is a non-dimensional exponent, β_i is the interaction regression parameter, η is the interaction exponent, and ε_d is the error term. The deforestation signal regressions do not contain intercepts, since the signal concentration should be zero for zero deforestation extent, and was not statistically different from zero ($p > 0.05$) for all regressions reported here.

The regression parameters in Equations (2)–(4b) were estimated in two ways. First, β_o and β_s were estimated using forested watersheds only, using Equation (2). Then, C_d for all watersheds was calculated, and the parameters in Equations (4a) and (4b) determined using non-urbanized watersheds of all deforestation extents. In the second estimation procedure, β_o, β_s, and β_d were determined in a multiple regression model, using non-urban watersheds of all deforestation extents, both as an additive model, and as an interaction model:

$$C_t = \beta_o + \beta_s S_{for} + \beta_d D^{\delta} + \varepsilon_d \tag{5a}$$

$$C_t = \beta_o + \beta_i (SD)^{\eta} + \varepsilon_d \tag{5b}$$

where the parameters are as defined in Equations (3), (4a), and (4b). For watersheds with urban populations, an additional regression was determined:

$$C_u = C_t - C_f - C_d \tag{6a}$$

$$C_u = \beta_u \log(U) \tag{6b}$$

where C_u is the signal concentration due to urban areas, C_d is estimated using Equation (4a) or (4b), C_f is estimated from Equation (2), β_u is the urban regression parameter, log is the base-10 logarithm, and U is the urban population density in persons/km^2, calculated as the total urban population in the watershed divided by the watershed area. The C_u and β_u were determined using only watersheds with urban populations. The log of U was used due to the wide range of urban population densities in the watersheds (0.5–1600). Using a linear regression on U results in strong influence of one or two outlier points with high urban population densities.

In-stream processing influences stream nutrient concentrations and fluxes for a range of watershed sizes (Triska et al. 1989; Howarth et al. 1996; Smith et al. 1997; Alexander et al. 2002a). We tested for the possible influence of watershed size and average channel travel distance to the sampling point by including an additional term in Equation (4a)

$$C_d = \beta_d D^{\delta} e^{-kd_a} + \varepsilon_d \tag{7}$$

where d_a is the mean flow distance to the watershed outlet in km, and k is the in-stream processing coefficient in 1/km. For urban populations, Equation (6) was modified to incorporate an in-stream processing term:

$$C_{\mathrm{u}} = \beta_{\mathrm{u}} \sum_{j=1}^{n} \log(U_j) \mathrm{e}^{-kd_j} \tag{8}$$

where U_j is the urban population density in urban area j, n is the number of urban areas in the watershed, and d_j is the in-stream distance from the urban center to the sampling location in km.

The regression parameters and their p-values in Equations (4)–(8) were determined using non-linear least-squares by the Gauss–Newton method (Matlab Version 6.0). In the Rondônia streams, the regression errors tended to increase with deforestation extent for chloride, total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP). Weighted regression is used to stabilize the variance with the weighting function indicated in Table 3.

Extrapolation beyond the range of calibration was necessary for predicting background concentrations of nitrate, since some deforested watersheds have lower sand content than any forested catchment. We did not allow for negative background concentrations, and assigned watersheds minimum nitrate and TDN concentrations equal to the lowest measured concentration in forested catchments (0.3–1.3 μM).

Stream chemistry

Stream water samples were collected from 77 locations in the dry season, August 1998, and 66 locations in the wet season, February 1999. See Biggs et al. (2002), for more detailed description of hydrologic conditions during sampling. Fifty of the dry season watersheds and 35 of the wet season watersheds had no urban populations. All non-urban watersheds represent hydrologically independent samples, and are non-nested. Seventeen samples were collected from watersheds with urban populations in the dry season, and 15 in the wet season. In some cases, samples from urban watersheds were collected downstream of non-urban sampling locations, but each sample from urban watersheds is hydrologically independent from the other urban samples. Each sample is both hydrologically and statistically independent from the other watersheds, reducing autocorrelation problems when estimating the parameters in Equations (2)–(8). Ten dry season and 16 wet season samples were collected along a transect of the Ji-Paraná River, the largest river basin in Rondônia, but these samples were not used to parameterize the regression equations due to potential autocorrelation problems. Additional samples were collected in two highly urbanized watersheds in the dry season of 2002.

Water samples were filtered in the field using 0.7 μM Whatman glass fiber filters, kept at 4 °C and frozen prior to transport for chemical analysis. Particulate nitrogen and phosphorus samples were collected on pre-ashed 0.7 μM glass fiber filters, air-dried overnight, and frozen prior to transport for analysis. Nitrate and chloride were determined with ion chromatography on a Dionex DX500. TDN and TDP concentrations were determined for the filtered water samples using simultaneous persulfate digestion (Valderrama 1981), followed by colorimetric determination of the resulting nitrate and phosphate with automated colorimetric flow injection analysis. Particulate nitrogen and phosphorus concentrations were determined using simultaneous persulfate digestion on the glass-fiber filters.

Watershed properties

Watershed boundaries were digitized into a GIS using 1:100,000 scale topographic maps and the coordinates of collection points recorded in the field with a global positioning system. Flow-path lengths (d_i and d_j) were calculated using a 90-m SRTM digital elevation model and a flow-accumulation algorithm in ARC/INFO.

Land cover was determined from a mosaic of eight Landsat TM images from 1998 classified using spectral mixture analysis (SMA) (Roberts et al. 2002). Given the difficulty of spectrally separating pasture from regenerating vegetation, the fraction of the catchment deforested (D) includes both pasture and regenerating vegetation, and represents a mosaic of clearings of different ages and regenerating forest in various stages of regrowth. Approximately 15% of cleared areas in Rondônia become secondary growth forests (Roberts et al. 2002), so the effect of regenerating secondary vegetation on stream nutrients is likely to be small. The deforestation extent (D) also does not include information on grazing intensity or the condition of riparian zones, which may affect stream nutrient concentrations (Carpenter et al. 1998; McFarland and Hauck 1999).

Soil organic carbon (OC), nitrogen, phosphorus, sand, silt and clay contents in the upper 20 cm were calculated for each watershed from digitized soil maps and soil profile analyses of the Sigteron project (Cochrane 1998). The contents were computed as the average content for the soil types present in each watershed weighted by the fraction of the watershed covered by each soil type (Biggs et al. 2002). Soil properties were calculated using soil profiles located in forested areas only (2152 of 2932 profiles in the database), which included biological reserves, areas with selective logging activity, and extractive reserves. In the Sigteron project, soil OC was determined using dichromate acid oxidation (Walkey and T.A. 1934), total nitrogen with Kjeldahl digestion (Bremner and Mulvaney 1982), and soil P with Mehlich-P1 extraction (Mehlich 1953).

Results

Watershed properties

The sampled watersheds include the range of soil types and deforestation extents encountered in Rondônia (Table 1). Catchments more than 75% deforested range from 2 to 300 km^2. Forested catchments (<25% deforested) tend to contain sandy

Table 1. Number of samples and average area, urban population density and soil properties of the sampled watersheds by deforestation extent. Values presented as mean and (range). Urban watersheds include watersheds with $U > 0$. Deforestation extent includes all areas cleared up to 1998.

	Watershed deforestation extent			Total
	0–25%	25–75%	75–100%	
Number of samples				
Dry season				
Non-urban	11	28	11	50
Urban	2	11	4	17
Jip-transect	2	8	0	10
Total	15	47	15	77
Wet season				
Non-urban	8	17	10	35
Urban	2	8	5	15
Jip-transect	2	14	0	16
Total	12	39	15	66
Area (km^2)				
Non-urban	1574 (63–12353)	148 (1.7–630)	106 (2.0–308)	425 (1.7–12353)
Urban	2130–2576	3183 (7–33,000)	557 (364–846)	967 (7–33,000)
Urban population density (persons/km^2), urban watersheds only	0.5–21	96 (1–579)	461 (2–1700)	215 (0.5–1700)
Soil properties				
OC (kmol/ha)	342 (319–356)	361 (322–393)	373 (329–392)	355 (319–393)
N (kmol/ha)	24.8 (23.3–26.3)	25.8 (23.3–27.7)	26.7 (23.7–28.2)	25.4 (23.3–28.2)
P (kmol/ha)	0.33 (0.24–0.65)	0.40 (0.23–0.69)	0.48 (0.24–0.63)	0.41 (0.23–0.88)
Sand %	68 (55–84)	54 (46–70)	52 (44–56)	55 (44–84)
Clay %	24 (12–34)	34 (22–41)	35 (30–42)	33 (12–42)

soils with lower OC, N and P contents compared with deforested catchments. The difference in soil properties between forested and deforested watersheds is not due to deforestation, but rather reflects the differences prior to disturbance, and likely reflects preferential deforestation on more fertile soils.

All soil nutrient concentrations correlate with soil texture and with other soil nutrients. Soil N, P, OC, C:N, and pH correlate positively with soil silt content (Table 2). Soil OC correlates with both soil N ($r = 0.98$) and soil P ($r = 0.57$). The significance levels of the coefficients did not depend on whether the Pearson parametric or Spearman rank non-parametric method was used. Table 2 includes the Pearson correlation coefficients.

