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Relationships Between Land Use and Stream Nutrient Concentrations in a Highly Urbanized Tropical Region of Brazil: Thresholds and Riparian Zones

F. Tromboni [1] · W. K. Dodds [2]

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Abstract Nutrient enrichment in streams due to land use is increasing globally, reducing water quality and causing eutrophication of downstream fresh and coastal waters. In temperate developed countries, the intensive use of fertilizers in agriculture is a main driver of increasing nutrient concentrations, but high levels and fast rates of urbanization can be a predominant issue in some areas of the developing world. We investigated land use in the highly urbanized tropical State of Rio de Janeiro, Brazil. We collected total nitrogen, total phosphorus, and inorganic nutrient data from 35 independent watersheds distributed across the State and characterized land use at a riparian and entire watershed scales upstream from each sample station, using ArcGIS. We used regression models to explain land use influences on nutrient concentrations and to assess riparian protection relationships to water quality. We found that urban land use was the primary driver of nutrient concentration increases, independent of the scale of analyses and that urban land use was more concentrated in the riparian buffer of streams than in the entire watersheds. We also found significant thresholds that indicated strong increases in nutrient concentrations with modest increases in urbanization reaching maximum nutrient concentrations between 10 and 46% urban cover. These thresholds influenced calculation of reference nutrient concentrations, and ignoring them led to higher estimates of these concentrations. Lack of sewage treatment in concert with urban development in riparian zones apparently leads to the observation that modest increases in urban land use can cause large increases in nutrient concentrations.

Keywords Total phosphorus · Total nitrogen · Water quality · Agriculture · Urbanization · Eutrophication

✉ F. Tromboni
flavia.tromboni@gmail.com

[1] Departamento de Ecologia, IBRAG, Universidade do Estado do Rio de Janeiro, Rio de Janeiro, RJ, Brazil

[2] Kansas State University, Manhattan, KS 66506, USA

Introduction

Nutrient pollution due to human activities is increasing globally (Carpenter et al. 1998) and causes problems worldwide because increasing nitrogen (N) and phosphorus (P) exports into downstream water bodies causes algal blooms and harms biotic integrity (Dodds et al. 2006; Smith and Schindler 2009; Dodds and Smith 2016). Among the many aspects of decreasing water quality associated with eutrophication (Smith 2003), the proliferation of harmful algal blooms is of particular concern (Paerl et al. 2001; Paerl and Otten 2013). Downstream transport of nutrients is causing eutrophication of coastal waters (Paerl et al. 2014) in addition to harming freshwaters, and has led to world-wide proliferation of "dead zones" (Diaz and Rosenberg 2008).

The majority of studies on impacts of human activities on water nutrient concentrations have been carried out in temperate regions, particularly in North America and Western Europe, where the density of fertilized cropland can be high (Foley et al. 2005). Studies in the tropics are fewer and report contradicting results, with decreases (Neill et al. 2001, 2006) and increases in nutrient concentrations associated with deforestation and agricultural land cover conversion (Germer et al. 2009; Silva et al. 2011, 2012).

Today more people on Earth live in urban areas than rural areas (UNFPA 2007) and tropical developing countries are experiencing the highest rates of growth due to population growth and rural-urban migration (UNFPA 2007). Ninety five percent of net global population increase is expected to happen in urban areas of developing countries (Grimm et al. 2008), where 90–95% of all sewage and 70% of industrial wastes are not treated (Millennium Ecosystem Assessment 2005). Globally, streams in populated areas exhibit common characteristics defined as the "urban stream syndrome" with some similarities (Meyer et al. 2005; Ramírez et al. 2009) but also unique characteristics due to differences in discharge, climate (Ramírez et al. 2009) and resource availability and infrastructure (Capps et al. 2016). Many urban areas display increased delivery of nutrients to streams (Paul and Meyer 2001). Urban pressures on water quality are expected to increase in developing tropical countries, but knowledge on urban impacts on streams is still limited in those countries (Capps et al. 2016). In the US, urban and agricultural streams have similar inorganic nutrient concentrations (greater than forested), but nitrate and total N are higher in agricultural streams than in urban (Wenger et al. 2009). Greater nutrients in agricultural areas than urban watersheds might be less common in developing countries where cities often lack adequate sewage treatment (Wenger et al. 2009) and agricultural practices may differ from those in temperate areas. Understanding site-specific differences among different areas of the world is important to set efficient water management priorities (Booth et al. 2016).

