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Urban influences on the nitrogen cycle in Puerto Rico

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Abstract. Anthropogenic actions are altering fluxes of nitrogen (N) in the biosphere at unprecedented rates. Efforts to study these impacts have concentrated in the Northern hemisphere, where experimental data are available. In tropical developing countries, however, experimental studies are lacking. This paper summarizes available data and assesses the impacts of human activities on N fluxes in Puerto Rico, a densely populated Caribbean island that has experienced drastic landscape transformations over the last century associated with rapid socioeconomic changes. N yield calculations conducted in several watersheds of different anthropogenic influences revealed that disturbed watersheds export more N per unit area than undisturbed forested watersheds. Export of N from urban watersheds ranged from 4.8 kg ha^{-1} year^{-1} in the Río Bayamón watershed to 32.9 kg ha^{-1} year^{-1} in the highly urbanized Río Piedras watershed and 33.3 kg ha^{-1} year^{-1} in the rural-agricultural Río Grande de Añasco watershed. Along with land use, mean annual runoff explained most of the variance in fluvial N yield. Wastewater generated in the San Juan Metropolitan Area receives primary treatment before it is discharged into the Atlantic Ocean. These discharges are N-rich and export large amounts of N to the ocean at a rate of about 140 kg ha^{-1} year^{-1}. Data on wet deposition of inorganic N ($NH_4^+ + NO_3^-$) suggest that rates of atmospheric N deposition are increasing in the pristine forests of Puerto Rico. Stationary and mobile sources of NO_x ($NO + NO_2$) and N_2O generated in the large urban centers may be responsible for this trend. Comprehensive measurements are required in Puerto Rico to quantitatively characterize the local N cycle. More research is required to assess rates of atmospheric N deposition, N fixation in natural and human-dominated landscapes, N-balance associated with food and feed trade, and denitrification.

Introduction

Human activities have caused unprecedented changes in the nitrogen (N) gaseous fluxes between the atmosphere and the Earth's ecosystems (Galloway et al. 1995; Holland et al. 1999; Matson et al. 1999; Socolow 1999). It is estimated that the application of fertilizers, the development of N-fixing crops (legumes and forages), and fossil fuel burning adds about 140 Tg of N per year to terrestrial environments (Vitousek et al. 1997). This rate matches the upper end of the natural N fixation rate associated with lightning and N-fixing algae and bacteria, estimated at 90–140 Tg per year prior to the Industrial Revolution (Galloway et al. 1996). In addition, human actions such as burning of forests, wood fuels, and grasslands, the draining of wetlands and the clearing of land for crops are depleting the N stored in soil organic matter and in tree biomass at a rate of about 60 Tg per year (Vitousek et al. 1997).

The impacts of these anthropogenic activities are evident in the atmospheric N budget and in the ecosystem functioning. For example, increased emissions of nitrous oxide (N_2O) are altering the heat balance of the Earth (Vitousek et al. 1997). This gas absorbs infrared radiation emitted by the Earth and is thought to contribute significantly to the greenhouse effect. In addition, N_2O contributes to the thinning of the stratospheric ozone layer that shields the Earth from damaging UV cosmic radiation. In urban areas, the production of nitric oxide (NO) from the combustion of fossil fuels controls ozone formation. High ambient ozone concentrations initiate and exacerbate respiratory illness (Townsend et al. 2003). In the atmosphere, NO is oxidized in two steps to form nitric acid (HNO_3), a compound that is responsible for increased rain acidity (e.g., Meixner 1994). Gaseous ammonia (NH_3), a byproduct of forest burning, of animal waste oxidation, and application of fertilizers, buffers the acidifying effect of NO (through its oxidation product HNO_3), and, therefore influences the chemistry of atmospheric aerosols, water vapor, and rain. When deposited to soil surfaces NH_3 can be considered as an acid, since it is rapidly nitrified in soils, a process that directly forms H^+ and NO_3^- (Galloway 1998).

Changes in the global N cycle create a cascade of effects with direct impacts on the global carbon cycle. The increase in wet and N dry deposition associated with increasing concentrations of atmospheric N species may promote plant growth and hence increase carbon sequestration by plants, particularly in N-limited ecosystems of the temperate and boreal regions (Vitousek et al. 1997). This increase in carbon storage may represent an important sink in the global carbon budget that counteracts the increase in atmospheric carbon dioxide associated with the combustion of fossil fuels. However, as these ecosystems become saturated with N, other elements such as phosphorus, calcium, and water may become limited thus reducing plant growth. This condition leads to high losses of N that have caused acidification of lakes and streams in some regions (Aber et al. 2003). Other ecosystem-level impacts associated with increased N inputs include changes in biodiversity, intensified trace gas (particularly NO and N_2O) exchange, increased cation leaching, and changes in estuarine trophic structure (Howarth et al. 1996; Aber et al. 1998; Matson et al. 1999).

The complex nature of interactions between humans and the global N cycle mandates the need for the determination of N fluxes at the regional and/or national level. Although research and environmental monitoring must continue in temperate regions where much of the anthropogenic N has been generated (Howarth et al. 1996), additional research is needed in developing tropical regions where particularly land-use change is expected to alter natural N fluxes (Matson et al. 1999; Trebs et al. 2006).

This paper evaluates the effects of human activities on the N flux in Puerto Rico, a densely populated tropical Caribbean island that has experienced drastic landscape transformations associated with rapid socioeconomic changes (Hunter and Arbona 1995; Thomlinson and Rivera 2000; López et al. 2001; Grau et al. 2004). Available hydrologic data are used to assess fluvial N fluxes from four watersheds in Puerto Rico with varying levels of human impacts and water yield. These are compared with N fluxes to the ocean from wastewater treatment plants located in urban centers. Collected data on rain chemistry were evaluated to estimate rates of N wet deposition. Fertilizer use in Puerto Rico was reviewed to assess its effect on local N budgets. Finally, future research needs are proposed to further improve our understanding of N dynamics in Puerto Rico and in the tropics.