Soil properties and stream nutrient concentrations

Soil properties affect the concentrations of all stream constituents except Cl. Stream nitrate concentrations correlate with watershed-averaged soil sand content, and

Table 2. Pearson correlation coefficients for soil attributes and stream solute concentrations.

	Soil property							
	Clay %	Silt %	N	P	C:N	N:P	OC	pH
Soil properties n = *61*								
Clay %	**1**							
Silt %	0.68*	1						
N	0.06	0.46*	1					
P	0.15	0.73*	0.53*	1				
C:N	0.58*	0.66*	0.42*	0.39**	1			
N:P	0.71*	0.27°	−0.09	−0.21	0.66*	1		
OC	0.21	0.58*	0.98*	0.57*	0.55*	0.05	1	
pH	−0.03	0.47*	0.29°	0.47*	0.63*	0.14	0.34*	
Defor (*D*)	0.49*	0.43*	0.43*	0.24°	0.40*	0.34*	0.50*	
Stream nutrient concentrations: all samples								
NO_3	−0.71*	−0.42*	0.26°	0.00	−0.14	−0.34*	0.17	0.19
TDN	0.08	0.50*	0.61*	0.64*	0.17	−0.27°	0.59*	0.19
TDP	0.12	0.47*	0.55*	0.58*	0.12	−0.27°	0.52*	0.14
PN	0.28	0.23	0.03	0.06	0.18	0.02	0.03	−0.29°
PP	0.13	0.44*	0.40*	0.55*	0.12	−0.23	0.39*	0.11

*$p < 0.01$, **$p < 0.1$.

stream TDP, particulate phosphorus (PP) and TDN concentrations correlate with soil P, OC, and N in both seasons (Table 2, Figure 2). Soil P has the most statistically significant β_s and was used to predict dry season C_f for TDN and TDP. Background concentrations C_f for dry season Cl and PN, and for wet season Cl, TDN, PN and PP were calculated as the average concentration in forested catchments, since the soil regression parameter was statistically insignificant using forested watersheds only.

Deforestation signal

Dry season concentrations of Cl and PP and signal concentrations of TDN, nitrate and TDP increase non-linearly with deforestation extent in non-urbanized watersheds (Figure 3). β_d is statistically significant and positive for all solutes except PN. δ is statistically significant ($p < 0.05$) for all solutes except PN and NO_3. The stream deforestation signal is not detectable for watersheds less than 66–75% deforested, and β_d is significantly different than zero only when watersheds greater than 66–75% deforested are included in the regression (Eqs. (4a) and (5a)). The interaction model (Eqs. (4b) and (5b)) gave the highest R^2 for both TDP and PP (Table 3). In the wet season, β_d is statistically significant for chloride and TDP only. Signal concentrations of nitrate increase slightly with deforestation. The detection of this signal depends on correcting for the influence of soil properties on pre-disturbance concentrations, since high nitrate concentrations occur in streams draining forested watersheds on sandy soils.

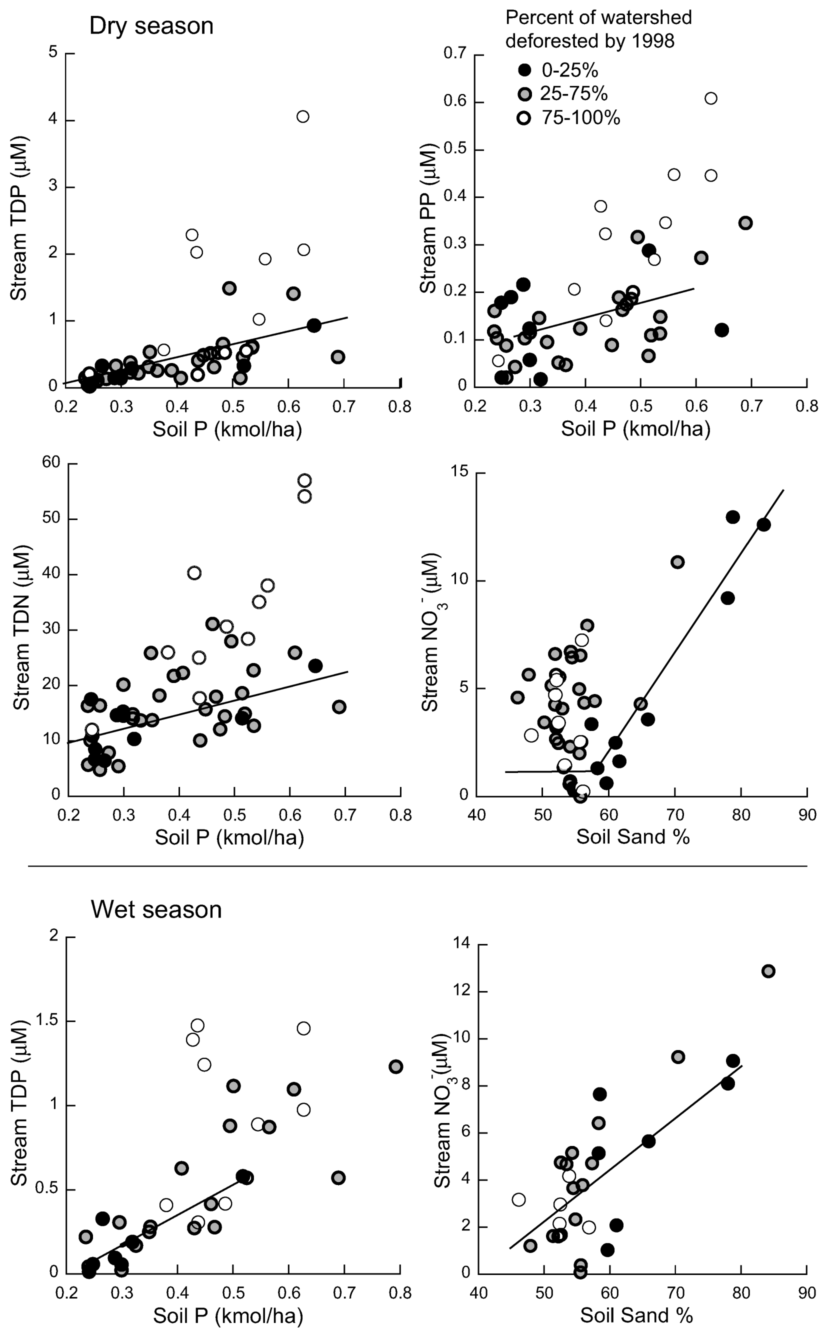

Figure 2. Stream nutrient concentrations as a function of watershed soil properties, dry and wet seasons. Non-urbanized catchments only. Lines represent regression lines for forested catchments only (Eq. (2)).