In Brazil, research on the impact of land use on streams has mostly focused on deforestation for conversion to pasture in the Amazon (Neill et al. 2001; Biggs et al. 2002, 2004; Germer et al. 2009) or on nitrogen cycle alteration (Downing et al. 1999; Filoso et al. 2003, 2006; Bustamante et al. 2015). Some studies on urban watersheds have focused on dissolved carbon and dissolved inorganic nutrients as responses to land use (Daniel et al. 2002; Andrade et al. 2011; Silva et al. 2012). However, in order to provide practical management guidelines to control eutrophication and freshwater quality, both organic and inorganic N and P should be considered, as they can be related to autotrophic and heterotrophic activity. Moreover, total N (TN) and total P (TP) can be stronger predictors of stream benthic algal biomass than are dissolved inorganic N (DIN) or P (Dodds et al. 1997). Gücker et al. (2016) found strong impacts of urban land use, followed by pasture, but a less important effect of agriculture on dissolved organic N and P in the transition between Cerrado and Atlantic Forest biomes in south Brazil. Similar results were found for São Paulo State, Brazil, where urbanization had stronger effects on total N and P in streams than agricultural land uses (Cunha et al. 2011). Brazil attempts to protect streams by legislating a minimum required forested riparian area to be preserved, but little is known about how this protection interacts with land use impacts.

Riparian protection has been used world-wide as a management practice to protect streams from nutrient loading and maintain water quality (Blinn and Kilgore 2001). Riparian land use can be a better predictor of in-stream nutrient concentration than watershed land use (Johnson et al. 1997) but watershed land use can overcome the capacity of riparian zones to protect streams depending on the land use intensity and area (Allan 2004). We are only aware of a few studies on the effectiveness of riparian buffer protection for maintaining water quality in tropical stream networks (Uriarte et al. 2011; Leal et al. 2016).

We investigated the relationships among land uses and TN and TP stream nutrient concentrations in a highly urbanized tropical region of Brazil (the State of Rio de Janeiro) to understand if responses to anthropogenic influences are similar in tropical and temperate streams, and to help define parameters that could guide management strategies to improve water quality in urbanized tropical areas. We analyzed both the riparian and watershed scales to investigate what scale better explains the variations in stream nutrient concentration and assess the efficiency of riparian areas in maintaining water quality. We also investigated thresholds for water nutrient concentration related to urban land use that could inform management strategies (Dodds et al. 2010). Finally, we used the data to estimate reference nutrients for this region using the regression approach of Dodds and Oakes (2004).

Materials and Methods

Study Area

We studied water quality in Rio de Janeiro State in Southeast Brazil (Fig. 1). The State is inside the Atlantic Forest Biome. Only 12% of the total original Atlantic Forest remains in Brazil and in Rio State, 30% remains in a highly fragmented condition (Ribeiro et al. 2009). The State has an area of 43,864 square kilometers, of which around the 57% is composed by pasture, 20% by agriculture and 4% by urban settlements (IBGE 2010). The entire state has a total population of almost 16 million inhabitants of which the 97.6% live in urban areas (IBGE 2010). Even if small in land cover percentage, the urban area includes the city of Rio de Janeiro (the state capital, and the second largest city in Brazil with 6.3 million inhabitants).

Agriculture and pasture lands are dominated by a large number of small family farms (that occupy the 23% of the rural land) and by larger-scale agriculture (covering 77% of agricultural lands) (IBGE 2006b). In the State of Rio, farms

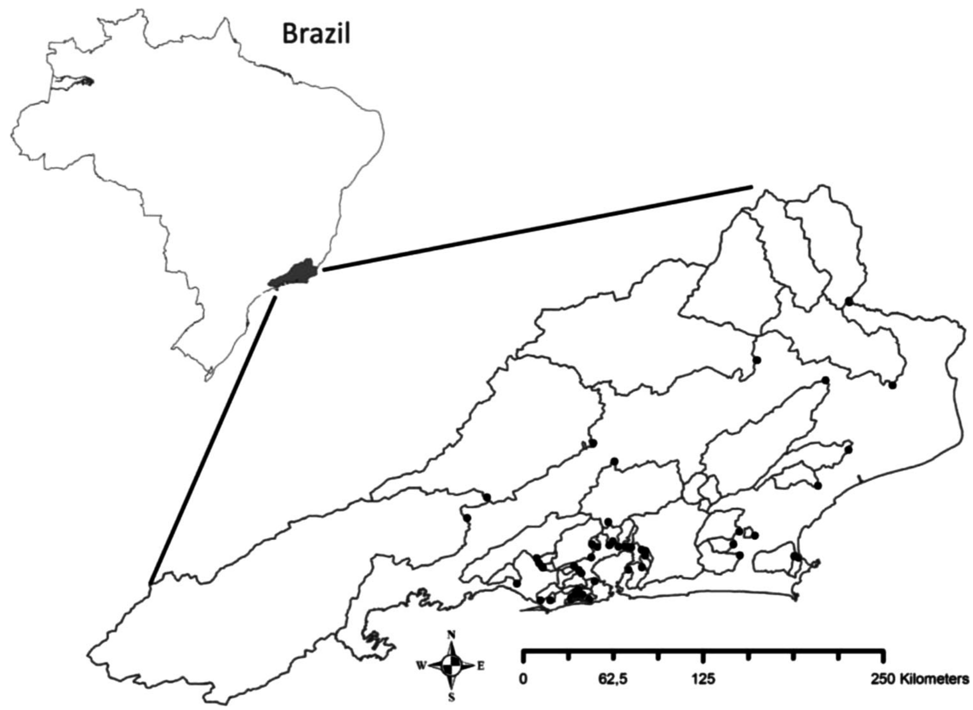

Fig. 1 Study area: the State of Rio de Janeiro with delineated watersheds above each sample station

are considered to be under family agriculture management when they are run only by family member labor force and have an area in between 1 and 140 hectares (IBGE 2006b). Pasture farms are characterized by a relatively low density of animals per km^2 (mostly less than ten animals per km^2 reaching 60–80 animals per km^2 is some small areas of the State) (IBGE 2006a).