Methods

The study site

With an area of 889,500 ha, Puerto Rico is the fourth largest island in the Caribbean (Figure 1). It is centered at 18°15′ N, 66°30′ W. The interior of the island has rugged topography with elevations reaching up to 1300 m above mean sea level. Geologic substrates include: alluvial, sedimentary, volcanic, limestone, and serpentine (Pico 1975). Average annual precipitation ranges from 2100 mm in the humid uplands, 1600 mm in the humid coastal plains, 1150 mm in the semiarid mountains and valleys, to 900 mm in the semiarid coastal plains. The average annual temperature is 24 °C in the humid uplands, 25 °C in the humid coastal plains, 26 °C in the semiarid mountains and valleys, and 26 °C in the semiarid coastal plains. On average, the island receives about 1753 mm of rain per year, of which 1057 mm are evaporated and transpired by vegetation, 622 mm are discharged to the ocean through rivers and underground aquifers, with the remaining stored in rivers, reservoirs, and cycled internally (DNER 2005). Seventeen major rivers drain the island, with the largest ones found on the Northern slopes, which are wetter than the Southern slopes.

During the 20th century, Puerto Rico experienced dramatic socioeconomic development of unprecedented proportions for many tropical countries. From its discovery in 1493 until 1899, when Puerto Rico became a United States possession, its population increased from about 30,000 to 953,243 inhabitants at an average rate of 2274 inhabitants year^{-1} (Picó 1975). Over the 20th century, the population increase was much faster, at a rate of 28,271 inhabitants year^{-1}. With a population of 428 inhabitants km^{-2} (Puerto Rico Planning Board 1995), Puerto Rico is one of the densest territories of the world. Major urban settlements are concentrated on the coastal plains in the cities of the San Juan Metropolitan Area (SJMA; e.g., Trujillo Alto, Bayamón, Carolina),

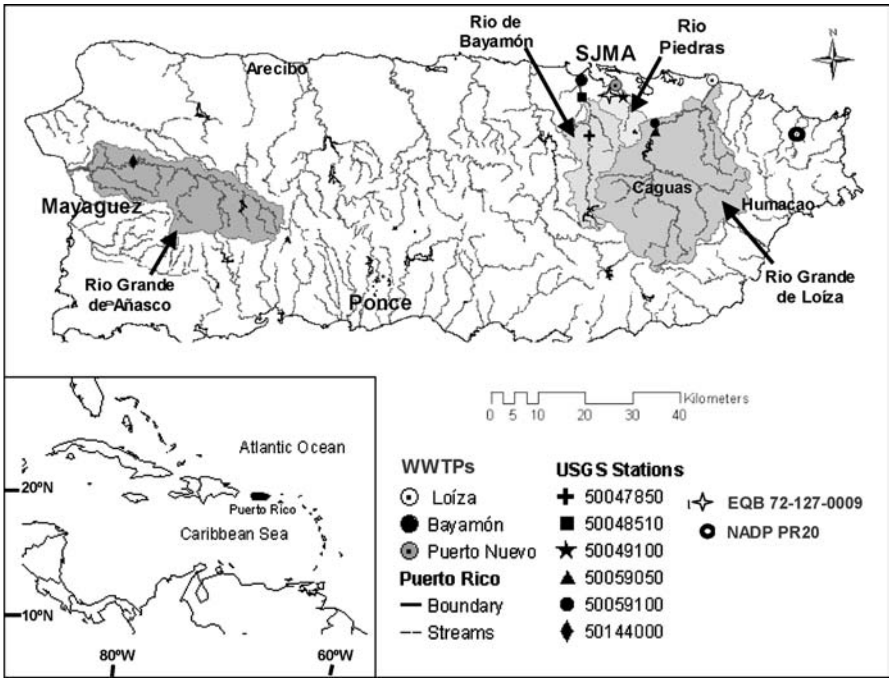

Figure 1. Location of wastewater treatment facilities, hydrologic USGS stations, and atmospheric deposition measurement stations in Puerto Rico referenced in this study.

Ponce, Mayaguez, Arecibo, and Humacao and inland cities such as Caguas (Figure 1). Rural areas, however, are heavily populated. Thus Puerto Rico can be considered to be an urban island. Only 35,000 ha or 4% of its territory are protected lands.

These demographic patterns have dramatically altered the Puerto Rican landscape. Puerto Rico was mostly forested in the 16th century. However, by 1828 only 61% forest cover remained due to timber cutting and development of non-forested land uses. By 1899, forest cover was reduced to 20% and coffee was the principal crop. By 1931, only 9% of forest remained while the production of coffee was declining. Boosted by an expansion of the sugar cane industry, deforestation continued. By late 1940, only 6% of the land area remained forested. In 1948, a new economic model based on manufacturing (Operation Bootstrap) was initiated and the sugar cane production began to decrease (Pico 1975). In 1952, Puerto Rico became a commonwealth associated with the United States. This political status allowed for the free trade of products and unrestricted immigration between the two countries. Between 1950 and 1980, Puerto Rico experienced rapid economic growth with >10-fold increase in its gross domestic product, labor wages, and personal annual income (Pico 1975; Dietz 1986). With industrialization, forest cover began to increase due to natural succession in abandoned agricultural lands, reaching

34% by 1985 (Birdsey and Weaver 1987) and 42% by 1992 (Helmer et al. 2002). The per capita GDP in Puerto Rico is one of the highest of Latin American and Caribbean ($16,800 in 2003 in purchasing power parity; http://www.cia.gov).

The socioeconomic transformations that led to reforestation in Puerto Rico also resulted in an increase in energy consumption. Because Puerto Rico is dependent almost exclusively on fossil fuels, per capita carbon emissions are among the highest in the Neotropics (about 2.5 Mg C person^{-1} year^{-1}; Grau et al. 2004). The effects of these emissions on the atmospheric deposition of N are still uncertain; however, there is consensus that N emissions associated with fuel combustion in Puerto Rico are increasing (DNER 1999).

