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Nutrient export and elemental stoichiometry in an urban tropical river

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Abstract. Nutrient inputs to surface waters are particularly varied in urban areas, due to multiple nutrient sources and complex hydrologic pathways. Because of their close proximity to coastal waters, nutrient delivery from many urban areas can have profound impacts on coastal ecology. Relatively little is known about the temporal and spatial variability in stoichiometry of inorganic nutrients such as dissolved silica, nitrogen, and phosphorus (Si, N, and P) and dissolved organic matter in tropical urban environments. We examined nutrient stoichiometry of both inorganic nutrients and organic matter in an urban watershed in Puerto Rico served by municipal sanitary sewers and compared it to two nearby forested catchments using samples collected weekly from each river for 6 yr. Urbanization caused large increases in the concentration and flux of nitrogen and phosphorus (2- to 50-fold), but surprisingly little change in N:P ratio. Concentrations of almost all major ions and dissolved silica were also significantly higher in the urban river than the wildland rivers. Yield of dissolved organic carbon (DOC) was not increased dramatically by urbanization, but the composition of dissolved organic matter shifted toward N-rich material, with a larger increase in dissolved organic nitrogen (DON) than DOC. The molar ratio of DOC:DON was about 40 in rivers draining forested catchments but was only 10 in the urban river. Inclusion of Si in the assessment of urbanization's impacts reveals a large shift in the stoichiometry (Si:N and Si:P) of nutrient inputs. Because both Si concentrations and watershed exports are high in streams and rivers from many humid tropical catchments with siliceous bedrock, even the large increases in N and P exported from urban catchments result in delivery of Si, N, and P to coastal waters in stoichiometric ratios that are well in excess of the Si requirements of marine diatoms. Our data suggest that dissolved Si, often neglected in watershed biogeochemistry, should be included in studies of urban as well as less developed watersheds due to its potential significance for marine and lacustrine productivity.

Key words: coastal; dissolved organic carbon; dissolved organic matter; dissolved organic nitrogen; dissolved silica; nitrate; nutrients; phosphate; stoichiometry; tropical; urban.

Introduction

Understanding the controls on temporal and spatial variability in water quality is a fundamental issue for aquatic ecology and environmental management. Numerous studies have documented the extent to which water resources have been degraded by human activities such as agriculture (Peierls et al. 1991), deicing of roads with road salt (Daley et al. 2009), or urbanization (Paul and Meyer 2001, Kaushal et al. 2014). This degradation leads to higher delivery of organic matter and nutrients to coastal ecosystems and the hypoxia that is associated with these inputs (Diaz and Rosenberg 2008). In most cases, the degradation of water quality is described as the extent to which nutrient criteria are exceeded or as the mass of a limiting nutrient such as nitrogen that is delivered from the land to the sea (Howarth et al. 1996). More recently, however, stoichiometric considerations have become more common, due to the realization that focus on reducing inputs of a single nutrient alone does not always yield the desired outcome of reduced eutrophication of nutrient-sensitive waters (Klausmeir et al. 2004, Dodds 2006, Elser et al. 2007). In freshwater systems, ecological stoichiometry traditionally focuses on the ratio of carbon to nitrogen to phosphorus (C:N:P; Frost et al. 2006, Elser et al. 2007), frequently comparing the availability of nutrients to the demands of phytoplankton (106 C:16 N:1 P) as established by Redfield (1934). The role of dissolved silica (Si) has been

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given relatively little consideration in studies of nutrient flux, despite the fact that its depletion has long been known to cause seasonal shifts of algal community composition in lakes (Kilham 1971, Conway et al. 1977) or limits to coastal marine diatom production (Malone et al. 1996).

Recent work highlights a growing realization that Si should receive more consideration in contemporary assessments of nutrient limitation (Downing et al. 2016). Increasingly, in both lentic freshwater and marine systems, the role of Si has been considered in the context of nutrient limitation (Garnier et al. 2010, Downing et al. 2016). Because land use changes such as urbanization and agriculture can dramatically alter the availability of Si as well as N and P that are delivered from land to surface waters (Carey and Fulweiler 2012), it is a potentially important consideration in management of water quality. Considerable evidence suggests that watershed alterations such as agricultural cultivation or urbanization can alter the flux of Si from formerly forested landscapes (Sferratore et al. 2006, Struyf et al. 2010). For nearshore marine ecosystems, alterations in the ratio of Si:N:P that is delivered from land to sea can shift communities from silica-demanding diatoms to other algae, which are often nuisance species (Garnier et al. 2010). Alterations to primary producers due to changes in stoichiometry can impact higher trophic levels as well (Díez et al. 2013), as demonstrated by manipulative experiments on Baltic Sea phytoplankton and zooplankton communities. Although increased Si availability many not alter productivity in lotic systems (Pringle et al. 1986), alterations in the relative amounts of Si, N, and P exported to marine ecosystems by streams and rivers could impact nearshore systems.

In urbanized watersheds, the overall stoichiometry of nutrients and organic matter in streams and rivers has received relatively little study. This is due in part to the fact that coastal cities are often treated as point sources that discharge nutrients directly to coastal waters from wastewater treatment facilities, with less focus on delivery of nutrients from the broader urban landscape. Major rivers such as those draining into the North Atlantic from Europe and America have received extensive study of their N loads (Howarth et al. 1996, Boyer et al. 2002), but similarly comprehensive assessments have not been made for their overall Si:N:P stoichiometry due to the long-recognized importance of N in limiting coastal marine productivity (Howarth and Marino 2006). In larger rivers such as the Rhine, reductions in P delivery to the river have caused a corresponding decline in Si uptake by diatoms, which appear to be the driver of increased riverine Si concentrations over the past several decades (Hartmann et al. 2011). Impoundment of rivers draining developed landscapes is known to decrease Si delivery to coastal ecosystems (Humborg et al. 2006), where interactions between N, P, and Si can be an important consideration in understanding the structure and function of coastal marine phytoplankton communities. In many of these examples, urban systems contribute nutrients that affect basin-scale stoichiometry, but the specific effects of urbanization on nutrient stoichiometry are difficult to determine.

Our understanding of spatial and temporal variability in urban elemental stoichiometry is even less developed than the overall effects of urbanization on nutrient stoichiometry. Seminal works on the "urban stream syndrome," for example, describe the overall degradation of water quality associated with urbanization, but do not address the effects of urbanization on elemental stoichiometry (Paul and Meyer 2001, Walsh et al. 2005, Wenger et al. 2009). Data on nutrient stoichiometry are available for cities with rudimentary waste treatment such as Kathmandu, where increases in C, N, and P concentration and flux were very large and Si was relatively unchanged as river chemistry evolved along the Bagmati River from headwaters to urban areas (Bhatt and McDowell 2007, Bhatt et al. 2014). In contrast, in urban areas in Maryland, USA, concentrations of Si increased substantially with impervious surfaces in study basins and appear to be affected by weathering of the built environment (Kaushal et al. 2017). In France, the Seine River receives both agricultural and urban wastewater inputs. In the late 1990s, levels of N greatly exceeded the Si:N stoichiometric demand of diatoms (about 1 Si:1 N molar ratio, Brzezinski 1985), with ratios of 0.2, but more recent upgrades to wastewater treatment facilities have resulted in increases in this ratio (Billen and Garnier 2007). In France and Belgium, the Scheldt River also drains a mix of urban and agricultural landscapes that frequently deliver N and P in excess of the Si flux that might limit the growth of coastal diatoms (Billen et al. 2005). Billen and Garnier (2007) proposed the Indicator of Coastal Eutrophication Potential (ICEP), based on the elemental stoichiometry of coastal diatoms and the extent to which riverine inputs deviate from this ratio. They have applied this approach globally, and find that most rivers exceed this ratio, particularly in the temperate zone, resulting in hypoxia (Garnier et al. 2010). They also stressed the extent to which more data are needed on Si flux in global rivers. Maguire and Fulweiler (2016) highlighted the importance of understanding Si fluxes from urban rivers and wastewater treatment effluents for the global carbon budget and marine productivity, but did not include any consideration of the nutrient or organic matter stoichiometry of urban rivers.