Water Chemistry

Data on in-stream TN and TP concentrations as well as soluble reactive phosphorus (SRP), ammonium (NH_4^+), nitrate (NO_3^-, the sum of nitrate and nitrite) and (DIN, the sum of NH_4^+ and NO_3^-), for the entire State of Rio de Janeiro were provided by Agência Nacional de Águas (ANA) but collected, analyzed and reported to ANA by INEA (Instituto Estadual do Ambiente) from the year 2000 to 2012. We selected 35 sampling stations that had at least five sampling dates available for both TN and TP and distributed along the year. We spatially located the 35 sampling stations using the latitude and longitude coordinates provided by ANA and with arcMap in ArcGIS 10.5. Sampling stations were spread across the entire State of Rio de Janeiro (Fig. 1).

Total nitrogen was measured with the Kjeldahl method that determines the organic nitrogen and ammonium with preliminary distillation and by the automated phenate method. Nitrate and nitrite were determined by ion chromatography (Clesceri et al. 1998) and the sum of nitrate plus nitrate and Kjeldahl N gives TN. TP was estimated by the persulfate digestion procedure and SRP measured by direct clorometric analyses procedures (Clesceri et al. 1998). We focused on total N and P given the problems with interpreting dissolved inorganic nutrients with respect to nutrient pollution (Dodds 2003) but also analyzed how other nutrient forms (SRP, NH_4^+ and NO_3^-) were related to different land use.

Watershed Delineation and Land Use Characterization

We downloaded Hydrological data and maps based on Shuttle Elevation Derivatives at multiple Scales (Hydro SHEDS) available online by the World Wildlife Fund (http://www.worldwildlife.org/pages/hydrosheds, last access January, 2017). Hydro SHEDS are based on a digital elevation model from the US National Aeronautics and Space Administration's Shuttle Radar Topography Mission (Lehner et al. 2006).

We used the 15 arc-second resolution flow direction, flow accumulation and river network shapefiles to delineate watersheds above each water sampling station with the spatial analyst watershed delineation tool in ArcGIS 10.5. The spatial visualization of the watersheds in arcMap allowed us to visualize and delete nested watersheds from our sample, we thus obtained a sample of 35 independent watersheds (Fig. 1). Watersheds size ranged from 12 to16,322 km^2, being on average 1516 km^2.

Each watershed was then intersected, using the ArcGIS geo-processing tool "Intersect", with a land use characterization shapefile for the year 2010, provided by IBGE

(Insituto Brasileiro de Geografia e Estadistica). This land-use characterization included nine land use categories (pasture with forest, agriculture with forest, natural pasture, planted pasture, trees plantations, natural grassland, forest, agriculture, and urban areas) that we grouped under five categories: natural (forest, natural vegetation, and natural grassland), agriculture (agriculture with forest and agriculture), pasture (planted and natural pasture) and urban. We then calculated the percentage of land use of each of the category in every watershed.

We also delineated 30 m riparian buffer areas around the entire stream network upstream of each sample site using the ArcGIS geo-processing tool "buffer". We then intersected them with the land use shapefile, using the same procedure as for the watersheds. The riparian width was chosen as the minimum width to accurately map riparian areas with the resolution of the land use maps available for the entire State of Rio de Janeiro. We thus obtained land use categories for riparian buffer upstream each sample site in order to identify which spatial scale (watershed or riparian) best described in-stream nutrient concentrations. Watersheds average characteristics in terms of land use and nutrient concentrations in the analyzed streams are reported in Table 1.