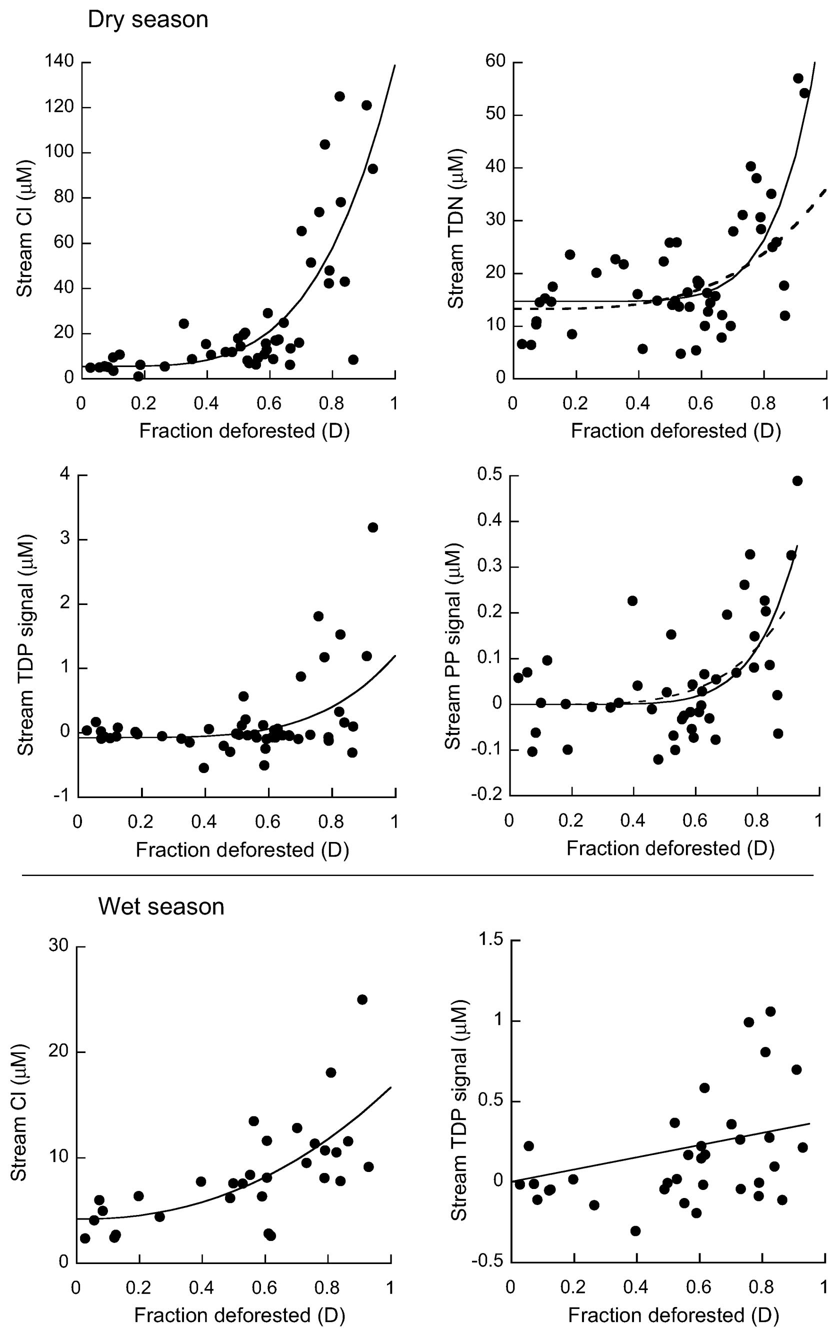

Figure 3. Stream chloride and nutrient concentrations versus total deforestation extent in the dry season, non-urban watersheds only. Solid lines are the best-fit lines for Equation (4a), dashed-lines represent the best-fit line excluding high outliers.

Table 3. Mean and standard deviations for regression parameters using non-urbanized watersheds. For dry season nitrate, dry season TDN, and wet season TDP, the top number in each cell is the parameter value for the separate background and signal regressions (Eqs. (2) and (4a)), and the bottom number is the parameter value for the combined, multiple regression (Eq. (5a)). The interaction parameter values were determined using Equation (5b). R^2soil and R^2 defor is calculated using the soil property or the deforestation extent as the only independent variable, and R^2 soil + *defor* is the variance explained using both variables.

	Additive models (Eqs. (2), (4a) and (5a))								
β_d	*Weight function*	*Soil property*	*Deforestation parameter* β_d	*Deforestation exponent* δ	*Soil parameter* β_S	*Intercept* β_o	R^2 *soil*	R^2 *defor*	R^2 *Soil + defor*
Cl									
Dry season	1/*D*	None	137 (25)[a]	4.3 (0.7)[b]	–	5.4 (0.6)[a]	–	0.63	0.63
Wet season	None	None	12.5 (3.0)[b]	2.2 (1.1)[c]	–	4.2 (1.5)[c]	–	0.46	0.46
TDN									
Dry season	None	Soil P	53 (17)[c]	8.3 (2.6)[c]	22 (11)[d]	ns	0.39	0.49	0.64
			52 (18)[c]	8.6 (2.8)[c]	39 (8)[c]	ns			
Wet season	None	Soil P	ns	ns	22.4 (7.9)[c]	11 (3.5)[c]	0.23	0.0	0.23
Nitrate									
Dry season	None	Sand%	3.8 (0.6)[c]	ns	0.46 (0.06)[b]	−25 (4)[b]	0.46	0.02	0.55
			5.1 (1.8)[c]	ns	0.37 (0.05)[b]	−19 (4)[b]			
Wet season	None	Sand%	ns	ns	0.22 (0.11)[c]	ns	0.62	0.0	0.62
TDP									
Wet season	$1/\sqrt{D}$	Soil P	0.33 (0.14)[c]	ns	1.6 (0.3)[b]	−0.4 (0.1)[c]	0.50	0.34	0.58
			0.38 (0.18)[c]	ns	1.7 (0.4)[b]	−0.4 (0.1)[c]			

Table 3. (continued)

	Interaction models (Eq. (5b))							
	Weight function	*Soil property*	*Interaction parameter* β_i	*Interaction exponent* η	*Intercept* β_o	R^2 *soil*	R^2 *defor*	R^2 *soil* $\times$ *defor*
TDP								
Dry season	1/D	Soil P	8.0 (3.6)[c]	2.2 (0.5)[a]	0.19 (0.02)[c]	0.39	0.49	0.65
PP								
Dry season	None	Soil P	1.8 (0.6)[c]	2.5 (0.5)[a]	0.1 (0.02)[c]	0.37	0.41	0.66
Wet season	None	Soil P	ns	ns	ns	0.13	0.0	0.14

[a]$p < 0.00001$, [b]$p < 0.001$, [c]$p < 0.05$, [d]$p < 0.10$, ns not significant ($p > 0.1$)

Chloride has the largest disturbance ratio (C_t:C_f) of all stream constituents (12.5 ± 6.4) followed by PP (1.9), NO_3 (2.6), TDP (2.3), and TDN (1.7) (Table 4). The disturbance ratio for all constituents decreases in the wet season, to 3.4 for Cl and 1.9 for TDP, and is not different from 1.0 for TDN, PP, NO_3, or PN.

In addition to using land cover data to define 'deforested' watersheds, we also use Cl to identify 'disturbed' watersheds. Chloride concentrations greater than those observed in forested catchments are assumed to have anthropogenic origin, so Cl serves as a general indicator of human disturbance (Herlihy et al. 1998). Both raw and signal concentrations of TDN and TDP correlate with stream Cl (Figure 4). Stream nitrate increases with chloride concentrations up to 25 ueq/L Cl, and does not increase further with increasing chloride (data not shown).

Urban signals

The urban regression coefficient β_u is statistically significant for Cl in the dry and wet seasons and for TDN and NO_3 in the dry season (Table 5, Figure 5). The dry season urban regressions are influenced by two highly urbanized watersheds with high solute concentrations (Figure 5). Stream TDP does not correlate with urban population density in either season. The highest concentrations of Cl, TDN, and TDP for all watershed sizes occur in urban watersheds (Figure 6).

Watershed size

The stream nutrient response to deforestation and urbanization decreases with increasing drainage area. Maximum Cl and TDN signals occur in small, urbanized watersheds and the signals decrease with increasing watershed area (Figure 6). Both Cl and TDN have positive signal concentrations for the largest watershed sampled (33,000 km^2). The in-stream processing coefficient (k) was not statistically significantly different from zero for non-urbanized watersheds for any stream nutrient except dry season NO_3 in urbanized catchments (Table 5).

Ji-Paraná transect

The Ji-Paraná River originates in forested catchments on sandy soils and proceeds through a region with deforested and urban areas (Figure 7). The Ji-Paraná shows increasing total (C_t) and signal concentrations (C_d) of Cl and TDN to the maximum watershed size of 33,000 km^2 (Figure 7). Note that C_d for the Ji-Paraná is the concentration due to both deforestation and urbanization, and no attempt is made to separate the signal into urban and deforestation effects. Background concentrations of NO_3 decrease as the river passes from forested, sandy soils to more clayey soils further downstream. Controlling for this natural trend, signal concentrations of NO_3 increase slightly downstream despite decreasing observed concentrations,

Table 4. Total, background and signal concentrations of nutrients and chloride, non-nested samples only. C_t are the observed concentrations. For deforested catchments, C_f and C_d were calculated using (2) and (3). For urban catchments, C_d and C_u were calculated using (5a) and (6a). All concentrations in µM. Values without standard deviations occur where a single value was used for background concentrations.

	Cl	TDN	NO_3	TDP	PN	PP
Dry season						
Forested ($D = 0$–25%)						
Total (C_t)	5.9 ± 2.8	13 ± 5	5.9 ± 5.8	0.25 ± 0.29	6.8 ± 6.3	0.12 ± 0.08
Deforested ($D = 75$–100%)						
Total (C_t)	74 ± 38	33 ± 14	3.9 ± 2.1	1.4 ± 1.4	6.2 ± 3.2	0.31 ± 0.16
Background (C_f)	5.9	18 ± 4	1.6 ± 0.1	0.59 ± 0.27	6.8	0.16 ± 0.02
Deforestation signal (C_d)	68 ± 38	14 ± 11	2.4 ± 2.2	0.82 ± 1.1	−0.6 ± 3.2	0.15 ± 0.14
Disturbance ratio (C_t:C_f)	12.5 ± 6.4	1.7 ± 0.5	2.6 ± 1.3	2.3 ± 1.5	0.9 ± 0.5	1.9 ± 0.8
Urban ($U > 5$ persons/km^2)						
Average $D = 56\%$						
Total (C_t)	96 ± 67	63 ± 49	18 ± 25	1.4 ± 1.5	24 ± 40	0.45 ± 0.43
Background (C_f)	5.9	15 ± 2	2.3 ± 2.4	0.4 ± 0.1	6.8	0.12
Deforestation signal (C_d)	22 ± 19	3 ± 3	2.2 ± 0.8	0.1 ± 0.1	0.0	0.05 ± 0.04
Urban signal (C_u)	68 ± 70	46 ± 49	16 ± 24	1.0 ± 1.4	14 ± 38	0.28 ± 0.43
Disturbance Ratio (C_t:C_f)	17 ± 12	4.2 ± 3.0	11 ± 17	3.4 ± 3.3	3.2 ± 5.6	3.7 ± 3.6‘
Wet season						
Forested ($D = 0$–25%)						
Total (C_t)	3.8 ± 1.5	19 ± 6	6.5 ± 3.8	0.17 ± 0.20	11 ± 8	0.34 ± 0.21
Deforested ($D = 75$–100%)						
Total (C_t)	12.5 ± 5.6	20 ± 4	2.6 ± 0.9	0.91 ± 0.46	7.3 ± 6.2	0.46 ± 0.18
Background (C_f)	3.8	18	2.0 ± 0.7	0.51 ± 0.15	15	0.37
Deforestation signal (C_d)	9.2 ± 5.5	2 ± 4	0.6 ± 0.6	0.40 ± 0.44	−8 ± 6	0.1 ± 0.2
Disturbance ratio (C_t:C_f)	3.4 ± 1.4	1.1 ± 0.2	1.3 ± 0.4	1.9 ± 1.1	0.5 ± 0.4	1.2 ± 0.5