Understanding the role of nutrient stoichiometry in determining the biological effects of materials delivered by tropical rivers to the global ocean has received scant attention in the literature, perhaps due to the focus on other topics such as understanding global carbon budgets (Richey et al. 1980), rates of weathering (Stallard and Edmond 1983), or global hydrologic inputs (Richey et al. 1989) that have been the impetus for early work on large tropical rivers. Work by Gücker et al. (2016*a*, *b*) shows that, for tropical inland streams in Brazil, pastures and urbanization increase concentrations of DOC, DON, and inorganic nutrients, and alter the stoichiometry of dissolved organic matter. The role of small tropical rivers in coastal nutrient dynamics is not as well understood, despite the disproportionately important role that those draining mountainous volcanic islands play in the global carbon cycle (Lloret et al. 2013). This is due to the proximity of upland sources to marine waters, the steep terrain with limited coastal plains, and to the rapid rates of weathering and erosion in these small islands (McDowell and Asbury 1994, Goldsmith et al. 2010, Lloret et al. 2013).

In this paper, we address the impact of urbanization on the stoichiometry of nutrients and organic matter delivered to the coastal zone by small, montane, tropical rivers in Puerto Rico. We do so by addressing the temporal variability in chemistry of a small urban river in a steep, wet, coastal site in the relatively aseasonal tropics. We focus on examining changes in weekly river chemistry and flux from the mouth of the river for a period of six years during which we also have comparable data from nearby undeveloped watersheds sampled just a few kilometers from the coast. In addition, we document the evolution of water chemistry along a gradient from relatively undisturbed headwater streams to downstream urban areas. Our primary questions are as follows: (1) To what extent does urbanization alter the concentration, stoichiometry, and flux of inorganic nutrients and organic matter in streams? (2) Is there predictable variation in nutrient stoichiometry along the urban drainage network? (3) Does the tropical urban stream syndrome vary from its better-studied temperate counterparts? and (4) To what extent might urbanization alter the potential nutrient limitation of tropical coastal waters?

Methods

Study sites

The island of Puerto Rico is the smallest of the Greater Antilles and is poised on the eastern edge of the Caribbean plate as the fulcrum between the Greater and Lesser Antilles (Fig. 1). The island is of volcanic origin, but the current geologic evidence suggests that the most recent active volcanism was 30 million years ago (MYA; McDowell et al. 2012). Some parts of the island contain uplifted carbonate sediments developed during a period when much of the current island was submarine, with recent uplift (5 MYA) resulting in the present configuration of mountains and narrow coastal plain (Brocard et al. 2015). Rainfall on the island ranges dramatically by elevation and orientation to the prevailing Trade Winds (Murphy et al. 2017), with values typically ranging from 2 to 5 m/yr. Our primary study site is the Río Piedras watershed, home to many of the inhabitants of the capital city of San Juan and its metropolitan area (Fig. 1). Originally settled in the 1500s and passing into U.S. hands in 1898 following the Spanish-American War, the city of

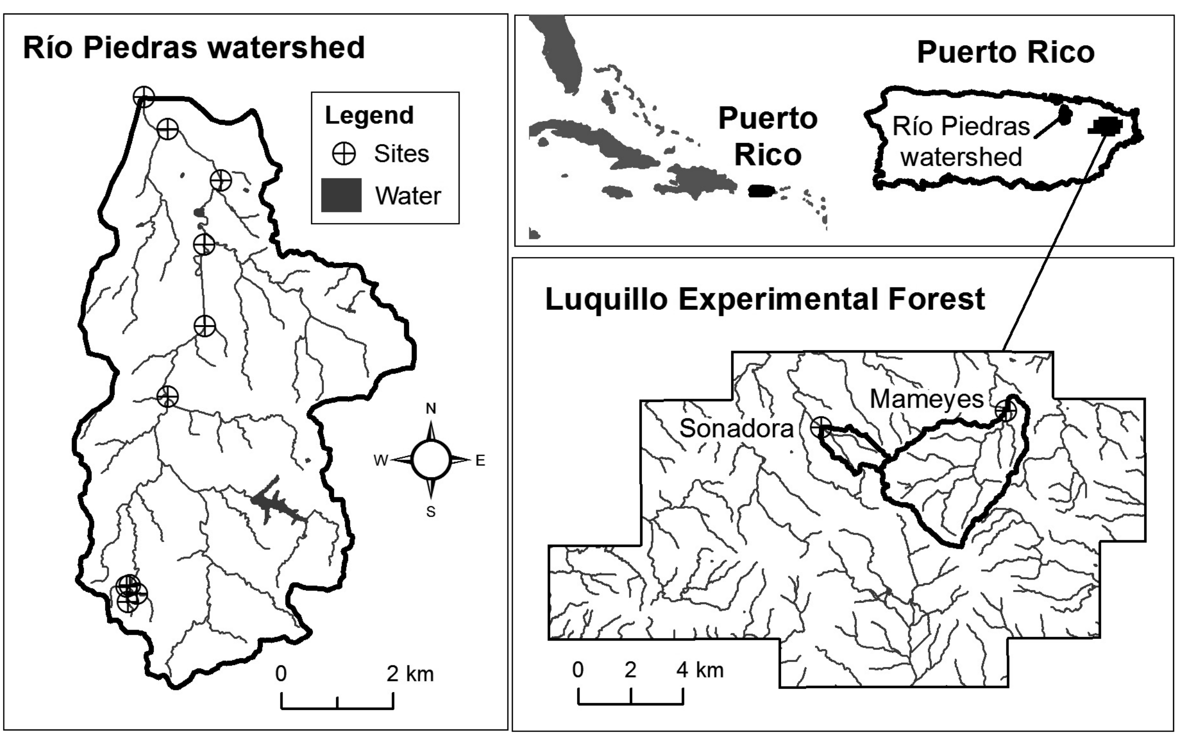

Fig. 1. Map of the study sites showing the three study watersheds as well as the location of individual sampling stations within the Río Piedras basin.

San Juan has undergone explosive growth since the 1940s. While originally confined to the easily fortified harbor area near the mouth of Bahia San Juan, growth spilled out into the Río Piedras basin with the advent of the industrialization associated with Operation Bootstrap, the name given to the Federal program of socioeconomic development that began in 1942. The urban infrastructure in the Río Piedras basin is thus of fairly recent construction, even though San Juan is a very old city.

Our focal urban watershed is defined by the USGS gauging station at Hato Rey, Puerto Rico (USGS 50049100). It has a watershed area of 39.4 km^2 and average daily discharge of 1.58 m^3/s for the period 1989–2015. Maximum elevation is 214 m above sea level (masl). In the 1880s, the river was used as a water supply (Lugo et al. 2011), but it is currently free-flowing throughout almost its entire length, with no significant water abstraction and no return of treated water from wastewater treatment facilities. Since the great majority of the human inhabitants of the basin are served by both public water and sewer (Potter et al. 2014), the river is, in theory, affected only by urban runoff from pavement and other impervious surfaces. In practice, however, this may be far from the case. As in other urban environments with extensive but aging infrastructure (Kaushal and Belt 2012, Kaushal et al. 2014), there appear to be many leaking water lines and sewer lines in the basin. The effects of these leaks on stream chemistry have recently been described by Ramírez et al. (2014) and Potter et al. (2014), who both documented the spatial variability in nitrogen, phosphorus, and major ion concentrations with extensive sampling throughout the Río Piedras basin. They were able to relate spatial variation in water quality to a variety of land cover drivers, and Potter et al. (2014) found that the volume of sewer pipe in an individual sub-basin was an excellent predictor of spatial variability in concentrations of nutrients and organic matter within the entire drainage network.