Statistical Analyses

We ran Spearman Rank correlation analyses to identify correlations among the land use categories (for both riparian land use percentage area and total watershed land use percentage area) and in-stream nutrient concentrations. Spearman Rank correlation was chosen as a conservative approach because many of the variables were not normally distributed. In particular, we found breakpoints in some of the relationships (see below), which are difficult to analyze with parametric methods. After identifying significant correlations, we used forward stepwise variable selections to define the best multiple linear regression that described relationships between land use categories and TN and TP in the water column. We ran separate models for the two analyzed spatial scales: the entire watershed and the riparian scales, because the two scales were cross-correlated. TN and TP data were log transformed in order to be normally distributed for parametric tests. In addition, we ran regression models using Mallow's Cp to test best models while controlling for over-fitting. Results were very similar to the multiple regression models, so we only present the multiple regression model results. We recognize that multicolinearity is an inescapable feature of proportional land use data,

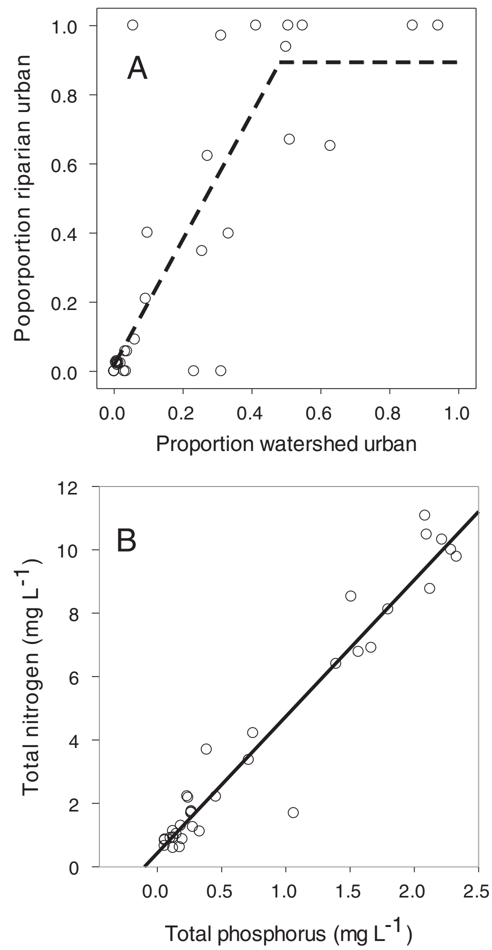

Fig. 2 Relationships between proportion of watershed and riparian zone with urban use (**a**) and between mean total N and total P for all watersheds (**b**)

Table 1 Analyzed watersheds descriptive statistics of the state of Rio de Janeiro

	N	Mean	Median	Minimum	Maximum	SD
TP (mg/L)	35	0.79	0.28	0.06	2.33	0.82
TN (mg/L)	35	3.85	1.75	0.59	11.07	3.62
SRP (mg/L)	35	0.04	0.01	0.00	0.19	0.06
NH_4^+ (mg N/L)	35	1.34	0.60	0.03	4.42	1.48
NO_3^- (mg N/L)	35	0.19	0.20	0.03	0.41	0.11
R urban	35	0.33	0.06	0.00	1.00	0.41
R natu	35	0.07	0.03	0.00	0.70	0.13
R agri	35	0.09	0.08	0.00	0.48	0.11
R pastu	35	0.48	0.60	0.00	0.97	0.35
W urban	35	0.20	0.05	0.00	0.94	0.26
W natu	35	0.23	0.19	0.00	0.67	0.20
W agri	35	0.17	0.15	0.00	0.46	0.11
W pastu	35	0.39	0.40	0.02	0.84	0.26

N referrers to the number of the watersheds in the sample and SD refers to standard deviation

R riparian scale, *W* watershed scale, *natu* natural land use, *agri* agricultural land use and *pastu* pasture land use