Urban ($U > 5$ persons/km^2)						
Average D = 56%						
Total (C_t)	20 ± 18	25 ± 8	7.7 ± 5.8	0.61 ± 0.72	7.0 ± 3.3	0.25 ± 0.11
Background (C_f)	3.8	18	3.5 ± 1.6	0.28 ± 0.12	15 ± 3.3	0.37
Deforestation signal (C_d)	5.0 ± 3.2	0.0	0.0	0.27 ± 0.02	−8	0.0
Urban signal (C_u)	12 ± 17	3.3 ± 11	4.1 ± 6.6	0.12 ± 0.46	0.3 ± 6.2	0.09 ± 0.18
C_t:C_f	5.1 ± 4.6	1.4 ± 0.4	2.5 ± 2.3	1.8 ± 1.5	0.5 ± 0.2	0.7 ± 0.3

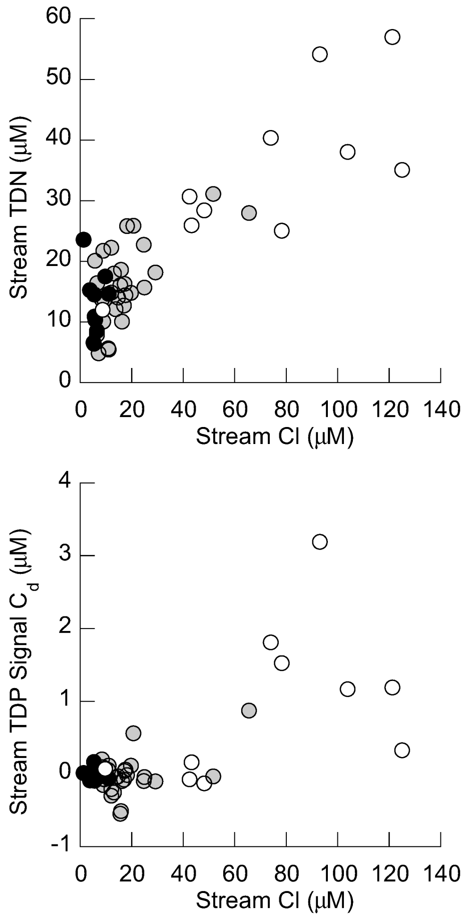

Figure 4. Stream TDN (C_t) and TDP signal concentrations (C_d) versus stream chloride, non-urban watersheds only. Symbols as in Figures 1 and 2.

Table 5. Urban regression parameters (Eq. 8). Number in parentheses is the standard deviation.

	Urban parameter β_u, for log(U)	In-stream processing coefficient k
Cl		
Dry season	37 (11)*	ns
Wet season	28 (11)*	ns
TDN		
Dry season	27 (8)*	ns
Wet season	ns	ns
NO_3^-		
Dry season	19 (7.5)*	0.74 (0.28)*
Wet season	ns	ns

**$p < 0.001$, *$p < 0.05$, ns not significant ($p > 0.05$).

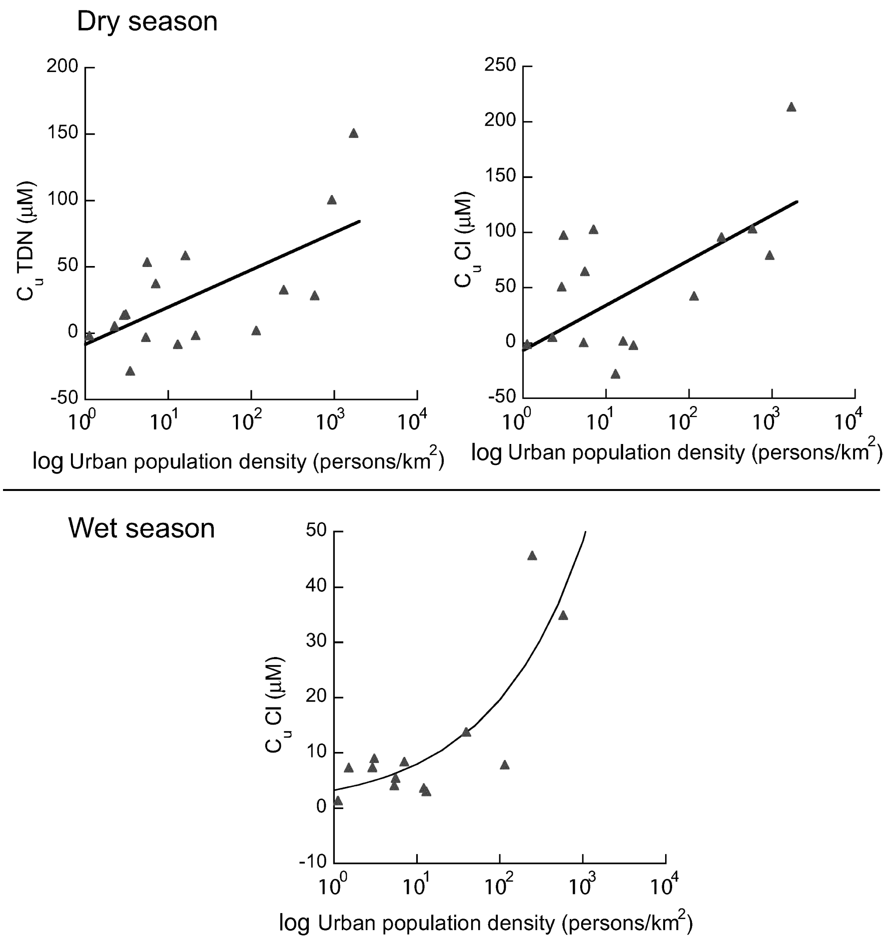

Figure 5. Stream chloride and TDN urban signal concentrations (C_u, Eq. (6a)) versus log Urban population density, urban watersheds only. For wet season Cl, the line indicates the best fit of a log–log regression.

demonstrating the importance of controlling for natural variability when determining anthropogenic effects on stream nitrate.

Discussion

The survey and analysis demonstrate four major points: (1) Soil type, namely texture and nutrient status, influence regional patterns in the concentrations of dissolved and particulate nutrients in the sampled streams, both before and following disturbance. (2) Watersheds more than 75% deforested have higher

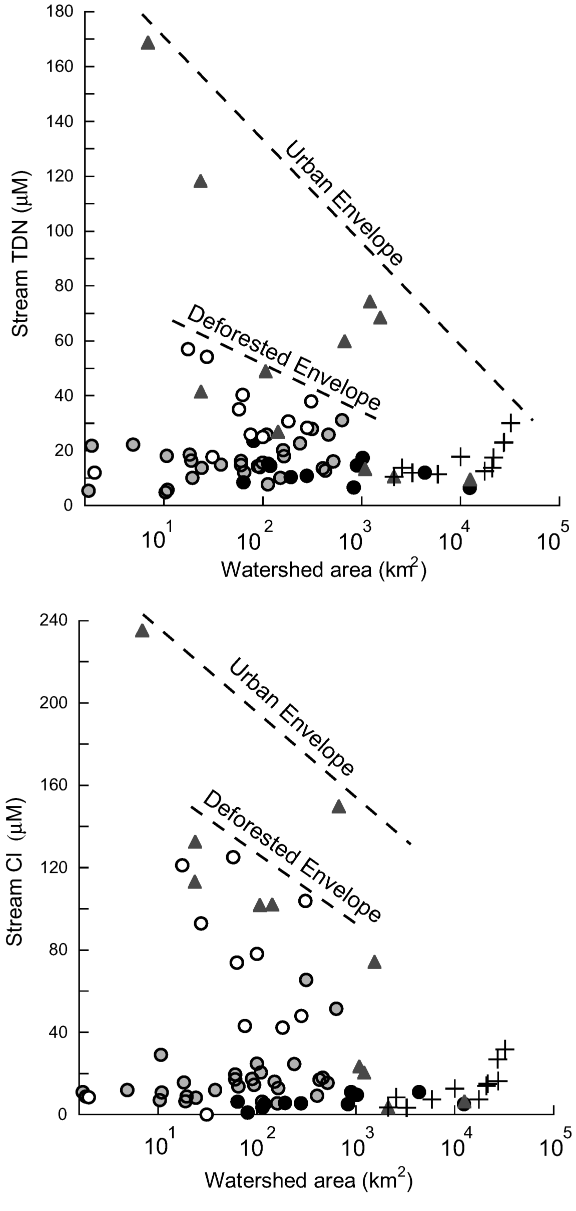

Figure 6. Chloride and TDN concentrations in stream water versus watershed area, dry season only. Symbols as in Figures 2 and 5. The urban envelope indicates the maximum concentrations observed for watersheds with urban population density greater than 5 persons per km^2. '+' signs indicate samples from the Ji-Paraná transect.