Fluvial export of nitrogen

Flow-weighted means of the total N concentration were calculated for four watersheds in Puerto Rico based on data collected at US Geological Survey (USGS) streamflow and water quality stations (Table 1). Total N concentration and instantaneous discharge data are available quarterly at each water quality station. At streamflow stations, mean daily discharge data are also available.

Río Grande de Loiza watershed

This is the largest watershed in Puerto Rico. The Río Grande de Loiza drains into the Atlantic Ocean near the municipalities of Loiza and Carolina. This watershed supplies the San Juan Metropolitan area with an average of 3.7×10^5 m^3 day^{-1} withdrawn from the Carraizo Reservoir. The reservoir was built in 1953, and its current capacity is estimated at 18.1×10^6 m^3; Ortiz-Zayas et al. 2004). Estimates of mean annual runoff below the reservoir are impacted by these extractions (Table 1). It is a semi-rural basin with about 13% of its area urbanized (Gould et al. 2005). According to Osterkamp (2001), about 21% of the watershed is forested and about 58% of this basin is dominated by agriculture and pasture. Two major wastewater treatment plants service most of the population in the watershed: the Caguas Regional Wastewater Treatment Plant and the Carolina Regional Wastewater Treatment Plant. The Caguas plant discharges secondary treated effluent back into the Río Grande de Loíza while Carolina discharges primary treated effluent to the Atlantic Ocean via a submerged outfall.

N export from the Río Grande de Loíza was calculated from data on total N collected at the Río Grande de Loíza below Trujillo Alto (station 50059100; Table 1) and discharge data collected at the Río Grande de Loíza below the dam site (station 50059050) as an approximation of that in station 50059100. Station 50059050 is located 4 km upstream from station 50059100 and there are no major tributaries discharging between the stations. To evaluate the relationship between discharge and N concentration at the 50059100 station, a linear regression was developed between the logarithm of the concentration of

Table 1. Summary of information on the water-quality stations in Puerto Rico analyzed. Based on data from Díaz et al. (2004).

Station name and number	Period of record		Elevation, m amsl	Drainage area, km^2	Runoff, mm $year^{-1}$	% Urban land in watershed[a]
	Start	End				
Río Grande de Loíza below dam site, 50059050	Dec-1986	Sep-2002	10	541.0	427[b]	13
Río Grande de Loíza below Trujillo Alto, 50059100	Jan-1981	Aug-2001	8	552.0	–	13
Río de Bayamón near Bayamón, 50047850	Oct-1988	May-2002	30	108.3	302	22
Río de Bayamón at flood channel, 50048510	Dec-1973	May-2002	5	186.2	–	22
Río Piedras at Hato Rey, 50049100	Dec-1973	Apr-2002	5	39.4	1208	63
Río Grande de Añasco nr San Sebastían, 50144000	Jan-1974	Sep-2002	31.6	244.2	1202	5

[a]Land use data based on Gould et al. (2005) and watershed boundaries of the USGS (2002).
[b]Water yield at this site is affected by water withdraws for water supply at the Carraizo Reservoir.

total N (TN, mg l^{-1}) and the logarithm of instantaneous discharge (Q, ft^3 s^{-1}) at the time of sampling for the period of record. The equation obtained, Log TN = 0.2069*log Q − 0.1784 (r^2 = 0.19, p-value < 0.0001), was used to estimate TN concentration from a mean daily discharge series at the 50059050 station. An average annual total N load (kg $year^{-1}$) was calculated by summing the mean daily N concentration for each year over the period of record. The N yield per unit area of watershed (kg ha^{-1} $year^{-1}$) was calculated as the mean of the annual concentration series divided by the watershed area (cf. McDowell and Asbury 1994; Swistock et al. 1997).

Río de Bayamón watershed

The Río de Bayamón watershed drains the Western part of the SJMA (Figure 1). This basin is highly influenced by human activities with about 22% of its area urbanized. Secondary-growth forests and fallow lands predominate in the upper watershed. The lower 6 km of the river are impacted by a straight earthen channel with raised levees for flood control. Cidra Reservoir, with a volume of 6.6×10^6 m^3 (Ortiz-Zayas et al. 2004) is located in the upper part of the watershed and provides water supply to the Guaynabo area (Ramos-Ginés 1997). The Bayamón Regional Wastewater Treatment Plant services the inhabitants of the watershed and nearby communities (Figure 1). This plant provides primary treatment to wastewater before it is discharged to the Atlantic Ocean through a submerged outfall.

The USGS operates a water-quality station located 5.1 km above the river mouth (50048510; Table 1) and a streamflow gauging station (50047850) located upstream (Figure 1). The lack of a significant relationship between total N concentration and instantaneous discharge at the time of water sampling suggests that total N in the lower Río de Bayamón is not sensitive to flow. Therefore, the concentration of total N from 1974 to 2002 was averaged (1.88 mg N/L; SD = 1.16). Mean daily flow at station 50048510 was obtained from a relationship developed between the instantaneous flow at station 50048510 and mean daily flow at station 50047850. A flow-weighted mean concentration of total N was calculated for each year as the product of the mean daily flow at station 50048510 and the mean concentration of total N. An average annual total N load was computed from the annual series. The N yield per unit area of the watershed was calculated as described above.

Río Piedras watershed

This watershed, located in the center of the SJMA (Figure 1), is the most urbanized of the four watersheds studied with urban land covering 63% of the watershed. While some rural sections in the upper watershed are not connected to the public sewer system, the lower section is connected to the Puerto Nuevo Wastewater Treatment Plant. This plant provides primary treatment to wastewater, which is then discharged to the ocean via the Bayamón submerged outfall.