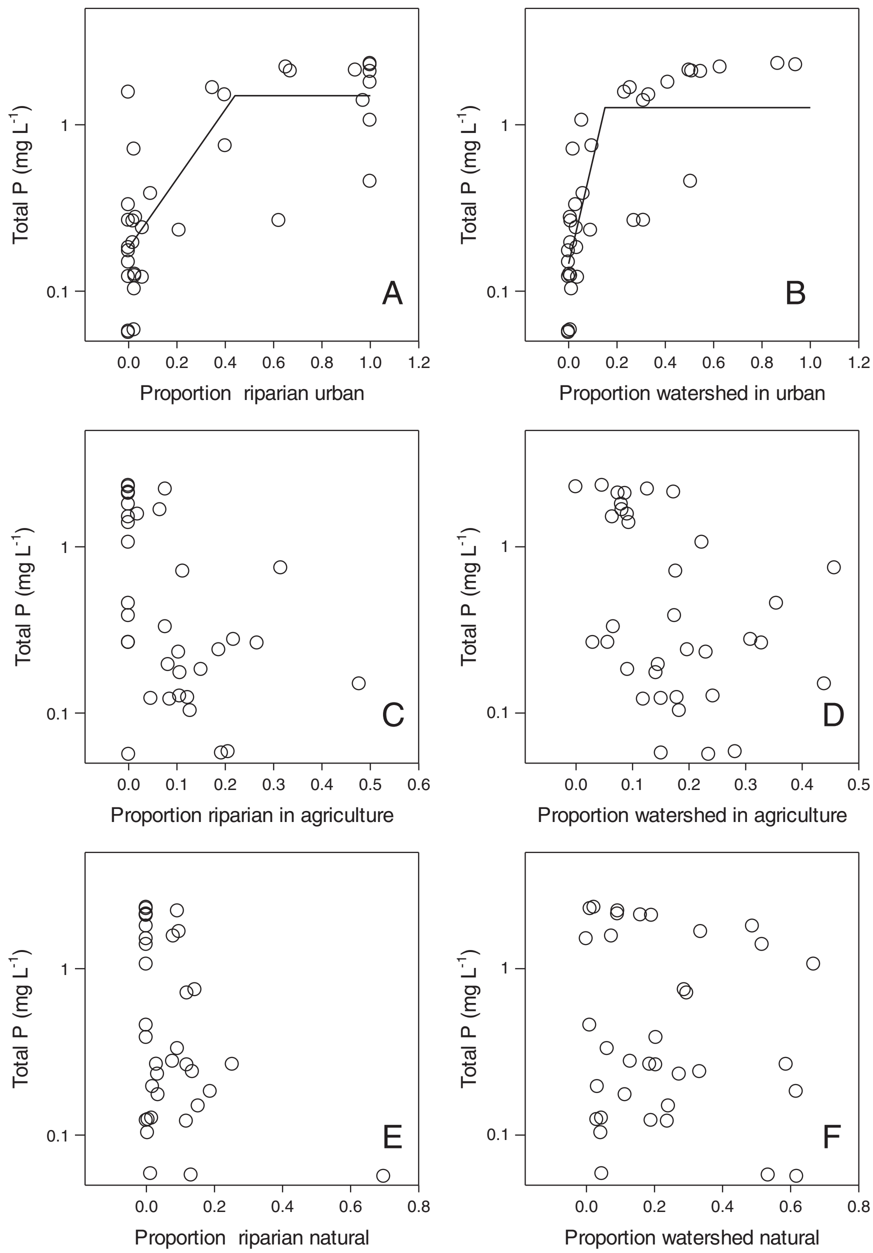

Fig. 3 Relationships of total P with proportion of urban riparian (**a**), urban watershed (**b**), agricultural riparian (**c**), agricultural watershed (**d**), natural riparian (**e**) and natural watershed (**f**). *Note* total P is on a log scale. *Lines* in **a** and **b** were determined by the program SEGREG to best fit the data via breakpoint regression

because when one land use dominates, another has to decrease. However, the stepwise regression still picks the land use most closely related to the nutrient concentration, and none of our models picked multiple land uses as statistically significant. Correlation and regression tests were done in Statistica v. 13 (Stat Soft Inc. Tulsa OK).

We observed plots of relationships with nutrients and found strongly non-linear relationships among urban land use and TN or TP as well as between the proportion of watersheds in urban land against the proportion of riparian zones in urban land. Thus, we used breakpoint regression to test if two lines fit the data better than one, and if so, what the confidence intervals around the breakpoints were. These analyses were done with the package SEGREG (http://www.waterlog.info/segreg.htm). This method tests not only if two lines fit the data better than one, but also if two lines do fit better, which of the possible relationships described by two lines fits best (e.g., one flat line and one sloped, or two lines that are linked vs. two that are discontinuous).

We used Dodds and Oakes (2004) regression approach to estimate background nutrient concentrations for the studied streams in the absence of anthropogenic influence. For analysis of background nutrient concentrations we only regressed urban land use against TN and TP and then used the resulting intercept (where urban land use was zero) and confidence intervals around the estimate to indicate reference nutrient concentrations and the confidence interval of those estimates.

Table 2 Spearman rank-order correlations among variables

	TP	TN	SRP	NH_4^+	NO_3^-	R urban	R natu	R agri	R pastu	W urban	W natu	W agri	W pastu
TP	1.00	0.92	0.78	0.83	−0.40	0.71	−0.46	−0.60	−0.53	0.86		−0.48	−0.52
TN	0.92	1.00	0.77	0.91	−0.39	0.73	−0.36	−0.55	−0.53	0.91		−0.44	−0.55
SRP	0.78	0.77	1.00	0.81	−0.66	0.61	−0.46	−0.75	−0.52	0.77		−0.58	−0.64
NH_4^+	0.83	0.91	0.81	1.00	−0.48	0.66	−0.40	−0.56	−0.49	0.86		−0.46	−0.55
NO_3^-	−0.40	−0.39	−0.66	−0.48	1.00			0.44	0.36	−0.39			0.46
R urban	0.71	0.73	0.61	0.66		1.00	−0.55	−0.58	−0.72	0.78			−0.65
R natu	−0.46	−0.36	−0.46	−0.40		−0.55	1.00	0.63		−0.45	0.48		
R agri	−0.60	−0.55	−0.75	−0.56	0.44	−0.58	0.63	1.00	0.45	−0.70		0.63	0.45
R pastu	−0.53	−0.53	−0.52	−0.49	0.36	−0.72		0.39		−0.55			0.87
W urban	0.86	0.91	0.77	0.86	−0.39	−0.78	−0.45	−0.70	−0.55	1.00		−0.56	−0.59
W natu							0.48				1.00		−0.43
W agri	−0.48	−0.44	−0.58	−0.46		−0.28		0.63		−0.56			
W pastu	−0.52	−0.55	−0.64	−0.55	0.46	−0.65		0.45	0.87	−0.59	−0.43		