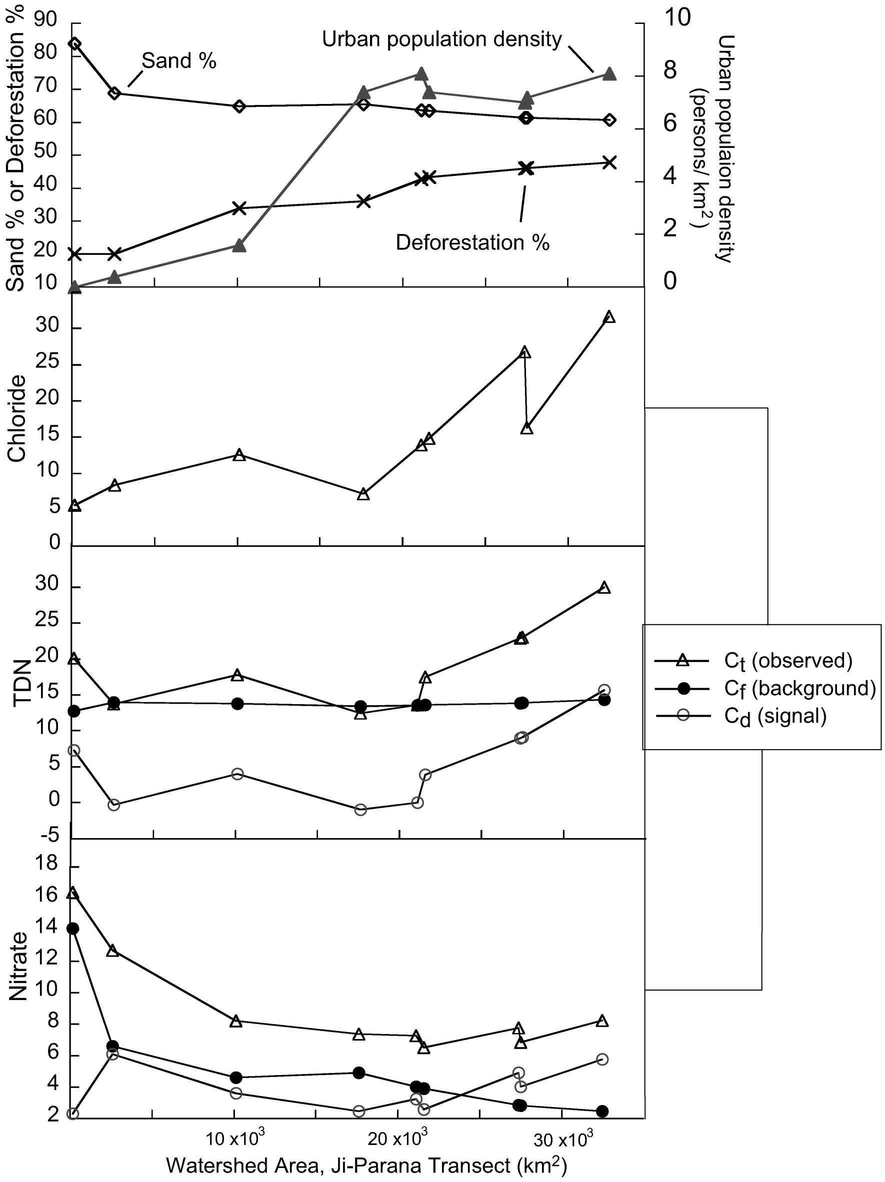

Figure 7. Watershed properties and stream Cl, TDN, and nitrate concentrations for a transect of the Ji-Paranà River, dry season only. The chloride transect shows total concentration (C_t) only. All concentrations in μM.

concentrations of all solutes in the dry season, though no stream nutrient disturbance is detected in watersheds less than 66–75% deforested. (3) Urban populations increase stream Cl and TDN concentrations over deforestation alone, though the response is highly variable, (4) A stream land use signal in Cl and TDN is observed for watersheds up to 33,000 km^2, suggesting that even relatively large rivers show signs of anthropogenic disturbance in this deforested and urbanized region.

Soil properties and stream nutrient concentrations

Terrestrial nutrient dynamics change with soil properties, resulting in regional patterns in nutrient cycling patterns. Nutrient stocks and cycling rates in terrestrial tropical forests increase with soil fertility (Vitousek and Sanford 1986), and nutrient transformation rates in terrestrial systems depend on soil texture (Silver et al. 2000; Vitousek and Matson 1988). In the Rondônia streams, soil properties also correspond to regional patterns in stream nutrient concentrations, suggesting that both terrestrial and aquatic nutrient dynamics are controlled in part by watershed soil properties. Stream P and NO_3 are the most affected by soil characteristics; TDN shows a slight but statistically significant effect of soil properties.

Stream nitrate concentrations might be expected to increase or decrease with soil clay content, depending on the relative importance of mobilization and transport. Nitrogen mobilization via mineralization and nitrification typically decreases with soil sand content in tropical soils (Vitousek and Matson 1988; Silver et al. 2000), while nitrate leaching rates typically increase with soil sand content due to decreased rates of nitrate adsorption (Gustafson 1983; Wong et al. 1990) and denitrification (Avnimelech and Raveh 1976) in sandy soils. If mineralization and nitrification in the soil were the principal control on stream nitrate concentrations, we would expect stream nitrate concentrations to decrease with increasing sand content. The fact that we observe the opposite in the Rondônia streams suggests that stream nitrate concentrations in minimally disturbed catchments are controlled more by the leaching characteristics of soils than by rates of mineralization and nitrification in the soil profile.

In contrast to nitrate, total dissolved nutrients (TDN and TDP) and PP correlate positively with soil nutrient status. In Hawaiian soils, fluxes of dissolved organic and inorganic phosphorus increase with available P in the soil, and P leaching increases with addition of P to the soil (Neff et al. 2000). The relationship between stream and soil concentrations of P is also observed for Ca, Mg, K, Si, and ANC in the same streams (Biggs et al. 2002), and stream P also correlates with soil and stream cation concentrations, suggesting that similar processes regulate the mobility of all of these rock-derived solutes. The correlation between soil P and stream P does not necessarily imply that stream P originates in the upper soil horizons; rather other watershed properties that correlate with soil P, such as depth to weatherable bedrock, may ultimately determine stream P concentrations (Biggs et al. 2002). Soil P content also influences decomposition and N mineralization rates in both temperate (Cornish and Raison 1977; Pastor et al. 1984) and humid tropical ecosystems, especially in soils of low P contents (Hobbie and Vitousek 2000), and may be partly responsible for the higher stream TDN concentrations observed on soils with high P contents.

Effect of deforestation

Stream nutrient concentrations appear resistant to disturbance from non-urban land use change up to a threshold level of approximately 66–75% deforestation, where significant but variable impacts occur in watersheds of 1.5 to 300 km^2. Stream nutrient disturbance is not detectable for watersheds less than 66–75% deforested, but streams draining heavily (>75%) deforested watersheds have up to 21 (Cl), 5.1 (PP), 4.7 (TDP), and 2.5 (TDN) times the forested background concentration. Resistance of stream nutrient concentrations to disturbance has been observed in other humid regions. Catchments on deep soils exhibit high nutrient retention capacity and small but persistent changes in stream nitrate concentrations following vegetation cutting (Swank and Vose 1997; Swank et al. 2001). In the central Amazon basin, nutrient concentrations increase significantly in soil and shallow groundwaters following forest cutting and burning (Williams et al. 1997). However, stream water concentrations of TDN and TDP do not change significantly following cutting and burning of forest, though annual export of nutrients increase due to increases in discharge caused by reductions in evapotranspiration (Williams and Melack 1997). Some of the nutrient retention capacity observed in other humid environments is likely due to sorption of both inorganic and organic forms of nitrogen and phosphorus in the soil column (Qualls et al. 2000, Qualls et al. 2002) and may be partly responsible for the low nutrient disturbance observed in the partially deforested Rondônia streams (<66–75% deforested).

We observe larger mean perturbations of stream nutrients in heavily deforested watersheds compared with other studies of small streams in Rondônia, though some of the streams from our survey also show the small perturbations observed in other studies. Small streams draining a pasture in Rondônia (drainage area ~ 1 km^2, Nova Vida site) have higher concentrations of ammonium, dissolved organic nitrogen and phosphate than do streams draining forests, though TDN and TDP concentrations remain relatively unchanged (Neill et al. 2001). Also at Nova Vida, Thomas et al. (in press) find no stream signal in TDN or TDP in a third-order (~ 52 km^2), partially deforested stream. The large Nova Vida stream is $\sim 40\%$ deforested, which is below the 75% deforested threshold observed in our statewide survey, and matches the low nutrient response observed for partially deforested watersheds (Figure 3).