The watershed has the greatest population density in the oldest areas of the city near the mouth of the river (Fig. 1), with an average density for the entire watershed of 2,215 inhabitants/km^2 (Census 2010). The original land cover is tropical evergreen forest, with rainfall averaging 2,000 mm across the basin (Webb and Gomez 1996). In the most recent NLCD assessment available (2001), the watershed is 19% forest and 30% impervious cover. Lithology of the basin is primarily volcaniclastic materials, with a small percentage of the land area underlain by carbonates of marine origin. We also compare data from the urbanized Río Piedras watershed to two other nearby, well-studied, forested watersheds: Río Mameyes (USGS 50065500) and Quebrada Sonadora (USGS 50063440; McDowell and Asbury 1994, McDowell et al. 2012, 2013). Located in the Luquillo Experimental Forest (USDA Forest Service), the Mameyes and Sonadora basins are almost entirely forested, with only scattered houses and research stations. The Mameyes is a Federally designated Wild and Scenic River. Forest age in both watersheds is mixed, with past disturbance (small-scale charcoal making, agriculture) that ceased in the early 1900s. Vegetation varies with elevation; older trees with shorter stature and lower biomass are found at high elevations (peak elevation is about 1,000 masl; McDowell et al. 2012). Extensive research on stream water chemistry has been conducted on the Mameyes and Sonadora (McDowell and Asbury 1994, Murphy and Stallard 2012; McDowell et al. 2013), although elemental fluxes have not been previously published for the years of our study. All three watersheds drain into the North Atlantic, have similar geology, and a similar record of weekly river sampling, allowing us to assess the impacts of urbanization within the Río Piedras watershed.

Sampling regime and analysis

Sampling in each study watershed occurred weekly for six calendar years (January 2009 to December 2014), which captured periods of both high and low flow. Samples were held on ice after collection until filtering through a pre-combusted and rinsed Whatman GF/F (nominal pore size 0.7 μm) and were analyzed for major cations and anions, dissolved silica, nutrients, and organic matter. Prior to analysis, samples were held refrigerated (dissolved Si) or frozen (other analytes) in acid-washed HDPE bottles. Major cations (Na^+, K^+, Ca^{2+} Mg^{2+}) and anions (F^-, Cl^-, SO_4^{2-}, NO_3^-) were analyzed using ion chromatography (Dionex ICS-1000, Thermo Fisher Scientific, Waltham, MA, USA, using methods EPA 300.7 and 300.1). Samples for dissolved Si (molybdate blue method), NH_4^+ (phenol hypochlorite), and soluble reactive P (SRP; ammonium molybdate) were analyzed with robotic colorimetry (Westco Smartchem, Unity Scientific, Brookfield, CT, USA). Dissolved organic carbon was measured as non-purgeable organic carbon on a Shimadzu TOC-V or TOC-CPH (Shimadzu Corporation, Columbia, MD, USA). Total dissolved N (TDN) was measured with the same instrument using the Shimadzu TN module that analyzes NOx production following high-temperature Pt-catalyzed oxidation (Merriam et al. 1996). Dissolved organic N (DON) was determined by subtracting the inorganic forms of nitrogen (NO_3^- and NH_4^+) from TDN.

Special care was taken to ensure that dissolved Si values were unaffected by our use of a glass fiber filter. Although previous work on dissolved Si in a variety of environments has relied on glass fiber filters (e.g., Heartsill-Scalley et al. 2007 for tropical rain and throughfall; Sferratore et al. 2006 for temperate river chemistry), use of a glass fiber filter is generally avoided in trace metal and isotopic geochemistry. We assessed the possibility of Si contamination by analyzing nine blanks of deionized water that were carried through the filtration process and found that there was no detectable Si (<0.02 mg/L as SiO_2) produced by the filtration process. We also compared the Si values obtained with GF/F and Whatman

Cellulose Membrane filters (0.45 μm pore size) as a further test of possible filter effects (both nominal pore size and filter materials) on reported values of riverine dissolved Si. For three replicate splits from each of our three study rivers, we found no statistically significant difference between the values obtained with the two filter types and no interaction effects between river and filter type on Si concentrations.

Data analysis

To determine whether the three watersheds had different water chemistry for the 14 solutes that we examined, we compared watersheds using a one-way ANOVA in R (v. 3.3.3; R Core Team 2017). If this showed a significant difference, we then used a post hoc Tukey Honestly Significant Difference test to determine which pairs of rivers differed significantly for the given solute. For both statistical analyses, we used a Bonferroni corrected alpha value of 0.00357 (0.05/14), as we made 14 separate comparisons.

Fluxes were calculated using the loadflex program (Appling et al. 2015), which is an enhancement of the widely used USGS LOADEST model (Runkel et al. 2004) as implemented in R. Both loadflex and LOADEST rely primarily on relationships between concentration of a solute and instantaneous discharge at the time of sampling to estimate concentrations when measured values of river chemistry are not available. In practice, and in our case, this often means that the 15-min record of discharge at a given station is paired with an estimate of concentration based on weekly grab samples that span a range of discharge conditions. Because other drivers (such as seasonal variation in concentration or long-term changes in atmospheric deposition) can also change stream solute concentrations, each program also incorporates the observed change in a solute over time into the estimates of flux. The loadflex program contains a number of features not available in LOADEST, including robust assessment of uncertainties in flux estimates and implementation of multiple approaches to estimate concentrations when weekly grab samples for stream chemistry are paired with a continuous record of discharge, including the composite method of Aulenbach and Hooper (2006). The composite method is particularly appropriate for data sets that show changes in concentrations that are neither seasonal nor monotonic (Aulenbach and Hooper 2006).

We calculated stoichiometric ratios for N:P, Si:N, Si:P, and DOC:DON using the average observed concentrations for all available samples. Due to small differences in sample sizes for the different nutrients, the stoichiometric ratios are not strictly conserved (e.g., Si:P is not equal to N:P times Si:N). To assess statistical uncertainty in the overall calculated nutrient ratios for each watershed, we used the boot package in R (v. 3.3.3) to calculate bootstrapped 95% confidence intervals. We did this by generating a bootstrapped average for each component of the ratio, then taking the ratio of the two elements of interest to get a bootstrapped stoichiometric ratio. We replicated this 10,000 times and created the 95% confidence intervals based on these results. This approach preserves nutrient concentration combinations from specific days, while also avoiding the mathematical issues that arise when taking an average of a ratio.

To characterize the spatial evolution of nutrient stoichiometry along the river network of our urban site, we used samples from headwaters to mouth that were originally reported in aggregate in Potter et al. (2014). In this paper, we use these data to assess stoichiometric relationships and examine changes in stoichiometry with impervious surface cover, which increases with distance downstream, neither of which was described or examined in our earlier paper. We examined the impact of impervious surface cover on nutrient stoichiometry using a linear regression in R.

Results

Overall, we observed higher concentrations of almost all solutes in the urban watershed and higher fluxes per unit watershed area for most solutes. The stoichiometry of nutrients also changed with urbanization, with large changes in Si:N, Si:P, and DOC:DON. The ratio of N:P was surprisingly similar between forested and urban watersheds, despite the fact that N and P fluxes were dramatically higher in the urban basin. On an annual basis, fluxes of N and P are greatly elevated and highly variable from year to year in the urban river. On a monthly basis, however, the stoichiometry of nutrients in the urban watershed was more predictable.