Since 1973, the USGS has monitored water quality at a station located in Hato Rey (Table 1). The USGS has also monitored streamflow at this station since 1988. There was no relationship between the concentration of total N and discharge indicating that total N in Río Piedras is not sensitive to streamflow. Therefore, the mean concentration of total N was calculated for the period of record (2.87 mg N/L; SD = 1.97). The average annual total N load and the N yield per unit area were calculated as described above.

Río Grande de Añasco watershed
This is a rural watershed located in Western Puerto Rico (Figure 1). Urban land cover is minimal (Table 1) and agricultural activity is sparse at mid and high elevations. Three reservoirs, located in the upper part of the watershed (Guayo, Prieto, and Yahuecas) transfer part of runoff generated in this watershed to an outside watershed for hydroelectric generation, irrigation, and water supply (Ortiz-Zayas et al. 2004).

The USGS operates a combined water quality and streamflow station in this watershed (50144000; Table 1). Water quality records are available since 1974 while streamflow data are available since 1963. Total N concentration and discharge were statistically related (Log TN = 0.5047*log Q − 1.1170; $r^2 = 0.43$, p-value < 0.0001), at this station, and thus the mean daily discharge series for the period of record was used to estimate the mean daily total N concentration. A flow-weighted mean concentration of total N was calculated for each year as the product of the mean daily flow at station 50014400 and the mean daily concentration of total N. An average annual total N load was computed from the annual series from which a nitrogen yield per unit area was calculated.

Nitrogen export via wastewater

Wastewater generated in the SJMA is treated in three regional wastewater treatment plants (WWTPs): Carolina, Puerto Nuevo, and Bayamón (Figure 1; Table 2). The three plants serve about 798,000 inhabitants and are operated by the Puerto Rico Aqueduct and Sewer Authority (PRASA). The WWTPs offer primary treatment to wastewater with up to 80% removal of suspended solids and up to 50% removal of organic matter (Table 2). The three plants discharge

Table 2. Design parameters of the wastewater treatment system for the SJMA. Data from PRASA (2005).

WWTP	Population served	Flow (mgd)	BOD_5		Total suspended solids	
			% Removal	Effluent quality (mg l^{-1})	% Removal	Effluent quality (mg l^{-1})
Bayamón	224,155	40	50	130	80	75
Puerto Nuevo	395,041	72	38	130	78	75
Carolina	178,901	45	–	130	57	70
Total	798,097	157				

their treated effluents to the Atlantic Ocean through two ocean outfalls: the Bayamón/Puerto Nuevo combined outfall and the Carolina outfall.

The WWTPs are not designed to remove N from wastewater. An unknown amount of organic N associated with the nitrogenous oxygen demand might be incidentally removed with primary treatment. However, given the low removal efficiency of organic matter, this amount would be small. Therefore, effluents discharged to the ocean are N-rich with a designed effluent concentration of inorganic N (nitrate, nitrite, and ammonium) of 54 mg l^{-1} (PRASA 2005).

The mean concentration of total N in wastewater and the total load of N discharged to the ocean from each of the three WWTPs were calculated based on historic flow and effluent chemistry data reported by PRASA in their discharge monitoring reports to EPA. PRASA does not have precise data on areas serviced by its WWTPs. Therefore, in order to estimate the N yield per unit area, the serviced area was estimated based on the product of the population served and the population density of each serviced area using data from the Puerto Rico Planning Board (2005). N yield per unit area associated with each of PRASAs sewer systems was estimated from the load and estimated serviced area of each WWTP.

Atmospheric N deposition

Data about total (wet + dry) atmospheric N deposition based on field measurements are lacking in Puerto Rico. There is only one field station on the island where rain water has been collected continuously since 1985. The field site (PR-20) is operated within the framework of the National Atmospheric Deposition Program (NADP) and is located in the Luquillo Experimental Forest in Northeastern Puerto Rico (Figure 1). Annual wet deposition data for inorganic N ($NH_4^+ + NO_3^-$) are available for the NADP site from 1985 to 2003 (http://www.nadp.sws.uiuc.edu). Rain water was also collected at two locations in the Luquillo Mountains (El Verde field station and Bisley Experimental Watersheds). Data from the initial years of operation of the NADP PR-20 station, as well as bulk precipitation chemistry in the Luquillo Mountains, were summarized by McDowell et al. (1990).

The most important contributors to N dry deposition are the atmospheric trace gases NH_3, HNO_3, HNO_2 (nitrous acid) as well as NO_x ($NO + NO_2$). Up to date, however, no measurements to quantify the surface-atmosphere exchange of these compounds have been carried out in Puerto Rico. The Puerto Rico Environmental Quality Board (EQB) has been monitoring NO_2 at a station located in the SJMA (EQB-72-127-0009; Figure 1) from May 2000 to June 2004. However, because micrometeorological quantities were not measured at this urban site and NO_2 measurements have been affected by strong local pollution, the data were not used to estimate surface-atmosphere exchange of this compound. In order to obtain a preliminary estimate of the expected total N (dry + wet) deposition in Puerto Rico our data for N wet deposition were related to results from Howarth et al. (1996), Galy-Lacaux et al. (2003), and Trebs et al. (2006).

Fertilizer use

Data on fertilizer use in Puerto Rico were compiled and published by the Association of American Plant Food Control Officials (AAPFCO 2002). These data, available from 1994 to 2002, were used to calculate N inputs to Puerto Rico from fertilizers. These data as well as cropland data (USDA 2004) were analyzed to compute N application indexes for Puerto Rico. N-fertilizer use in Puerto Rico was compared to other Latin American and Caribbean countries based on similar indexes developed by Martinelli et al. (this issue). An indirect parameter to evaluate the efficiency of the N-fertilizer use is the ratio of total cereal production to N fertilizer consumption for all crops, which in turn is a crude proxy of the N use efficiency (NUE) (Cassman et al. 2002).