The weak wet-season signals observed for nutrients in the Rondônia streams match results from smaller watersheds, which also find no significant difference between streams draining forest and pasture in the wet season (Neill et al. 2001). While storm runoff typically has higher concentrations of solutes than base or inter-storm discharge in forested (Williams and Melack 1997) and deforested (Markewitz et al. 2000) watersheds, enhanced stormflow concentrations are diluted by increased groundwater base flow in the wet season. Wet season base flow has relatively low nutrient concentrations, and shows no difference between forest and pasture watersheds, even in small watersheds (Neill et al. 2001).

The modest but detectable increase in nitrate concentrations with deforestation extent contrasts with observations in smaller watersheds, where pasture streams have significantly lower nitrate concentrations and higher ammonium concentrations than forested streams (Neill et al. 2001). The difference between small and large watersheds may be due in part to in-stream nitrification, which converts an average of 20–30% and up to 60% of experimentally added ammonium to nitrate for a wide geographic range of streams (Newbold et al. 1983; Peterson et al. 2001), including high rates (60%) in tropical catchments.

Stream P response to deforestation and pasture establishment increases with soil P content. High soil fertility increases the nutrient content of biomass (Vitousek and Sanford 1986), so the stock of nutrients mobilized by slash and burn agriculture is likely to be higher on nutrient-rich soils, possibly resulting in higher stream nutrient disturbances. Other factors, such as average pasture age, the intensity of land use, and cattle stocking densities may also correlate with soil nutrient status and contribute to the higher stream disturbances on fertile soils.

Stream nutrient and chloride responses to deforestation show a wide range of response, which might be expected in a regional survey where only watershed-aggregated soil properties and disturbance measures have been used. We have not accounted for clearing age, vegetation regeneration, or the condition of riparian vegetation, all of which may influence stream nutrient levels in disturbed areas (Vitousek and Reiners 1975; Peterjohn and Correll 1984; Lowrance et al. 1997). The observed variability in stream nutrient response requires extensive sampling to capture the range of nutrient disturbances, and complicates the extrapolation of results from single small streams.

Effect of area

Chloride and TDN concentrations decrease with watershed area, and the largest stream nutrient disturbances for both deforestation and urbanization occur in small watersheds (Figure 6). In the case of chloride, the decrease in signal with watershed area is due to decreasing deforestation extent and decreasing urban population density as watershed area increases, since in-stream processing of Cl should be minimal. For TDN, the regression technique used here does not indicate a strong effect of channel distance or watershed area on signal concentrations from non-urbanized watersheds. Nitrate shows some statistical evidence of in-stream processing, but only due to high nitrate signals in small, urbanized catchments. In-stream processing exerts important controls on stream nutrient budgets in temperate (House and Warwick 1998; Alexander et al. 2002b; Seitzinger et al. 2002) and tropical watersheds (Merriam et al. 2002), and in-stream processing likely affects stream nutrient concentrations in Rondônia. The lack of a strong effect in the Rondônia streams results from high variability in the nutrient concentrations in streams draining small watersheds, some of which show little or no stream nutrient disturbance. This variability in small stream response obscures clear statistical evidence of in-stream processing.

Deforestation signal sources

Given the high nutrient retention capacity observed in other humid watersheds experiencing vegetation disturbance (Swank and Vose 1997; Williams and Melack 1997; Qualls et al. 2000), why do the Rondônia streams exhibit marked changes for heavily deforested watersheds? The association of Cl with enhanced TDN, and TDP signals in non-urbanized streams suggests that cattle or rural human populations contribute to the nutrient concentrations of disturbed streams, and may be responsible for the enhanced concentrations. Cutting of vegetation alone may result in substantial changes in stream Cl concentrations (Kauffman et al. 2003), but a simple mass-balance on Cl suggests that this is unlikely in the Rondônia watersheds. Using data on Cl content of leaves and wood of tropical savanna forest biomass (McKenzie et al. 1996), and biomass estimates from Rondônia (Brown et al. 1995), we estimate that Rondônia forest biomass contains between 0.6 and 6.0 kmol Cl per hectare. Combustion volatilizes an average of $72 \pm 22\%$ of biomass C (McKenzie et al. 1996). While atmospheric deposition may return some of this volatilized Cl to the surface, we assume here that atmospheric deposition is well distributed over the study area and is part of the background concentration observed in both forested and deforested catchments. Given these stocks and volatilization rates, the net Cl input to the soil surface is between 0.18 and 1.6 kmol/ha. By comparison, the input of Cl from cattle salts is between 0.28 and 0.56 kmol/ha per year for stocking rates of 1 and 2 cattle per hectare (H. Schmitz, Fundação Fauna e Flora Tropicais Rondônia, personal communication, 1998). At these rates, the total input of Cl to the watershed from cattle salt would exceed the total input from burned biomass in 0.5–5 years following burning. In addition, Cl concentrations typically decrease rapidly following cutting (Kauffman et al. 2003), while the most heavily deforested Rondônia watersheds have average pasture ages greater than 10 years as estimated from a time-series of Landsat TM imagery (Roberts et al. 2002). Any Cl pulse from biomass has likely already leached during the first years following deforestation, and the observed Cl signals are most likely due to contamination from cattle, especially in non-urbanized catchments. The correlation between TDN and Cl further suggests that signal nutrient concentrations also may be derived from cattle and/or rural human inputs, and not from burned biomass. A more detailed Cl and N budget with more precise estimates of the Cl content of vegetation and atmospheric deposition will provide more accurate tests of this hypothesis.

Urban influence

Urban populations have strong impacts on Cl and TDN in some streams, though the effect is highly variable. The highest concentrations of Cl, TDN and TDP observed for watersheds of different sizes occur in urbanized watersheds (Figure 6, TDP data not shown), and watersheds with urban populations have higher stream Cl and TDN concentrations than non-urbanized watersheds of similar deforestation extent. However, the statistical significance of the urban regression parameter in the dry season depends on one or two watersheds with both high urban population densities and high stream solute concentrations (Figure 6). The variability of response, particularly for Cl, suggests that loading of Cl and TDN from urban areas to the stream network is spatially heterogeneous. The locations of industries, such as dairy and meat processing plants, were not accounted for in this study, and might explain some of variability observed in urban watersheds.

The higher average TDN and Cl in urbanized watersheds match observations in more heavily urbanized regions in the southeast of Brazil. Urbanized watersheds in the Piracicaba River basin in São Paulo State have stream chloride and ammonium concentrations that are 315 and 55 μM greater than non-urbanized catchments (watershed area range 11–130 km^2) (Martinelli et al. 1999). Stream chemistry disturbance in the Piracicaba Basin correlates closely with a land-use index that is controlled by urban land cover (Ometo et al. 2000). The Rondônia streams of this study show greater variability in watershed response to urban populations than the Piracicaba watershed, which may be due to the high fraction of residences served by sewage collection systems in the Piracicaba basin compared with the nearly exclusive use of septic systems in the urban areas of Rondônia (IBGE 2000). A high proportion of the population in the Piracicaba basin has sewage collection (92%), but virtually none of the sewage is treated (4%) and most is disposed of to local surface waters untreated (Martinelli et al. 1999). In areas with septic systems like Rondônia, subsurface disposal likely attenuates nitrogen and phosphorus concentrations, resulting in lower and more variable nutrient loading to streams. Other activities in and near urban areas, such as dairy and meat processing plants, may also account for the variability seen in stream nutrient response of urban areas (personal observation).

Despite the wide variability seen in urbanized watersheds, the TDN and Cl signals observed in intermediate-sized watersheds (1000–3000 km^2, Figure 6) exceed the signals observed all non-urban, pasture watersheds measured here and in other studies of small watersheds in Rondônia (Neill et al. 2001), suggesting that the TDN signals in the intermediate watersheds cannot be obtained by averaging signals from small pastures. We conclude that the most severe impacts on large rivers will not likely result from establishment of pastures that commonly follow deforestation in the Amazon, but rather from urban areas and their associated industrial and agricultural processing activities.