Note that correlations where $p > 0.05$ are not listed

R riparian scale, *W* watershed scale, *natu* natural land use, *agri* agricultural land use and *pastu* pasture land use

Table 3 Regression of total N and total P concentrations against proportion (Prop.) watershed urban land use and riparian urban land use

Dependent variable	Independent variable	*B*	SE	*p*-value	Adj. R^2
Total P (mg/L)	Intercept	0.25	0.092	0.011	0.73
	Prop. urban watershed	2.67	0.279	<0.001	
Total N (mg/L)	Intercept	1.45	0.415	0.001	0.72
	Prop. urban watershed	11.79	1.261	<0.001	
Total P (mg/L)	Intercept	0.28	0.116	0.019	0.59
	Prop. urban riparian	1.53	0.221	<0.001	
Total N (mg/L)	Intercept	1.76	0.563	0.003	0.49
	Prop. urban riparian	6.29	1.076	<0.001	

Results

We found a non-linear relation between riparian and watershed urban land use (Fig. 2a). Breakpoint regression indicated the best fit model was rapidly increasing urban cover in the riparian zone ahead of that occurring in the whole watershed until a maximum proportion of development was reached. The TN in each site was generally 4.6 times greater than TP as indicated by the slope of the relationship between the two as determined by linear regression ($r^2 = 0.94$) between TN and TP (Fig. 2b).

Non-linear relationships were found between land use and total nutrients (Fig. 3a and b). Thus, our initial data exploration was with the non-parametric Spearman Rank Correlation test (Table 2). Total P in the water related to land uses (Fig. 3). Given the strong correlation between TN and TP (Fig. 2), similar plots for TN provide the same patterns, so we only present TP here. Interestingly, NO_3^-correlated negatively with TN and NH_4^+, but TN and NH_4^+ were closely and positively correlated. In addition, NO_3^- was positive-related to pasture and agriculture at a riparian scale and to pasture at a watershed scale, while NH_4^+ was negatively related to those two land uses at all scales. NO_3^- was also negatively correlated with urban land use, while NH_4^+ and SRP had a positive relation with urban land use (Table 2).

The proportions of urban land use (riparian or in the watershed) were most strongly related to TN and TP. As expected, natural areas had a negative correlation with TN and TP, but surprisingly, riparian agriculture and whole watershed agriculture were also negatively correlated with TP and TN at riparian and watershed scales. In the same way, proportion of pasture correlated negatively to TP and TN at both spatial scales (Table 2). However, stepwise regression analyses showed that urban land use was the dominant predictor of in-stream nutrient concentration at both riparian and watershed scales. Agriculture and pasture land use did not improve the model and were not selected by the stepwise regressions (Table 3). Watershed urban land use explained slightly more of the variability of in-stream

Table 4 Breakpoints and confidence intervals of regression for total P and total N against proportion of urban in the watershed and the riparian

All data	Total P	Total N
Breakpoint riparian urban	0.24	0.20
90% CI riparian breakpoint	0.03	0.02
Breakpoint watershed urban	0.46	0.10
90% CI watershed urban	0.05	0.01

Table 5 Total N and P baseline reference values calculated with all data and just data with urban area below breakpoints. All values are in mg/L

All data	Watershed data	Riparian data
Total N	1.294	1.358
Low 95%	0.991	0.989
High 95%	1.689	1.863
Total P	0.198	0.195
Low 95%	0.140	0.136
High 95%	0.280	0.280
Below urban breakpoints		
Total N	0.878	1.148
Low 95%	0.697	0.826
High 95%	1.108	1.596
Total P	0.165	0.179
Low 95%	0.114	0.115
High 95%	0.238	0.279

nutrient concentration than riparian land use (R^2 values were greater when riparian proportional land uses were used for the independent variables TN and TP).

There were significant breakpoints in the regressions of TP (and TN) against urban area of watershed or of riparian zone (Table 4). The breakpoints all provided better model fits than a single regression line fit to proportion urban and log TN or log TP (data not shown). The best general model had an initial steeply increasing linear relationship between proportion urban and TP or TN as the proportion of urban land use increased from zero. This was followed with a breakpoint somewhere between 10 and 40% urban land use, and then a flat line following that with a slope of zero with constant TN or TP at greater proportions of urban cover. While the breakpoints were variable, they all occurred at relatively low proportions of urbanization regardless of whether riparian or watershed urban areas were used as a predictive variable. We did not find significant breakpoints related to the other land use categories.