Concentrations of nutrients, organic matter, and chloride were all significantly elevated in the Río Piedras watershed relative to its wildland counterparts, the Sonadora and Mameyes (Table 1). Concentrations of DOC, DON, NH_4^+, NO_3^-, SRP, and SO_4^{2-} in river water were all highly elevated in the Río Piedras, with levels 2–50 times higher in the urban river than in the two forested watersheds (Table 1). Although higher than in the forested watersheds, NO_3^- concentration in the urban Río Piedras was not nearly as elevated as NH_4^+ (15-fold vs. 50-fold increase, respectively; Table 1). Organic matter was elevated in the urban catchment to a lesser extent than inorganic nitrogen, with DON levels fivefold higher in the urban river while dissolved organic carbon (DOC) was only about 75% higher. Large differences were seen for many other solutes. Concentrations of Na and Cl, for example, were three to four times higher in the urban catchment than the forested catchments (Table 1).

Differences in nutrient exports were not as large as those observed for nutrient concentration but were still substantial (Table 1). For soluble reactive P, inorganic N, and DON, area-normalized fluxes in the Río Piedras were at least three times those of the forested watersheds (Fig. 2). For most other solutes such as Na, Cl, and Mg, fluxes were about 50–100% higher in the Río Piedras than the wildland rivers (Fig. 2). The only fluxes that were lower per unit watershed area in the urban than the

TABLE 1. Concentration and export (mean ± SE) of inorganic nutrients, dissolved organic nitrogen (DON), total dissolved nitrogen (TDN), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), dissolved Si as SiO_2, and major cations and anions for weekly samples collected over six study years (2009–2014) in the Río Piedras (RP), Río Mameyes (MPR), and Quebrada Sonadora (QS), Puerto Rico, USA.

	Concentration (mg/L)			Export ($kg \cdot ha^{-1} \cdot yr^{-1}$ ± SE)		
Compound	RP	MPR	QS	RP	MPR	QS
NH_4^+-N	0.38^A	0.006^B	0.006^B	7.15 ± 1.39	0.18 ± 0.03	0.23 ± 0.05
NO_3^--N	0.741^A	0.046^B	0.053^B	8.17 ± 0.67	1.53 ± 1.04	1.32 ± 0.36
DON	0.33^A	0.06^B	0.06^B	6.72 ± 3.98	2.19 ± 0.35	2.62 ± 0.36
TDN	1.62^A	0.11^B	0.13^B	19 ± 0.82	4.1 ± 0.6	4.36 ± 0.34
SRP	0.074^A	0.006^B	0.002^B	1.11 ± 0.26	0.16 ± 0.02	0.1 ± 0.01
SiO_2	26.9^A	19.5^C	10.78^B	286 ± 7.13	484 ± 14.3	346 ± 13.6
DOC	3.48^A	2.09^B	1.89^C	65.6 ± 6.25	66.2 ± 7.2	119 ± 16.5
Na^+	21.8^A	6.23^B	4.68^C	245 ± 8.23	161 ± 3.51	169 ± 3.79
K^+	2.71^A	0.6^B	0.26^C	38.8 ± 1.8	16.2 ± 0.36	9.3 ± 0.45
Ca^{2+}	18.8^A	7.82^B	2.71^C	251 ± 12.4	198 ± 6.35	94.6 ± 3.28
Mg^{2+}	9.17^A	1.98^B	1.65^C	106 ± 5.02	45.75 ± 1.33	50.7 ± 1.77
Cl^-	24.6^A	7.46^B	7.05^B	270 ± 9.06	203 ± 4.03	267 ± 5.96
SO_4^{2-}-S	3.78^A	1.04^B	0.53^C	46.8 ± 1.79	27.4 ± 0.89	20.5 ± 0.43
F^-	0.05^A	0.031^A	0.018^B	0.38 ± 1.32	0.65 ± 0.08	0.52 ± 0.07

Notes: We compared solute concentrations among the three rivers using an analysis of variance (ANOVA) and a post hoc Tukey test using Bonferroni-corrected alpha values ($\alpha = 0.00357$). Statistically significant differences are noted with different superscript letters, with "A" denoting the highest value. Fluxes are calculated using loadflex (Appling et al. 2015), and SE refers to the standard error of the average of the six annual flux values.

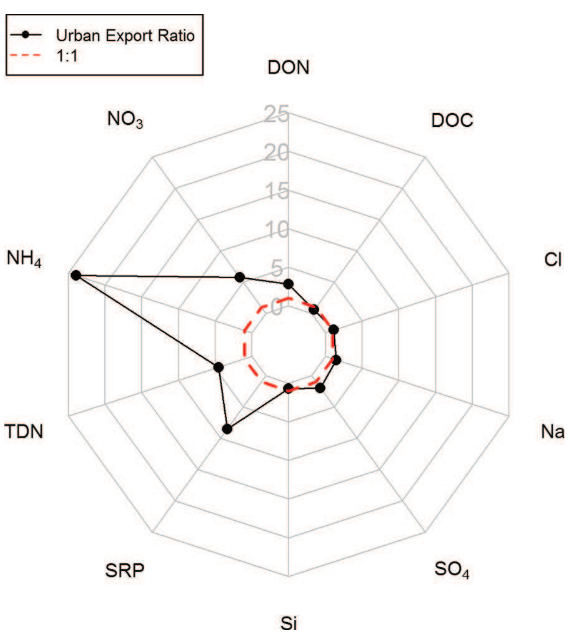

FIG. 2. Radar plot showing the ratio of average annual flux ($kg \cdot ha^{-1} \cdot yr^{-1}$) of nutrients, organic matter, and major ions in the urban Río Piedras watershed relative to the average annual flux in the forested Mameyes and Sonadora watersheds. DON, dissolved organic nitrogen; DOC, dissolved organic carbon; Si, dissolved silica; SRP, soluble reactive phosphorus; and TDN, total dissolved nitrogen. The red interior dashed line is the 1:1 ratio, and the other radar lines are corresponding ratios.

forested watersheds were DOC and Si (Table 1, Fig. 3). Fluxes of nutrients and major ions were typically more stable from year to year in the forested watersheds than in the urban Río Piedras (Fig. 3; Appendix S1, Tables S1–S3 and Fig. S1).

By most measures, the stoichiometry of nutrients and dissolved organic matter was altered dramatically in the urban watershed. Based on average concentrations over the study period, the ratios of Si:N, Si:P, and DOC:DON were all considerably lower in the Río Piedras than in the forested watersheds, and the 95% confidence intervals for these ratios in the Río Piedras did not overlap with those of the Mameyes or Sonadora (Table 2). The ratios Si:N and Si:P were about 80–90% lower, and the ratio of DOC:DON in DOM was about 75% lower. There was considerable variation when stoichiometry was examined on a weekly, sample by sample basis, but the same trends were evident on a monthly basis, with the urban river consistently lower in Si:N, Si:P, and DOC:DON (Fig. 4). In the Río Piedras, molar Si:N often approached or reached 1:1; in the forested watersheds, in contrast, the ratio was frequently above 50, especially in the Mameyes. Although it varied over time, the Si:N ratio in the forested watersheds never approached 1:1 (Fig. 4). The stoichiometry of organic matter (as expressed by the molar DOC:DON ratio) was fundamentally different in the urban watershed, with a large shift from N-poor material (C:N often exceeding 40) to N-rich material (C:N typically near 10; Fig. 4). No seasonal variation in stoichiometry was evident in any of the ratios (Fig. 4). The ratio of N:P was not appreciably different in the Río Piedras than in the forested watersheds, as variation in the urban watershed was bracketed by that seen in the two forested watersheds (Fig. 4a; Table 2). On a monthly basis, molar N:P ranged from about 16–60 among all the study watersheds.