Results

Fluvial fluxes of nitrogen

Land use in the studied watersheds ranged from highly urbanized in the Río Piedras (63% urban) to rural areas in the Río Grande de Añasco (5% urban) with some agriculture mainly of bananas, coffee, citrus, plantains, and yams (Sotomayor-Ramirez et al. 2004). These watersheds and others with published N export data were grouped into three land use categories: urban, agricultural-rural, and forested (Table 3).

In general, urban and agricultural-rural watersheds had similar and highly variable N yields (Table 3). Export of N from urban watersheds ranged from 4.8 kg N ha^{-1} $year^{-1}$ in the Río Bayamón watershed to 32.9 kg N ha^{-1} $year^{-1}$ in the highly urbanized Río Piedras watershed. Published N yields for urban sewered and unsewered watersheds in Puerto Rico (Ramos-Ginés 1997) were within this range. N export rates in agricultural-rural watersheds ranged from 6.9 kg N ha^{-1} $year^{-1}$ in one of the tributary watersheds to Lago de Cidra to 33.3 kg N ha^{-1} $year^{-1}$ in the Río Grande de Añasco watershed, a value similar to that computed for the urban Rio Piedras watershed. Both urban and agricultural-rural watersheds had higher N yields than forested watersheds, which ranged from 2.7 to 9.8 kg N ha^{-1} $year^{-1}$ (Table 3).

Among all the watersheds, the Río Grande de Añasco and the Río Piedras watersheds had the highest runoff (>1200 mm $year^{-1}$; Table 1). To evaluate the relationship between runoff and N yield, linear regression analysis was developed for each land use category. No significant relationship was observed between N yield and mean annual runoff for the urban and rural-agricultural

Table 3. N yield of the studied watersheds and comparison with published estimates for other watersheds in Puerto Rico.

Land use	Basin	N yield, kg N ha^{-1} year^{-1}	References
Urban	Río Grande de Loiza	16.4 (3.8)	This study
	Río de Bayamon	4.8 (0.7)	This study
	Río Piedras	32.9 (3.0)	This study
	Lago de Cidra Site 4 (sewered)	6.6	Ramos-Ginés (1997)
	Lago de Cidra Site 5 (unsewered)	17.1	Ramos-Ginés (1997)
Agricultural-Rural	Río Grande de Añasco	33.3 (6.4)	This study
	Lago de Cidra Site 2	6.9	Ramos-Ginés (1997)
	Lago de Cidra Site 3	8.6	Ramos-Ginés (1997)
Forested	Río Icacos	9.8	McDowell and Asbury (1994)
	Quebrada Toronja	4.4	McDowell and Asbury (1994)
	Quebrada Sonadora	5.9	McDowell and Asbury (1994)
	Lago de Cidra Site 1	2.7	Ramos-Ginés (1997)

Values in parenthesis represent the standard error of the mean.

watershed groups. A significant relationship, however, was found when the watersheds from these two land use categories were combined. Similarly, the N yield from forested watersheds was significantly related to mean annual runoff (Figure 2). This analysis revealed that N yield in watersheds in Puerto Rico is related to runoff and that under similar runoff conditions, urban and agricultural-rural watersheds export more N per unit area than forested watersheds.

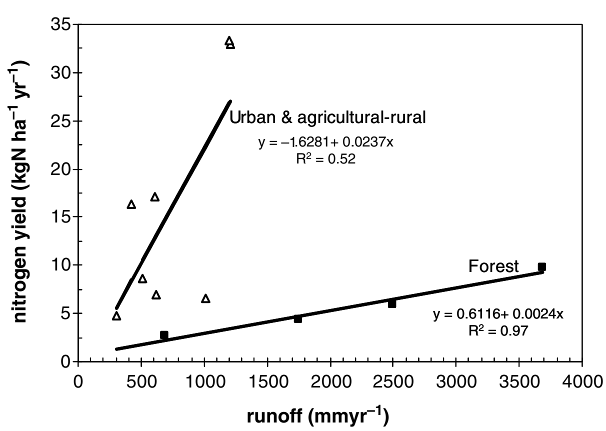

Figure 2. Relationship between runoff and N yield for two land use categories in Puerto Rico. The regression lines are significant at the $p = 0.05$ level.

Nitrogen export via wastewater

The average concentrations of total N in treated wastewater ranged from 18.0 mg l^{-1} at the Puerto Nuevo WWTP to 54 mg l^{-1} at the Carolina WWTP. Average effluent flow ranged from 25.8 million gallons per day (mgd) at Carolina to 55.6 mgd at Puerto Nuevo (Table 4). Per capita N load varied between facilities from 3.5 at Puerto Nuevo to 11.8 kg N person^{-1} year^{-1} at Bayamón. The average of the three facilities (9.6 kg N person^{-1} year^{-1}) is higher than that reported by Meybeck et al. (1989) (3.3 kg N person^{-1} year^{-1}) as a global average for sewered populations. When evaluated on a per unit area basis, N export through wastewater (mean = 139.6 kg N ha^{-1} year^{-1}; Table 4) is four times higher than the maximum rate of fluvial export reported for an urban-agricultural rural area (33.3 kg N ha^{-1} year^{-1}; Table 3) and as much as 52 times that of some forested basins in Puerto Rico (Table 3).

Atmospheric nitrogen deposition

In Puerto Rico, annual N_2O emissions have increased 11% per year from 1990 to 1994 from 395 tons year^{-1} (full molecular basis) to 569 tons year^{-1}, while NO_x emissions have increased 2.4% per year over this period from 97,307 to 106,544 tons year^{-1} (DNER 1999). Under a 'business as usual' scenario, N_2O and NO_x emissions are expected to continue to increase in the future at 7.8 and 1.1% per year, respectively, from the 1994 level (Figure 3). Fuel combustion, either from stationary or mobile sources, is the primary source of these emissions. Burning of agricultural waste and fertilizer use are considered to be negligible sources of NO_x and N_2O. No emission estimates exist for NH_3.