Conclusion

This survey of stream nitrogen and phosphorus address the four questions outlined in the introduction: (1) Stream nutrient concentrations vary with regional changes in soil texture and soil nutrient status. The detection of deforestation's impact on stream solute concentrations depends on controlling for this natural variability. The influence of deforestation would be overestimated in the case of TDN and TDP, and underestimated in the case of nitrate, since forested catchments occur on sandy, nutrient-poor soils that have high stream concentrations of nitrate and low stream concentrations of TDN and TDP. (2) Stream TDN, TDP and Cl are elevated in heavily deforested, non-urban watersheds, and deforestation extent is the dominant watershed control on stream TDN and Cl in non-urban watersheds. The sampled streams show resistance to nutrient disturbance from deforestation up to a threshold; only heavily deforested watersheds (66–75% deforested) show stream nutrient signals. (3) Watersheds of up to 3000 km^2 with urban populations have higher stream nutrient concentrations than any non-urban, deforested catchment, though the relationship between urban population density and stream signal response is highly variable. Anthropogenic changes in stream Cl and TDN concentrations can be detected in urbanized watersheds as large as 33,000 km^2. (4) The association of stream nutrient concentrations and chloride concentrations in non-urban watersheds suggests that processes besides vegetation conversion impact stream nutrient concentrations in non-urbanized watersheds; establishment of cattle populations is hypothesized to be important, though more field data is required to fully test the hypothesis. Urbanized watersheds have the highest concentrations of TDN and Cl for all watershed sizes. Comparison with the industrialized south of Brazil suggests that urban point sources are likely to dominate over non-point sources of N, particularly as the urban areas develop sewage collection systems. We conclude that regional deforestation and urbanization impact stream N and P for a wide range of stream sizes, from small pasture streams to large rivers systems.

Acknowledgements

Reynaldo Victoria and Thomas Ferreira Domingues from the Centro de Energia Nuclear na Agricultura, Eraldo Matricardi of Planafloro, Harald Schmitz of the Fundação Fauna e Flora Tropicais Rondônia, and Maria Alves da Silva Bahia of Centro de Aguas e Esgoto de Rondônia helped with field logistics and data acquisition. R.B. Alexander, John Melack, Oliver Chadwick and one anonymous reviewer provided valuable comments on the manuscript. Jim Sickman, Frank Setaro and Bob Petty assisted with chemical analyses. This work was supported by the National Aeronautic and Space Agency – EOS (Earth Observing System) Amazon Project NAGW-5233, and by a NASA Earth System Science graduate student fellowship.

References

Aitkenhead J.A. and McDowell W.H. 2000. Soil C:N as a predictor of annual riverine DOC flux at local and global scales. Global Biogeochem. Cycles 14: 127–138.

Alexander R.B., Elliott A.H., Shankar U. and McBride G.B. 2002a. Estimating the sources and transport of nutrients in the Waikato River Basin, New Zealand. Water Resour. Res. 38: art.no. 1268.

Alexander R.B., Johnes P.J., Boyer E.W. and Smith R.A. 2002b. A comparison of models for estimating the riverine export of nitrogen from large watersheds. Biogeochemistry 57: 295–339.

Avnimelech Y. and Raveh J. 1976. Nitrate leakage from soils differing in texture and nitrogen load. J. Environ. Qual. 5: 79–82.

Beaulac M.N. and Reckhow K.H. 1982. An examination of land use-nutrient export relationships. Water Ressour. Bull. 18: 1013–1024.

Bettencourt J.S., Tosdal R.M., Leite Jr. W.B. and Payolla B.L. 1999. Mesoproterozoic rapakivi granites of the Rondônian Tin Province, southwestern border of the Amazonian craton, Brazil. I. Reconnaissance U–Pb geochronology and regional implications. Precambrian Res. 95: 41–67.

Biggs T.W., Dunne T., Domingues T.F. and Martinelli L.A. 2002. The relative influence of natural watershed properties and human disturbance on stream solute concentrations in the southwestern Brazilian Amazon basin. Water Resour. Res. 38(8): art. no. 1150, doi 10.1029/2001WR000271.

Bormann F.H. and Likens G.E. 1979. Pattern and Process in a Forested Ecosystem. Springer-Verlag, New York.

Bremner J.M. and Mulvaney C.S. 1982. Nitrogen-total. In: Page A.L., Miller R.H. and Keeney D.R. (eds) Methods of Soil Analysis, Part 2. Chemical and Mircrobiological Properties. American Society of Agronomy, Madison. pp. 595–624.

Browder J.O. and Godfrey B.J. 1997. Rainforest cities: urbanization, development, and globalization of the Brazilian Amazon. Columbia University Press, New York.

Brown I.F., Martinelli L.A., Thomas W.W., Moreira M.Z., Ferreira C.A.C. and Victoria R.A. 1995. Uncertainty in the biomass of Amazonian forests – an example from Rondônia, Brazil. For. Ecol. and Manage. 75: 175–189.

Bruijnzeel L.A. 1991. Nutrient input–output budgets of tropical forest ecosystems: a review. J. Trop. Ecol. 7: 25–36.

Carpenter S.R., Caraco N.F., Correll D.L., Howarth R.W., Sharpley A.N. and Smith V.H. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecol. Appl. 8: 559–568.

Clark E.A. 1998. Landscape variables affecting livestock impacts on water quality in the humid temperate zone. Can. J. Plant Sci. 78: 181–190.

Cochrane T.T. 1998. Sigteron: Sistema de Informação geográfica para os terrenos e solos do estado de Rondônia, Brasil. Tecnosolo/DHV Consultants BV, Porto Velho.

Companhia de Pesquisa de Recursos Minerais 1997. Mapa Geológico do Estado de Rondônia. Porto Velho.

Cornish P.S. and Raison R.J. 1977. Effects of phosphorus and plants on nitrogen mineralisation in three grassland soils. Plant and Soil 47: 289–295.

Creed I.F. and Band L.E. 1998. Export of nitrogen from catchments within a temperate forest: evidence for a unifying mechanism regulated by variable source area dynamics. Water Resources Research 34: 3105–3120.

Dillon P.J. and Kirchner W.B. 1975. The effects of geology and land use on the export of phosphorus from watersheds. Water Res. 9: 135–148.

Downing J.A., McClain M., Twilley R., Melack J.M., Elser J., Rabalais N.N., Lewis Jr. W.M., Turner R.E., Corredor J., Soto D., Yanez-Arancibia A. and Howarth R.W. 1999. The impact of accelerating land use change on the N-cycle of tropical aquatic ecosystems: current conditions and projected changes. Biogeochemistry 46: 109–148.

Grayson R.B., Gippel C.J., Finalyson B.L. and Hart B.T. 1997. Catchment-wide impacts on water quality: the use of 'snapshot' sampling during stable flow. J. Hydrol. 199: 121–134.

Guggenberger G., Haumaier L., Thomas R.J. and Zech W. 1996. Assessing the organic phosphorus status of an Oxisol under tropical pastures following native savanna using P-31 NMR spectroscopy. Biol. Fert. Soils 23: 332–339.

Gustafson A. 1983. Leaching of nitrate from arable land into groundwater in Sweden. Environ. Geol. 5: 65–71.

Herlihy A.T., Stoddard J.L. and Johnson C.B. 1998. The relationship between stream chemistry and watershed land cover data in the Mid-Atlantic region. US Water Air Soil Pollut. 105: 377–386.

Hill A.R. 1978. Factors affecting the export of nitrate-nitrogen from drainage basins in southern Ontario. Water Res. 12: 1045–1057.

Hobbie S.E. and Vitousek P.M. 2000. Nutrient limitation of decomposition in Hawaiian forests. Ecology 81: 1867–1877.

House W.A. and Warwick M.S. 1998. A mass-balance approach to quantifying the importance of in-stream processes during nutrient transport in a large river catchment. Sci. Total Environ. 210/211: 139–152.

Howarth R.W., Billen G., Swaney D., Townsend A., Jaworski N., Lajtha K., Downing J.A., Elmgren R., Caraco N., Jordan T., Berendse F., Freney J., Kudeyarov V., Murdoch P. and Zhao-Liang Z. 1996. Regional nitrogen budgets and riverine N and P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry 35: 75–139.

Instituto Brasileiro de Geografía e Estatisticas IBGE 1996. Contagem da População. Brasilia.

Instituto Brasileiro de Geografia e Estatística IBGE 2000. Pesquisa Nacional de Saneamento Básico. Rio de Janeiro.

Instituto Nacional de Pesquisas Espaciais INPE 2000. Monitoring of the Brazilian Amazonian Forest by Satellite, 1998–1999. São Jose dos Campos.

Jones D.W., Dale V.H., Beauchamp J.J., Pedlowski M.A. and O'Neill R.V. 1995. Farming in Rondônia. Resour. Energy Econ. 17: 155–188.

Kauffman S.J., Royer D.L., Chang S. and Berner R.A. 2003. Export of chloride after clear-cutting in the Hubbard Brook sandbox experiment. Biogeochemistry 63: 23–33.

Kirchner W.B. 1974. An examination of the relationship between drainage basin morphology and the export of phosphorous. Limno. Oceanogr. 20: 267–270.

Lowrance R., Altier L.S., Newbold J.D., Schnabel R.R., Groffman P.M., Denver J.M., Correll D.L., Gilliam J.W., Robinson J.L., Brinsfield R.B., Staver K. and Lucas W. 1997. Water quality functions of riparian forest buffers in Chesapeake Bay watersheds. Environ. Manage. 21: 687–712.

Malmer A. 1996. Phosphorus loading to tropical rain forest streams after clear-felling and burning in Salbah, Malaysia. Water Resour. Res. 32: 2213–2220.