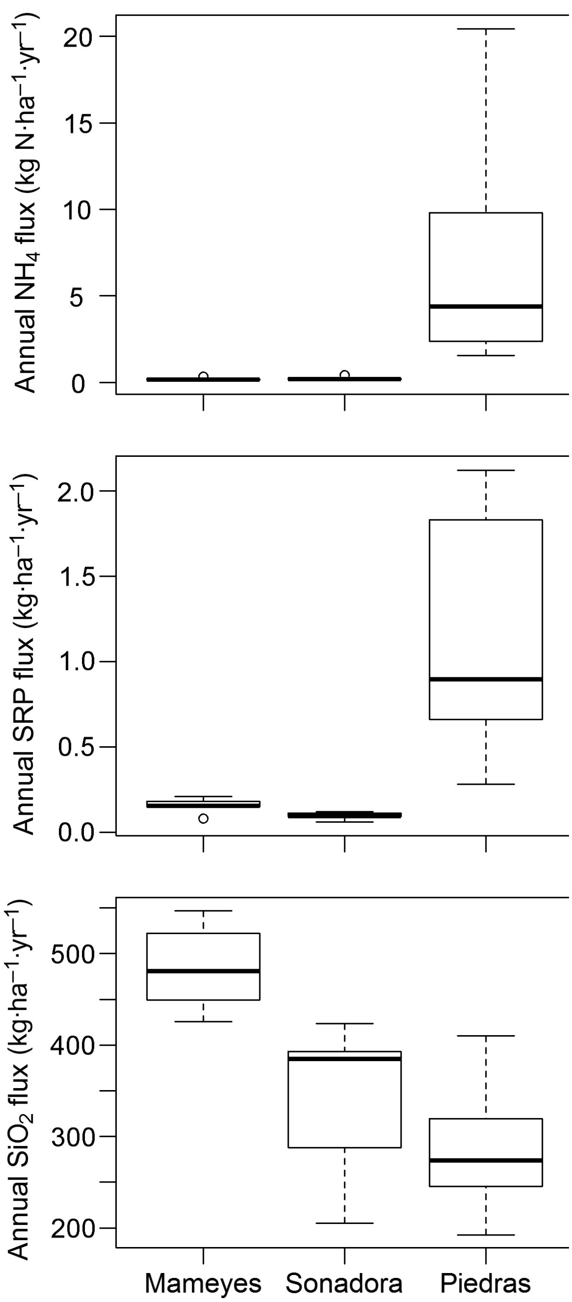

Fig. 3. Box plots showing annual variability in flux of major nutrients from forested (Mameyes, Sonadora) and urban (Río Piedras) watersheds over 6 yr of sampling (2009–2014). The median value is represented by the central line, the upper and lower bounds of the box represent the upper and lower quartiles, respectively, and the whiskers represent the range of the data, excluding outliers. Outliers, points greater than 1.5 times the interquartile range above the upper quartile or below the lower quartile, are represented by points.

Although urbanization strongly affected overall nutrient concentrations and fluxes, it also decreased the short-term variability of nutrient stoichiometry. On a weekly and monthly basis, the Si:N ratio in the two forested watersheds was highly variable, for example, and this variability was reduced in the urban watershed (Fig. 4b). The Sonadora and Río Mameyes averaged Si:N ratios of about 20 and 40 (Table 2), but weekly values ranged from 4.2 to 182 and 2.3 to 93, respectively. In contrast, Si:N ratios were more constrained in the urban, nitrogen-enriched Río Piedras watershed, with an average Si:N of 4.5 and a weekly range of 0.58–21.1). For the forested watersheds, variability in Si:N is primarily driven by lower concentrations of TDN during these weeks, rather than increased Si.

The differences in nutrient flux and nutrient stoichiometry between the forested watersheds and the Río Piedras were also evident along the main stem of the Río Piedras, which is characterized by an increase in population density, urban development, and impermeable surface cover with distance downstream (Potter et al. 2014). Along the gradient in impermeable surface that occurs with distance downstream, Si:N ratios dropped from about 12 to about 5, and DOC:DON also showed a general decline but considerable spatial variability. Unlike the data from the mouth of the Río Piedras, where N:P ratios were similar to the wildland rivers (Fig. 4), there was a large drop in N:P ratio as urbanization increased with distance downstream (Fig. 5).

Discussion

Urbanization has a profound influence on the concentrations and fluxes of most solutes relative to those in nearby forested watersheds. In addition to the obvious potential impacts of increased N and P loading, the stoichiometry of these urban inputs is likely to be important in determining their ecological effects on coastal ecosystems. Even though the export of DOC from mountains to the coast is similar per unit area in the forested and urban watersheds, for example, the stoichiometry of that organic matter is dramatically altered, as DOM shifts to much more N-rich material in the urban system and DON increases fivefold in concentration. Similar results were observed by Gücker et al. (2016*a*) in their study of small tropical urban catchments, where DOC:DON declined from 26 to 6 when comparing forested to urban sites sampled on multiple dates during the wet season. Because DON is potentially available to both phytoplankton and microbes (Seitzinger and Sanders 1997, Bronk et al. 2007), increased delivery of DON from urban runoff can change the trophic status of coastal systems. DON from anthropogenic sources appears to be particularly susceptible to microbial mineralization (Seitzinger et al. 2002), as is often the case with organic substrates that are rich in N relative to C (Magill and Aber 1999). Much of the additional DON from the Río Piedras watershed appears to be from leaking or ineffective sewage infrastructure, as total volume of sewer pipe in a sub-basin is the best predictor of spatial variability in stream DON concentrations within this watershed and all sewage is exported out of the watershed for treatment (Potter et al. 2014). Any DON that is derived from sewage leaks or overflows is much more likely to be easily mineralized than the DON found in rivers

TABLE 2. Comparison of observed stoichiometric ratios in the three study rivers.

	Río Piedras		Río Mameyes		Quebrada Sonadora	
	n	Mean (95% CI)	*n*	Mean (95% CI)	*n*	Mean (95% CI)
N:P	285	48.9 (44.7–52.7)	303	39.6 (36.3–43.2)	306	107 (98.9–115)
Si:N	260	4.05 (3.67–4.3)	284	41.1 (38.1–44.1)	299	20.6 (19.6–21.8)
Si:P	261	197 (170–220)	282	1670 (1560–1780)	297	2220 (2060–2370)
DOC:DON	281	11.8 (10.9–13.7)	306	28.8 (26.5–31.1)	302	35 (33–37.1)

Notes: Molar ratios of DOC:DON, TDN:SRP (N:P), Si:TDN (Si:N) and Si:SRP (Si:P) are derived from average values presented in this table for each site. We calculated 95% confidence intervals by bootstrapping our sample points 10,000 times.

receiving treated effluent that have been the subject of previous papers (Seitzinger and Sanders 1997). On the island of Puerto Rico, modern sewage treatment is very effective at reducing BOD, and the nitrogen load in treated sewage effluent is dominated by NO_3^- (Figueroa-Nieves et al. 2014), suggesting that minimizing these apparent sewage leaks would greatly reduce bioavailable nitrogen loads.