The NADP PR-20 Luquillo Experimental Forest station is located upwind from the SJMA and represents the rain chemistry associated with oceanic moisture carried by the Easterly Trade Winds. Concentrations of inorganic N (NO_3^- andNH_4^+) in precipitation have been increasing at this site over the last

Table 4. Export of N from primary WWTP in the SJMA. TN is total nitrogen.

WWTP	Average effluent conditions		Total N load, (kg year^{-1})	Per capita N load, kg N person^{-1} year^{-1}	Serviced area (ha)	N yield, kg N ha^{-1}year^{-1}
	Flow (mgd)	TN (mg l^{-1})				
Bayamón[a]	39.6	48.6	2,650,802	11.8	11,429	231.9
Puerto Nuevo[b]	55.9	18.0	1,387,403	3.5	11,259	123.2
Carolina[c]	25.7	54.0	1,910,437	10.7	19,956	95.7
All	121.0	40.2	5,948,642	9.6	42,644	139.5

[a]Data based on discharge monitoring reports from March 2002 to March 2004.
[b]Data based on discharge monitoring reports from February 1997 to March 2004.
[c]Data based on discharge monitoring reports from January 2000 to March 2004.

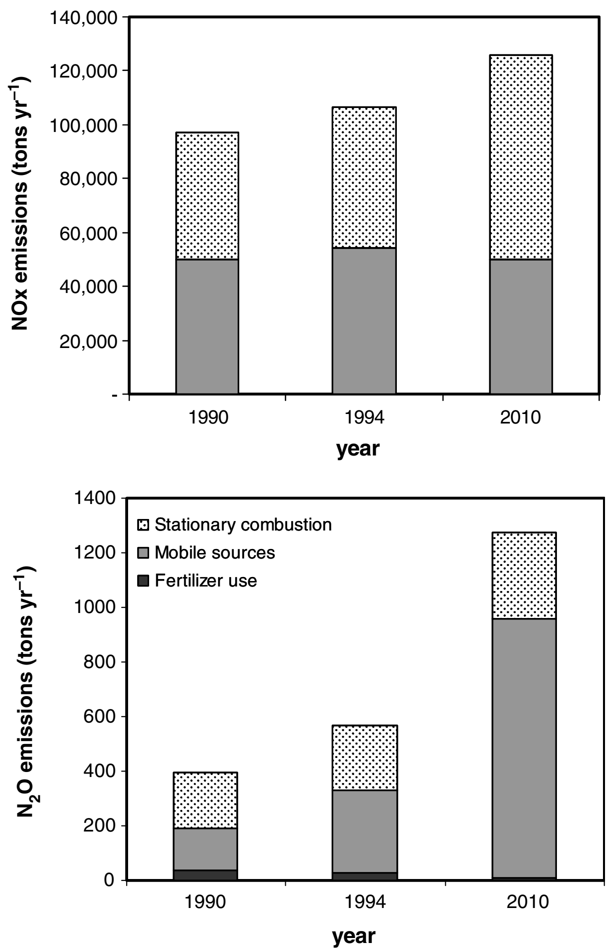

Figure 3. Change in NO_x and N_2O emissions by source from 1990 to 1994 and forecasts based on a 'business as usual' scenario. Data published by the Energy Affairs Administration of the Puerto Rico DNER. Emission rates are expressed on a full molecular basis.

18 years at a rate of 0.08 kg N ha^{-1} $year^{-1}$ (Figure 4). Over the last five years, the wet input of N to the site was on average 2.7 kg N ha^{-1} $year^{-1}$. Howarth et al. (1996) estimated NO_y (ensemble of NO_x and its reservoirs, such as HNO_3 and N_2O_5) and NH_x ($NH_3 + NH_4^+$) deposition for the Caribbean by applying estimates of N wet + dry deposition to the North Atlantic region modeled by Propero et al. (1996). They estimated that, in the Caribbean, modern NO_y is deposited at a rate of 2.1 kg N ha^{-1} $year^{-1}$ (wet + dry). Pre-industrial rates were estimated to 0.7 kg N ha^{-1} $year^{-1}$ with the difference of 1.4 kg N ha^{-1} $year^{-1}$, obviously attributed to anthropogenic activities. NH_x deposition (wet + dry) was estimated to 1.82 (modern), 0.83 (pre-industrial), with a difference of

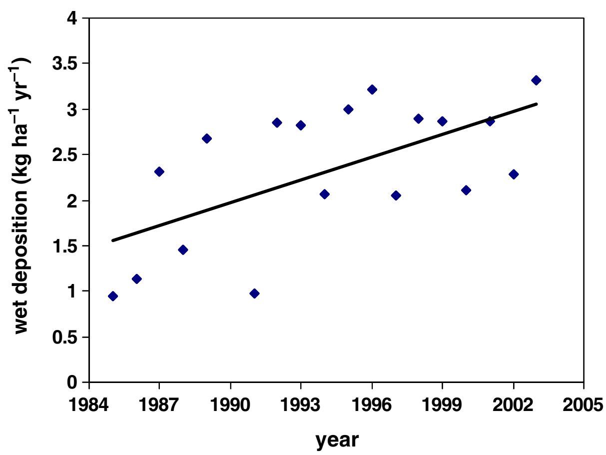

Figure 4. Wet deposition of inorganic N (NH_4^+ and NO_3^-) at the NADP PR-20 station located at El Verde. The trend line is significant at the $p < 0.01$ level.

0.99 kg N ha^{-1} year^{-1} related to anthropogenic activities. The measured N wet deposition rates in the Luquillo Experimental Forest station (1999–2003 average = 2.7 kg N ha^{-1} year^{-1}) are lower than the total modern estimate of 3.92 kg N ha^{-1} year^{-1} (for NO_y and NH_x; dry + wet deposition) by Howarth et al. (1996). The difference is due to the fact that N dry deposition in Puerto Rico is not included because of the lack of available data.