Markewitz D., Davidson E.A., Figueiredo R., Victoria R.L. and Krusche A.V. 2000. Control of cation concentrations in stream waters by surface soil processes in an Amazonian watershed. Nature 410: 802–805.

Martinelli L.A., Krusche A.V., Victoria R.L., de Camargo P.B., Bernardes M., Ferraz E.S., de Moraes J.M.D. and Ballester M.V. 1999. Effects of sewage on the chemical composition of Piracicaba River, Brazil. Water Air Soil Pollu. 110: 67–79.

McFarland A.M.S. and Hauck L.M. 1999. Relating agricultural land uses to in-stream stormwater quality. J. Environ. Qual. 28: 836–844.

McKenzie L.M., Ward D.E. and Hao W.M. 1996. Chlorine and bromine in the biomass of tropical and temperate ecosystems. In: Levine J.S. (ed) Biomass Burning and Global Change, Vol 1. Remote Sensing, Modeling and Inventory Development, and Biomass Burning in Africa. MIT Press, Cambridge, Mass, pp. 241–248.

Melich, A. 1953. Determination of P, Ca, Mg, K, Na, and NH4 NCSU Soil Test Division Mimeograph. Raleigh, NC.

Merriam J.L., McDowell W.H., Tank J.L., Wollheim W.M., Crenshaw C.L. and Johnson S.L. 2002. Characterizing nitrogen dynamics, retention and transport in a tropical rainforest stream using an *in situ* 15N addition. Freshwater Biol. 47: 143–160.

Mortatti J., Probst J.L. and Ferreira J.R. 1992. Hydrological and geochemical characteristics of the Jamari and Jiparana river basins (Rondonia, Brazil). GeoJournal 26: 287–296.

Neff J.C., Hobbie S.E. and Vitousek P.M. 2000. Nutrient and mineralogical control on dissolved organic C, N and P fluxes and stoichiometry in Hawaiian soils. Biogeochemistry 51: 283–302.

Neill C., Piccolo M.C., Steudler P.A., Melillo J.M., Feigl B.J. and Cerri C.C. 1995. Nitrogen dynamics in soils of forests and active pastures in the western Brazilian Amazon basin. Soil Biol. Biochem. 27: 1167–1175.

Neill C., Deegan L.A., Thomas S.M. and Cerri C.C. 2001. Deforestation for pasture alters nitrogen and phosphorus in small Amazonian streams. Ecol. Appl. 11: 1817–1828.

Newbold J.D., Elwood J.W., Schulze M.S.R.W.S. and Barmeier J.C. 1983. Continuous ammonium enrichment of a woodland stream: uptake kinetics, leaf decomposition, and nitrification. Freshwater Biol. 13: 193–204.

Novotny V. and Chesters G. 1981. Handbook of Nonpoint Pollution: Sources and Management. Van Nostrand Reinhold, New York.

Nye P.H. and Greenland D.J. 1960. The Soil Under Shifting Cultivation. Commonwealth Bureau of Soils, Harpenden, UK.

Ometo J.P.H.B., Martinelli L.A., Ballester M.V., Gessner A., Krusche A.V., Victoria R.L. and Williams M. 2000. Effects of land use on water chemistry and macroinvertebrates in two streams of the Piracicaba river basin, south-east Brazil. Freshwater Biol. 44: 327–337.

Pastor J., Aber J.D., McClaugherty C.A. and Melillo J.M. 1984. Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. Ecology 65: 256–268.

Pedlowski M.A., Dale V.H., Matricardi E.A.T. and da Silva Filho E.P. 1997. Patterns and impacts of deforestation in Rondonia, Brazil. Landscape Urban Plan. 38: 149–157.

Peterjohn W.T. and Correll D.L. 1984. Nutrient dynamics in an agricultrual watershed: observations on the role of a riparian forest. Ecology 65: 1466–1475.

Peterson B.J., Wollheim W.M., Mulholland P.J., Webster J.R., Meyer J.L., Tank J.L., Martí E., Bowden W.B., Valett H.M., Hershey A.E., McDowell W.H., Dodds W.K., Hamilton S.K., Gregory S. and Morrall D.D. 2001. Control of nitrogen export from watersheds by headwater streams. Science 292: 86–90.

Pote D.H., Daniel T.C., Nichols D.J., Sharpley A.N., Moore Jr. P.A., Miller D.M. and Edwards D.R. 1999. Relationship between phosphorus levels in three ultisols and phosphorus concentrations in runoff. J. Environ. Qual. 28: 170–175.

Qualls R.G., Haines B.L., Swank W.T. and Tyler S.W. 2000. Soluble organic and inorganic nutrient fluxes in clearcut and mature deciduous forests. Soil Sci. Soc. Am. J. 64: 1068–1077.

Qualls R.G., Haines B.L., Swank W.T. and Tyler S.W. 2002. Retention of soluble organic nutrients by a forested ecosystem. Biogeochemistry 61: 135–171.

RADAMBRASIL 1978. Levantamento de recursos naturais. Ministerio das Minas e Energia, Rio de Janeiro.

Rignot E., Salas W.A. and Skole D.L. 1997. Mapping deforestation and secondary growth in Rondonia, Brazil, using imaging radar and thematic mapper data. Remote Sens. Environ. 59: 167–179.

Roberts D.A., Numata I., Holmes K., Batista G., Krug T., Monteiro A., Powell B. and Chadwick O.A. 2002. Large area mapping of land-cover change in Rondônia using multitemporal spectral mixture analysis and decision tree classifiers. J. Geophys. Res. 107: 8073, JD000374.

Seitzinger S.P., Styles R.V., Boyer E.W., Alexander R.B., Billen G., Howarth R.W., Mayer B. and Van Breemen N. 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochemistry 57/58: 199–237.

Silver W.L., Neff J., McGroddy M., Veldkamp E., Keller M. and Cosme R. 2000. Effects of soil texture on belowground carbon and nutrient storage in a lowland Amazonian forest ecosystem. Ecosystems 3: 193–209.

Smith R.A., Schwartz G.E. and Alexander R.B. 1997. Regional interpretation of water-quality monitoring data. Water Resour. Res. 33: 2781–2798.

Sombroek W.G. 1966. Amazon Soils: a Reconnaissance of the Soils of the Brazilian Amazon Region. Centre for Agricultural Publications and Documentation, Wageningen.

Sonzogni W.C., Chesters G., Coote D.R., Jeffs D.N., J.C.K , R.C.O and Robinson J.B. 1980. Pollution from land runoff. Environ. Sci. Technol. 14: 148–153.

Swank W.T. and Vose J.M. 1997. Long-term nitrogen dynamics of Coweeta forested watersheds in the southeastern United States of America. Global Biogeochem. Cycles 11: 657–671.

Swank W.T., Vose J.M. and Elliott K.J. 2001. Long-term hydrologic and water quality responses following commercial clearcutting of mixed hardwoods on a southern Appalachian catchment. For. Ecol. Manage. 143: 163–178.

Thomas S.M., Neill C., Deegan L.A., Krusche A.V., Ballester V.M. and Victoria R.L. Influences of land use and stream size on particulate and dissolved materials in a small Amazonian stream network. Biogeochemistry (in press).

Triska F.J., Kennedy V.C., Avanzino R.J., Zellweger G.W. and Bencala K.E. 1989. Retention and transport of nutrients in a third-order stream: channel processes. Ecology 70: 1877–1892.

Uhl C. and Jordan C.F. 1984. Succession and nutrient dynamics following forest cutting and burning in Amazonia. Ecology 65: 1476–1490.

Valderrama J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. Marine Chem. 10: 109–122.

Vitousek P.M. and Reiners W.A. 1975. Ecosystem succession and nutrient retention: a hypothesis. BioScience 25: 376–381.

Vitousek P.M. and Sanford R.L.J. 1986. Nutrient cycling in moist tropical forest. Ann. Rev. Ecol. Syst. 17: 137–167.

Vitousek P.M. and Matson P.A. 1988. Nitrogen transformations in a range of tropical forest soils. Soil Biol. Biochem. 20: 361–367.

Vitousek P.M., Gosz J.R., Grier C.G., Melillo J.M., Reiners W.A. and Todd R.L. 1979. Nitrate losses from disturbed ecosystems. Science 204: 469–474.

Vollenweider R.A. 1971. The Scientific Fundamentals of Lake and Stream Eutrophication with Particular Reference to Phosphorus and Nitrogen as Eutrophication Factors. OECD, Paris

Walkey A.and T.A.B. 1934. An examination of the Degtjareff method for determining soil organic matter, and a proposed modification of the chromic acid titration method. Soil Sci. 37: 29–38.

Williams M.R. and Melack J.M. 1997. Solute export from forested and partially deforested catchments in the central Amazon. Biogeochemistry 38: 67–102.

Williams M.R., Fisher T.R. and Melack J.M. 1997. Solute dynamics in soil water and groundwater in a central Amazon catchment undergoing deforestation. Biogeochemistry 38: 303–335.

Wong M.T.F., Hughes R. and Rowell D.L. 1990. Retarded leaching of nitrate in acid soils from the tropics: measurement of the effective anion exchange capacity. J. Soil Sci. 41: 655–663.