The urban Río Piedras watershed exported inorganic N and P at levels similar to what would be expected based on studies of temperate urban ecosystems, exporting 8.5 times more soluble reactive phosphorus, ~5 times more NO_3^- and TDN, and 24 times more NH_4^+ than similar forested systems. Thus, the degraded water quality associated with the "urban stream syndrome" appears to be widely prevalent in both temperate and tropical streams (Walsh et al. 2005), as has been noted in previous studies of tropical urbanization (Ometo et al. 2000, Ramírez et al. 2014, Silva et al. 2011, Gücker et al. 2016*a*). If we expand the scope of the "urban stream syndrome" to consider the full range of nutrients, however, it appears that there may be some significant differences between temperate and tropical urban systems. First, it appears that urbanization may be unlikely to appreciably increase Si fluxes in much of the tropics, contrary to what has been observed in the temperate zone. Carey and Fulweiler (2012) showed that for a large regional data set that includes a wide range of geologic settings, urban export of Si is almost double that of fully forested sites in New England, USA. They attributed this result to the loss of Si uptake and storage by the biomass that is harvested during urbanization. We did not observe this pattern in the Río Piedras, however, with lower, not higher, fluxes in the urban environment. Similar results were reported by McDowell et al. (1995), who observed that, in rural catchments in the Caribbean, highest silica fluxes were observed in those sites with the lowest human population density. Studies of additional tropical urban watersheds across a range of runoff and lithology are needed to assess the generality of this finding, as recently called for in two syntheses of tropical and global urban stream research (Booth et al. 2016, Capps et al. 2016). Second, whether or not urbanization decreases Si export, many tropical watersheds export much more Si than their temperate counterparts (White and Blum 1995). This means that in many tropical regions N and P additions to coastal waters must be considerable before they exceed the index of coastal eutrophication potential (Billen and Garnier 2007).

Unlike temperate zone systems, which often have relatively low Si values (White and Blum 1995), the montane rivers of the Caribbean, including the Río Piedras, all have high concentrations of dissolved Si (McDowell and Asbury 1994, McDowell et al. 1995, Goldsmith et al. 2010). This appears to be part of a global pattern in tropical rivers, in which silicate weathering is typically the dominant contributor to the total dissolved solid load (Gaillardet et al. 1999). The Si flux from all three of our study watersheds is much larger than values predicted from temperate data sets that relate Si flux to forest cover (Carey and Fulweiler 2012). Our two forested watersheds (100% forest cover) export greater than an order of magnitude more Si than is predicted for temperate rivers (194 $kg \cdot ha^{-1} \cdot yr^{-1}$ Si in our tropical rivers, 17.9 $kg \cdot ha^{-1} \cdot yr^{-1}$ in temperate rivers). The Río Piedras watershed, which is ~19% forested, exports over five times as much Si (133.6 $kg \cdot ha^{-1} \cdot yr^{-1}$) than a similar temperate watershed would export (24.6 $kg \cdot ha^{-1} \cdot yr^{-1}$ Si; Carey and Fulweiler 2012). The baseline export of Si is much higher in most tropical streams and rivers than their temperate counterparts (McDowell et al. 1995, Gaillardet et al. 1999), likely due to the high and steady temperature that has been identified as a key driver of chemical weathering rates (White and Blum 1995). In their study of 68 watersheds around the globe with lithologies ranging from granitic to high grade metamorphic gneisses, White and Blum (1995) found that weathering and silica export were strongly related to precipitation and rainfall, with the humid tropics yielding the greatest Si export and temperate watersheds yielding only moderate Si flux per watershed area. While not all tropical terrain is siliceous or easily weathered, the substantial weathering of Si from tropical watersheds is well established and of global significance (Gaillardet et al. 1999).

The response of tropical watersheds to urbanization, and in particular their high Si load relative to their temperate counterparts, could play an important role in the community composition of nearshore marine algae or large reservoirs downstream of urban environments. Although marine diatoms typically have a Si:N ratio of 1:1 (Brzezinski 1985), they can be competitively dominant under high Si, low N conditions (Si:N > 25, Sommer 1994). Given the importance of Si:N stoichiometry in the

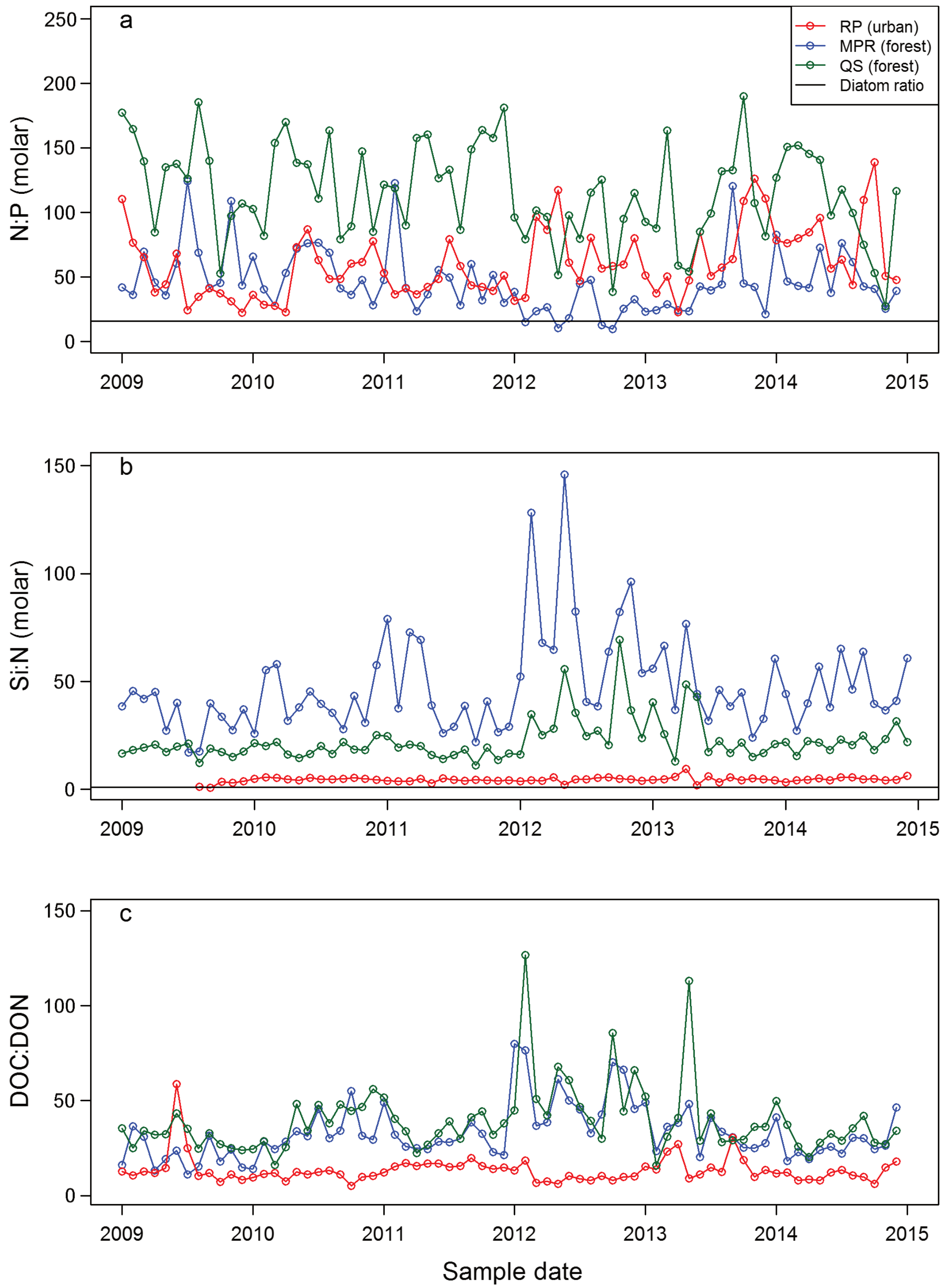

FIG. 4. Monthly variation in nutrient and dissolved organic matter stoichiometry over the 6 yr of weekly sampling for our three study watersheds, the Río Piedras (RP), Río Mameyes (MPR). and Qebrada Sonadora (QS). (a) molar N:P; (b) molar Si:N; (c) molar DOC:DON. The horizontal line represents typical algal stoichiometry for the N:P ratio (16:1, Redfield ratio) and the Si:N ratio of 1:1 (typical diatom ratio; Billen and Garnier 2007).