We applied the Dodds and Oakes (2004) regression approach to estimate background nutrient concentrations, where the intercept gives the expected value in the absence of anthropogenic inputs, and these estimates provided substantially lower nutrient concentrations than the means for the data set. The whole watershed data gave lower reference values than the riparian data alone (Table 5). Urban land use at a riparian and watershed scales were non-linearly related to TN and TP, so the linear regression approach using a single straight line to estimate background reference values could overestimate reference. Thus, we used just the line derived from the data below the breakpoint of urban land use, and found consistently lower baseline reference values than those derived from a single straight line fit to all the data (Table 5).

Discussion

Urban land use was the most important driver of in-stream TN and TP concentrations in the State of Rio de Janeiro regardless of whether whole watershed or riparian scales were considered. Significant impacts of urban land use on nutrient concentrations have been found in other studies from Brazil. Biggs et al. (2004) found urban-dominated areas had ten times the TDN concentrations than did forested areas. Urban streams in Brazil can be very different from forested, with low dissolved oxygen concentrations, high respiration rates, and high concentrations of carbon dioxide, dissolved inorganic nitrogen, and dissolved inorganic carbon (Andrade et al. 2011; Cunha et al. 2011). These authors however did not investigate the effects of riparian land use, or the existence of land use thresholds.

Given the importance of urban land use, we were interested in how riparian vs. watershed land uses influenced nutrient concentrations in our streams. Traditionally people inhabit areas with freshwater access, and 50% of the population lives within 3 km of streams (Kummu et al. 2011). In Rio State, many watersheds are quite steep and it is easiest to inhabit areas near rivers and streams. Consequently, riparian buffers had a larger percentage of urban area (33%) compared to the entire watershed (20%) and we observed a non-linear relationship between urban land use at a riparian and at a watershed scale, indicating that in urban areas of this region, human habitations tend to cluster around streams as opposed to uplands. These data indicate that the riparian forest protection by the Brazilian Forest Code might not always be applied or enforced (riparian areas in our study streams were on average only 7% forested, Table 1) and riparian protection might be not present in urban areas, exacerbating urban pressure on stream ecosystems.

In developed countries like the US, cropland is a key driver of stream nutrient concentrations (Omernik et al. 1981; Dodds and Oakes 2004; Secchi et al. 2011). Given the importance of agriculture to in-stream TN and TP in temperate studies, we were surprised that multivariate regression indicated that agricultural land did not increase nutrient concentration in our study streams. We also found non-significant increases in nutrient concentrations due to pasture. The study region however is characterized by non-intensive type of agriculture and pasture with a modest number of cattle (IBGE 2006a). Low intensity grazing can have lower impacts on stream chemistry than fertilized agriculture in temperate watersheds (Clark 1998). Thus, agriculture in Rio State may not reflect that in other areas including temperate areas that are more heavily studied.

Our results were more consistent with tropical studies on agricultural influences on water quality. In the Amazon, forested streams had higher nitrate concentrations than pasture streams (Neill et al. 2001), probably due to lower extractable nitrate and lower rates of N mineralization and net nitrification in the pasture soils than forested soils. But the authors found similar ammonium concentrations and lower phosphorus concentrations in forest compared to pasture streams in the same Amazonian region (Neill et al. 2006). However, in Southeast Brazil, stream water nutrient concentrations were generally greater in pasture and agricultural sites including higher total dissolved N (Silva et al. 2011).

Additionally, agricultural cover was relatively low in many of our watersheds. The watersheds in our study had an average percentage of non-urban deforestation (agriculture and pasture) that ranged from 20 to 84% for pasture and 0 to 45% for agriculture. It is possible that with an increase in the percentage of deforestation for non-urban uses we could observe what Biggs et al. (2004) noted in their study in the Amazon. They saw an increase up to 4.7 times for total dissolved phosphorus (TDP) and 2.5 times for total dissolved nitrogen (TDN) in deforested streams compared to forested, but only in watersheds with more than 66–75% of deforestation.

Values of TN and TP were highly correlated and behaved similarly with respect to land use. These results differ from Dodds and Oakes (2006) from a temperate watershed dominated by rangeland and row crop agriculture who found that land use was correlated to TN but less strongly to TP and they found no statistically significant urban influences on nutrient concentration in their streams. However, the urban area in their study was very small (a town of 760 people in a 1000 km^2 watershed). At a broader (continental) scale, Dodds and Oakes (2004) did find significant responses to urban land uses or higher population density, but the influence still was not as great as seen in our study. Dodds and Oakes (2006) also found that TN was better explained by riparian land use characteristics but TP concentrations were not significantly related to watershed or riparian land use. In our study, watershed-scale land uses have higher r^2 values when predicting TN and TP than riparian-scale land uses. In contrast, in Puerto Rico land cover of the 60 m wide riparian area was a better predictor of in-stream TN but it was not for TP concentration, which was driven by a sub-watershed land use scale (Uriarte et al. 2011). In their study TP levels were greater in pasture sites, followed by agriculture, urban and the lowest in forest; and TN levels were greater in pasture and urban. These authors suggest that improvement of sewage treatment plants reduced the impact of urban areas in Puerto Rico, improving water quality, and that agriculture intensity level was low. In contrast, in Rio State sewage plants are not common and do not remove nutrients.