To date, there are only few studies that give estimates of N dry deposition in tropical environments based on field measurements. Galy-Lacaux et al. (2003) have estimated N wet + dry deposition to different ecosystems in West-central and South Africa (DEBIT study). The relative contributions of dry N deposition to the total N deposition rates in Africa given by Galy-Lacaux et al. (2003) are 65% for dry savanna, 73% for wet savanna, 75% for forest, 59% for rural dry Savanna and 37% for industrial area. Trebs et al. (2006) have estimated wet + dry N deposition for a pasture site in the state of Rondônia (Brazil), which is located in the Southwestern part of the Amazon Basin. Trebs et al. (2006) found that during the late dry season (biomass burning) in September 2002, about 46% of the total N deposition was attributed to dry deposition and the contribution of dry deposition to the total N deposition dropped to only 31 and 22% during October (transition period) and November (onset of the wet season, clean conditions), respectively. Thus, on average N dry deposition may contribute approximately 30% to the total N deposition at the disturbed Amazonian site.

Puerto Rico's tropical climate is strongly affected by the Northeast trade winds with significant maritime influence from the Atlantic Ocean, whereas evergreen forest regions in West-central Africa are largely influenced by continental flows associated with the Northeast or Southeast trade winds. While in Puerto Rico atmospheric chemistry is a complex mixture of marine aerosols, fuel combustion and others, in Rondônia, the main sources of atmospheric N deposition are biomass burning and cattle ranching. Thus, neither the African nor the Amazonian site may completely represent atmospheric N deposition patterns in Puerto Rico. However, considering that the contribution of N dry deposition to the total N deposition was about 70% for the African ecosystems determined during the DEBIT study we would obtain a dry N deposition rate of 6.3 kg N ha^{-1} $year^{-1}$ for the pristine Puerto Rican forest site. On the other hand, taking into account the average contribution of 30% obtained by Trebs et al. (2006) for the Amazonian pasture site, N dry deposition would be 1.16 kg N ha^{-1} $year^{-1}$, which is much lower than the African estimate. Hence, N dry deposition to the Puerto Rican forest site may be expected to range from 1.16 to 6.3 kg N ha^{-1} $year^{-1}$. The resulting total N deposition would vary between 3.86 and 9.0 kg N ha^{-1} $year^{-1}$. Nevertheless, it should be noted that (i) the wet deposition estimate for the pristine forest does not include the potentially important organic N fraction (cf. Cornell et al. 2003), (ii) N deposition rates are probably much higher in regions of the island that are directly affected by urban pollution from the SJMA, and (iii) intensive field measurements are needed to reliably quantify Puerto Rican N dry + wet deposition rates.

Other nitrogen fluxes

In Puerto Rico, there is evidence that links modern agriculture with increased nitrogen loading to ground water (Conde-Costas and Gómez-Gómez 1998). However, contrary to the increasing trend in the use of N fertilizers worldwide (Galloway and Cowling 2002; Howarth et al. 2002), the use of N fertilizer had decreased in Puerto Rico from a maximum use of 10,093 tons N $year^{-1}$ in 1996 to a minimum of 5067 tons N $year^{-1}$ in 2002 (Figure 5), a reduction of 50%. Over this period, cropland area in Puerto Rico decreased by 16% from 329,969 in 1993 to 271,440 ha in 2002 (USDA 2004). This decrease was counteracted by a 20% increase in food imports from 1995 to 2004 from $1705.1 M to $2052.2 M (Puerto Rico Planning Board 2005b). Table 5 shows that N applications in Puerto Rico are low compared to the Latin American-Caribbean region and the World. This reflects that Puerto Rico is a low-intensity agriculture country, dependent almost exclusively on food imports. It is expected that significant amounts of N enter Puerto Rico through food imports; however, the exact N fluxes associated with this activity are unknown.

Discussion

Nitrogen fluxes in tropical regions

Howarth et al. (1996) documented that N fluxes per unit area to the North Atlantic Ocean were the highest in the highly disturbed watersheds of Northern

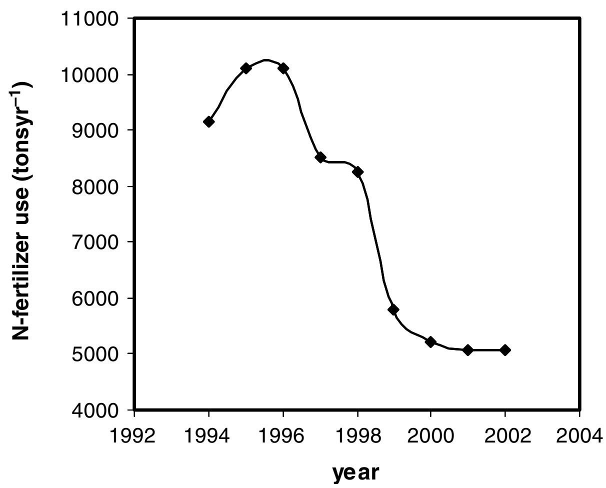

Figure 5. Annual N fertilizer use in Puerto Rico. Data from AAPFCO (2002).

Table 5. Comparison of N fertilizer use in Puerto Rico during 2002 and regional estimates for Latin American/Caribbean region and the World based on Martinelli et al. (this issue).

	Puerto Rico	LA-Ca	World
Fertilizer per unit area, kg N/ha (2002)	16.9	34	60
Per capita fertilizer consumption, kg N/person	1.2	9	14

Europe and Northeastern United States (14.5 and 10.7 kg N ha^{-1} year^{-1}, respectively) Atmospheric deposition of N and the application of fertilizers have been considered the two major sources of N in these regions. In temperate regions, N fixation becomes important only in the intensively cultivated Mississippi Valley, where N-fixing crops are abundant.