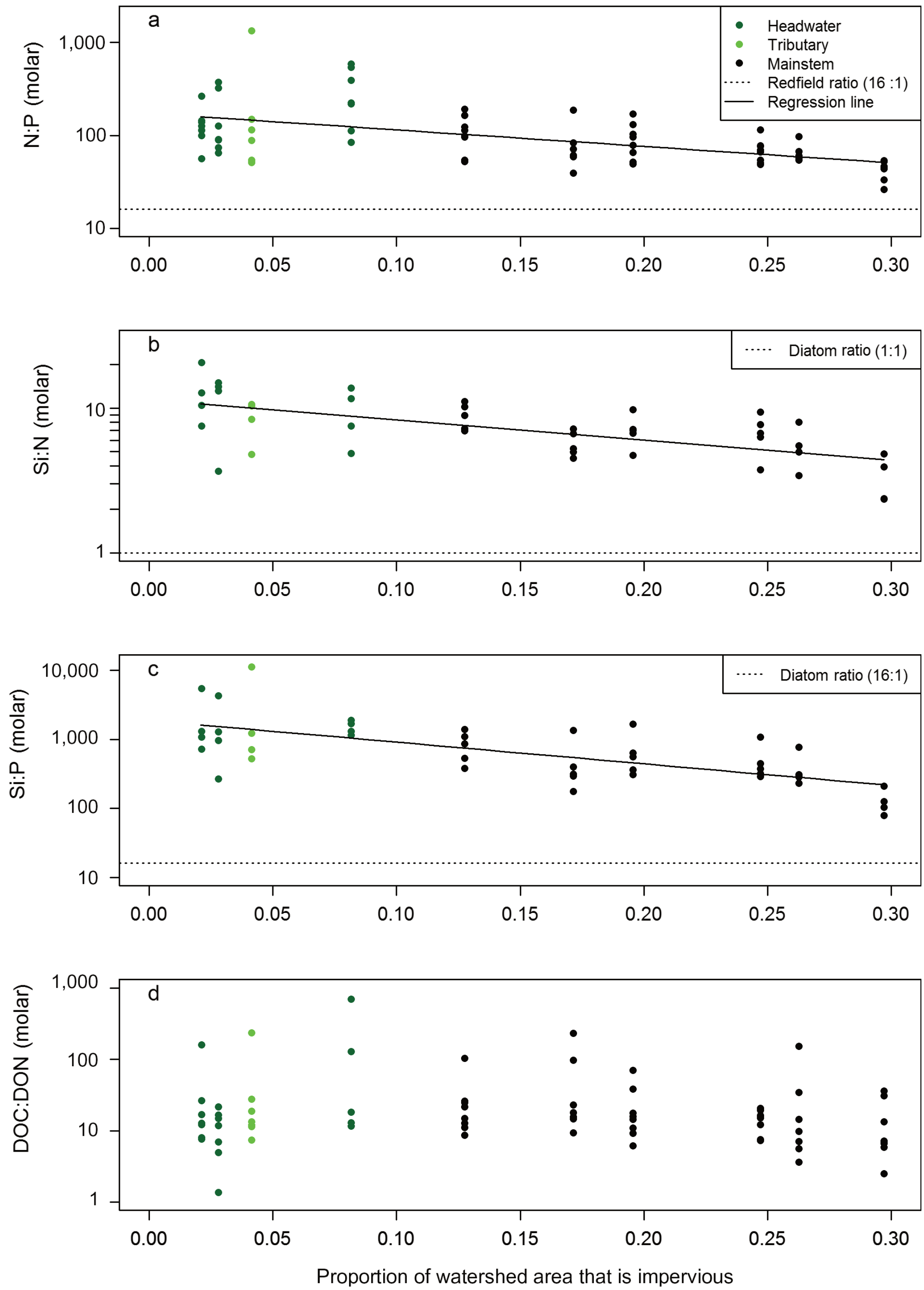

FIG. 5. Variation in nutrient stoichiometry (a, molar N:P; b, molar Si:P; c, molar Si:N) and the stoichiometry of dissolved organic matter (d, molar DOC:DON) along a range of impervious surface cover within the Río Piedras watershed from annual sampling in late February to early April, 2004 to 2010. Green points represent sampling from three different headwater streams in a given year, the light green points represent the tributary into which all three headwater streams flow, and black points represent samples from the mainstem Río Piedras. In general, urbanization increases with distance downstream. Note the log scale on the Y axes.

relative competitive dominance of diatomaceous and non-diatomaceous marine algae, the increase in N flux and large decrease in Si:N that we have observed in our tropical watersheds is an important aspect of the tropical urban stream syndrome. Because non-diatomaceous species are often nuisance algal species (Garnier et al. 2010), these shifts could have direct impacts on ecosystems and humans via increased harmful algal blooms.

In comparison with larger watersheds also draining the North Atlantic (Howarth et al. 1996), the areal flux of N is higher in the Río Piedras than all major watersheds of the continental United States and four times as high as an urban stream in Baltimore with a similar population density (Kaushal et al. 2014). Sanitary sewer leaks also have been found in the Baltimore watershed (Kaushal and Belt 2012), so the existence of sewage inputs of N into the Río Piedras cannot by itself explain the large flux of TDN. A plausible explanation is that leaks are more extensive in the Río Piedras than in Baltimore, or that illicit or unrecognized connections to storm sewers are more common in the Río Piedras than in other urban watersheds. A recent analysis by Reisinger et al. (2018) suggests that nitrogen flux in Baltimore streams is related to the frequency of combined sewer overflows (CSOs) as well as infrastructure condition. Because the Río Piedras watershed does not have combined sewers, such overflows cannot explain the high TDN there.

In contrast to nitrogen export, however, the concentration of NO_3^- in the Río Piedras is below that which might be expected based on global variation of riverine NO_3^- concentrations as a function of human population density (Fig. 6). One explanation for this lower than expected concentration, but relatively high dissolved N flux, is the high runoff in this basin (about 1.3 m annually). Additional factors driving this relatively high N flux but low NO_3^- concentration include the relatively low ratio of NO_3^-:NH_4^+ (Table 1) and the apparent oxygen limitation to nitrification observed by Potter et al. (2014) in an extensive study of spatial patterns in nitrogen concentrations at 40 sampling sites throughout the basin. Finally, the relatively low NO_3^- concentrations might be the result of high rates of denitrification in the basin. Past research in Puerto Rico, including in the Río Piedras watershed, shows that denitrification occurs at relatively high rates in these tropical streams and is a particularly large fraction of the total N uptake that occurs within the stream channel relative to temperate streams (Potter et al. 2010). Other comparisons between urban tropical streams and their wildland counterparts also show surprisingly little response of NO_3^- to urbanization. Silva et al. (2011) report an almost fivefold increase in NO_3^- of urban streams in the Cerrado region of central Brazil, but NO_3^--N was still relatively low (0.095 mg/L; Table 3). In central Brazil, small watersheds with significant urban cover had a median NO_3^--N concentration of only 0.22 mg/L (Gücker et al. 2016*b*), considerably lower than those in the Río Piedras.