In addition to differences in land use effects, our reference values (Table 5) differ from those from the United States, indicating that tropical biomes could have different reference values than more temperate areas. If this is correct, a nutrient-ecoregional approach to baseline nutrients is warranted and use of values from the US in other countries may be problematic. For the US, reference values were obtained with the regression approach we used (Dodds and Oakes 2004) and a modeling approach (Smith et al. 2003). Our background values for TP were greater than all of those reported for the United States by Smith et al. (2003) and comparable only to those reported for the Texas-Louisiana costal and Mississippi alluvial plains and the Xeric west by Dodds and Oakes (2004). Our background levels for TN were also greater that those reported by Smith et al. (2003) but were within the range of values reported by Dodds and Oakes (2004). In our study we found higher TP concentrations (60–2320 μg/L) compared to Castillo (2010) (14–386 μg/L), showing that also our pristine sites had higher phosphorus concentrations compared to streams in Venezuela. Our reference TP and TN values were closer to the Gambia river concentrations (TP of 70 and TN of 1145 μg/L) reported by Lewis Jr (1986). We do not know why our reference values differ from those reported in the US and this is an area that warrants further study.

Our analysis did suggest a unique issue with using the regression approach to estimate reference nutrients. The thresholds meant that including data above the threshold progressively increased the estimated reference condition. As this method is based on extrapolating to zero anthropogenic influence (in our case zero urban land use), we think that the extrapolation becomes more accurate if only data close to the reference condition are included. In all cases, restricting data to the lower portion of the distribution led to lower concentration estimates for reference nutrient concentrations.

Urban areas strongly increased TN and TP in streams. The TP concentrations we observed in our study are similar to those that delineate the boundary between mesotrophic and eutrophic lakes (Nürnberg 1996), indicating that receiving waters from these urban areas have high potential to cause eutrophication problems including harmful algal blooms. The Redfield ratio N:P by mass is 7:1 (16:1 by moles the composition of algal mass under balanced growth, Dodds and Whiles (2010)). Above this ratio, N is expected to limit algal growth (P is in excess), and below there is an N deficit (Howarth 1988), so a value of 4.6 N:P by mass that we found in our study indicates that P is being exported by these streams in excess of algal demand relative to N. Most detergents used in Brazil are phosphate-based, which could explain the relatively low TN:TP ratios we observed.

Thresholds can have important implications for management because they can indicate levels of anthropogenic impact above which drastic change is expected (Booth and Jackson 1997; Groffman et al. 2006; Dodds et al. 2010). We found that relatively small proportions of the watershed or the riparian zone converted to urban areas rapidly increased nutrient concentrations and high nutrient concentrations were relatively constant when more than 40% of the riparian area or 20% of the watershed area were converted to urban land use. Controlling nutrient pollution by limiting upland development may have limited practicality in areas, where sewage is not treated and where riparian areas are intensively developed. It is possible if development occurred in watershed with adequate riparian protection that higher proportions of urbanized areas could be achieved without such large influences on stream nutrient concentrations. The thresholds we found for anthropogenic effects of urbanization on environmental quality are similar to those reviewed by Brabec et al. (2002) and Allan (2004) for effect of increased impermeable surfaces associated with urbanization and water quality. We need to be clear that a threshold as we describe it in this paper does not necessarily delineate an alternative stable state, where it is difficult to return to the original condition if the system is moved back below the threshold (Dodds et al. 2010). We cannot predict how stream quality would respond to restoration from urbanized to natural conditions.

Our study suggests that water management in tropical developing countries might need to employ strategies that have already been adopted in many temperate developed countries. This is particularly true for highly urbanized areas where a proper sewage treatment is lacking and where there are no restrictions on phosphate-containing detergents. In addition, in the study area sediment control is not regulated so possibly erosion is greater in urban sites exacerbating water quality problems. If mechanized agriculture with intensive nutrient addition became more pervasive in the State of Rio, efforts might need to be focused more on agriculture as a source of nutrients to rivers and streams.

Most urban riparian restoration efforts in developed countries have focused on restoring riparian areas and planting trees adjacent to the stream channel (when this was possible by space availability and property issues). Riparian buffers can improve stream health in urbanized contexts (Bernhardt and Palmer 2007). The low nutrient concentrations that we found in forested sites suggest that replanting urban buffers could be a useful strategy to mitigate nutrient loading in the tropics but only after a proper sewage treatment and sediment erosion control are implemented. The lack of sewage treatment and sediment control together with urban population clustering around the streams and potential lack of enforcement of the Forest Code indicate that current practices do not protect water quality in the highly urbanized State of Rio de Janeiro.

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Compliance with Ethical Standards

Conflict of Interest The authors declare that they have no competing interests.

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