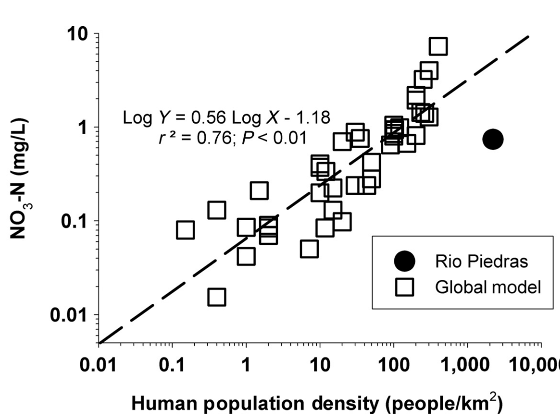

Fig. 6. Nitrate concentration (mg N/L) in river water as a function of human population density (inhabitants/km^2) for a global compilation of developed watersheds (Cole et al. 1993) and our urban study watershed, the Río Piedras, Puerto Rico, USA.

Export of phosphorus from the urbanized Río Piedras was in the same range as export from mixed land use watersheds in the northeastern United States (Howarth et al. 1996), but concentrations were higher than those observed in other tropical watersheds with a significant fraction of urban land use. Previous work in Puerto Rico and the Caribbean shows a modest range in SRP concentrations (2–11 μg/L) and molar N:P (8–50) in watersheds with low to moderate population density (McDowell and Asbury 1994, McDowell et al. 1995). Among small South American watersheds, concentrations of SRP ranged from 2 to 35 μg/L across various land uses (wildland, agriculture, pasture, urban; Gücker et al. 2016*a*). Gücker et al. (2016*b*) showed a clear pattern of increasing SRP in response to urbanization in Brazilian Cerrado watersheds, with concentrations doubling (17–35 μg/L) and N:P ratio increasing dramatically relative to their undeveloped watersheds. These urban sites in Brazil were half the average value that we obtained in the highly urbanized Río Piedras watershed (74 μg/L), likely due to its very high human population density. It should be noted that the range of natural variation in phosphorus concentrations and flux is very high in the tropics. At an unusual undisturbed rain forest watershed in La Selva, Costa Rica (the Arboleda), geothermally altered groundwater enters via deep groundwater flowpaths and increases SRP to over 230 μg/L (Ganong et al. 2015). No other sites with such extraordinarily high values have been reported in the literature from either urban or wildland sites in the tropics, nor have they been observed at other sites with geothermal influence (Ganong et al. 2015).

The consistent response of some of the major ions to urbanization is intriguing and suggests that the "urban stream syndrome" should be expanded to include a broader examination of the full range of water quality impacts as well as nutrient stoichiometry (Table 3). In many urban sites throughout the world, almost all solutes are elevated in concentration in urban environments and nutrient stoichiometry varies widely (Table 3). Although some of these increases can be attributed to direct human

TABLE 3. Comparison of Río Piedras chemistry to surface waters of other urban watersheds receiving no direct wastewater treatment effluent.

Parameter	No effluent	Río Piedras	Atibala River	Brazilian Cerrado	Bagmati	Ipswich
NH_4^+-N	0.04	0.380	0.637	0.11	20.4	0.021
NO_3^- -N	0.51	0.741	0.950	0.09	0.19	0.30
DON	0.42	0.33		0.30	3.27	0.37
SRP	0.07	0.074	0.040	0.004	2.94	0.002
DOC	10.3	3.48	27.06	1.76	13.1	9.13
SiO_2		26.9	1.55		17.6	2.10
SO_4^{2-}	27.4	11.34	26.49	0.37	5.65	8.76
Cl^-	26.8	24.6	8.62	1.14	48.9	44.0
Na^+	36.3	21.8	18.71	1.60	60.2	23.0
K^+	3.46	2.71	3.90	0.62	14.4	1.26
Ca^{2+}	29.2	18.8	5.99	1.38	11.2	13.8
Mg^{2+}	10.6	9.17	1.80	0.29	4.70	2.80
N:P	30.6	43.3	87.1	274	17.9	764
Si:N		4.3	0.2		0.2	0.7
Si:P		187	19.9		3.1	541
DOC:DON	28.6	11.4		6.9	4.7	28.8

Notes: All concentrations are mg/L. Average molar ratios of TDN:SRP or DIN:SRP (N:P), dissolved Si:TDN (Si:N), and dissolved Si:SRP (Si:P) are derived from average values presented in this table for each site. “No effluent” column is from a summary of multiple sites by Steele et al. (2010); Bagmati River, samples from downstream reaches in Kathmandu from Bhatt et al. (2007); Ipswich River, Massachusetts, from Williams et al. (2005); Atibala River, Piracicaba basin, Brazil from Williams et al. (2001); Brazilian Cerrado from an average of three small streams draining watersheds with 6–27% urban land cover (wet season values), from Silva et al. (2011).

impacts, such as inputs of C, N, and P from leaking or malfunctioning sewage infrastructure as has been suggested for the Río Piedras (Potter et al. 2014), not all of them are easily explained. Magnesium, for example, is elevated in both concentration and flux in the Río Piedras (Table 1) and is primarily derived from weathering rather than direct anthropogenic or atmospheric inputs in forested Puerto Rican watersheds (McDowell and Asbury 1994). Given the similar lithology of the three watersheds (dominantly volcaniclastic), this increased Mg level in the urban river suggests a variety of possible scenarios: that weathering of parent material occurs more rapidly due to urbanization, that urbanization provides new weatherable materials not present in forested catchments (e.g., concrete; Sferratore et al. 2006, Moore et al. 2017, Kaushal et al. 2017), or that direct inputs into the urban watershed or river occur for solutes not typically thought of as being derived from anthropogenic inputs. Further investigation of the drivers behind some of these less intuitive patterns in major ion export is needed to fully understand the urban stream syndrome.

We propose that the stoichiometry of nutrient and organic matter fluxes should be added to routine assessments of water quality in urban basins. Although the seminal papers on urban streams and the “urban stream syndrome” (Paul and Meyer 2001, Walsh et al. 2005, Wenger et al. 2009) included explicit recognition of the elevated concentrations of N and P typically seen in urban waters, Si and stoichiometric considerations were not included. Specifically, we suggest that the “urban stream syndrome” as originally described should be expanded conceptually to include consideration of both concentrations and stoichiometry of N, P, Si, and organic matter as each can contribute to changes in the trophic status of receiving waters, either through influences on primary production or through oxygen depletion due to mineralization of organic matter (Dodds 2006). Our initial assessment of the literature (Table 3) suggests that the data available for a comprehensive assessment of the ways in which nutrient and organic matter stoichiometry vary in urban environments are surprisingly limited, with most authors focusing on either nutrients and nutrient limitation in aquatic ecosystems (inorganic, N, P, and perhaps DOM) or on watershed-scale silica fluxes as an important indicator of weathering rates. The power of an integrated assessment has been demonstrated by Billen and Garnier (2007), who provide one of the most comprehensive attempts to include Si in assessment of the effects of urbanization and land cover change on nutrient and major element delivery to coastal waters. Understanding the impacts of watershed alterations on freshwater ecosystems remains a central focus in aquatic ecology, but it is important to consider the role of many nutrients that are not typically the centerpiece of these studies, such as Si. These alterations may play particularly important roles as we consider anthropogenic impacts holistically, across multiple time scales and from headwaters to the sea, explicitly coupling freshwater and marine ecosystems.

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Supporting Information

Additional supporting information may be found online at: http://onlinelibrary.wiley.com/doi/10.1002/eap.1839/full

Data Availability

Data are available from EDI Data Portal at https://doi.org/10.4211/hs.142c59757ed54de1816777828c9716e7