In the American tropics, Lewis et al. (1999) summarized N yields from 17 minimally disturbed watersheds in the Americas. They reported that N fluxes averaged 5.08 kg N ha^{-1} year^{-1} (range = 0.73–9.98) and that are strongly correlated to mean annual runoff. When compared to Northern temperate rivers (Howarth et al. 1996), these findings suggest that tropical undisturbed watersheds have lower N yields. Apparently, in these tropical watersheds, lower population densities, lower fertilizer applications, extensive mature forests, and lower atmospheric N deposition kept these fluxes at a minimum.

Future land and demographic changes in the tropics associated with globalization, however, may change the role of tropical watersheds in the global N budget. This is because nearly 40% of global N fertilizer applications are already taking place in the tropics and subtropics, a fraction that is expected to increase to 75% by 2020 (Matthews 1994; Matson et al. 1999). Moreover, it is estimated that about 75% of the global fuel-related N emissions will occur in the tropics and subtropics (Galloway et al. 1994). If development and industrialization occurs in tropical developing countries as it has in the temperate Northern developed countries, it is expected that atmospheric N deposition will increase rapidly, such that tropical N-deposition may move to levels higher than those of present industrialized temperate countries (Downing et al. 1999).

In fact, some tropical regions are already experiencing rapid landscape transformations that match or exceed the N export from temperate industrialized areas. For example, the Piracicaba River is a heavily developed watershed located in Southeastern Brazil with a mean annual runoff of 403 mm. Fluvial N export in this watershed averaged 17.5 kg N ha^{-1} $year^{-1}$ (Filoso et al. 2003). Remarkably, fluvial N export in the Piracicaba River basin is similar to the basins reported in this study of similar runoff (Cidra and Río Grande de Loiza). The fluvial N export rates reported for the Piracicaba River, Río Piedras, and the Río Grande de Añasco basins are higher than those reported for the most impacted industrialized zones in Northern Europe (Howarth et al. 1996). This suggests that the role of disturbed tropical watersheds in the global N flux to oceans may be more important than previously thought.

Tropical regions are considered important global carbon sinks (Schlesinger 1991). Because tropical forests are not generally N-limited (Martinelli et al. 1999) it is expected that under a future scenario of increased N deposition, forest primary productivity in tropical regions may decrease due to increased soil acidity and loss of soil fertility due to depletion of base cations (Matson et al. 1999). Thus, increases in N fluxes in tropical regions can have significant effects on the global carbon balance with negative consequences for tropical societies, particularly on islands due to the effects of increased N fluxes on N-limited coastal waters (Corredor et al. 1999a, b).

Challenges for nitrogen control in developing tropical islands

Land use change and water pollution control

While industrialization may have reached a steady state in most Northern developed countries, developing tropical regions will likely experience rapid land and demographic transformations as their economies change from agrarian to industrial (e.g., Grau et al. 2003). A demographic trend that favors natural reforestation of abandoned croplands due to human migration from rural areas to cities has been documented in Puerto Rico and the Dominican Republic (Zweifler et al. 1994; Aide and Grau 2004). In these islands, inhabitants from rural mountainous areas that depended on agriculture for subsistence have migrated to urban centers out-competed by the highly efficient modern farmers typically concentrated in the lowlands and attracted by the wider job opportunities of coastal cities. This has resulted in the natural reforestation of abandoned agricultural highlands.

N fluxes in these countries are likely to change with reforestation favoring N sequestration and urbanization increasing N losses. Pre-development N export in tropical rivers averages 5 kg N ha^{-1} $year^{-1}$ (Lewis et al. 1999; McDowell 2002). For Puerto Rico, N export from forested watersheds ranges from 3 to 10 kg ha^{-1} $year^{-1}$ (Table 3). With urban growth, there is an increase in wastewater generation and a need for proper treatment and disposal. Without adequate wastewater treatment, pollution of inland and coastal waters occurs. In 2000, the World Health Organization (WHO) reported that about 77% of the population in Latin American and the Caribbean did not have access to adequate water sanitation systems (Gleick et al. 2002). The WHO defines adequate sanitation broadly as the hygienic separation of human feces from human contact. In coastal urban centers, such as those in Puerto Rico, this implies primary treatment of wastewater, which does not remove N. This result in an increase in the load of N to the ocean of about two orders of magnitude higher than the load associated with urban and forested watersheds (Table 3; Figure 2).

Although the current waste treatment practices generally meet regulatory standards, they alter the nutrient balance and biogeochemical processes of Caribbean coastal ecosystems (Corredor and Capone 1985; Corredor et al. 1992, 1999a, b; Morel and Corredor 1993; Corredor and Morel 1994; Mosquera et al. 1998). In tropical developing islands, such as Puerto Rico, improvements of the wastewater treatment system for nutrient removal, particularly N, are necessary to protect coastal ecosystems. This can be accomplished with tertiary treatment technology or less conventional procedures such as terrestrial application of wastewater or constructed wetlands.

Currently, the WWTPs in the SJMA are granted waivers that allow for disposal of sewage receiving primary treatment only into receiving waters. The waiver was granted by the U.S. Environmental Protection Agency following guidelines established under Section 301(h) of the Clean Water Act. This waiver allows eligible WWTPs that met environmentally stringent criteria to receive a modified National Pollutant Discharge Elimination System permit waiving the secondary treatment requirements for the conventional pollutants biochemical oxygen demand (BOD_5), suspended solids (SS), and pH. Under the waiver, EPA requires PRASA (among other requirements) to protect and propagate a balanced indigenous population of shellfish, fish, and wildlife in the receiving waters, to meet water quality standards set by EPA and by the Puerto Rico EQB, to establish a monitoring program to assess impacts. In 2000, the EPA and the Puerto Rico Commonwealth reached an agreement by which PRASA will upgrade its primary WWTPs to provide secondary treatment by year 2020. The capital investments associated with these improvements are large and thus represent a challenge to Puerto Rico. However, the health benefits associated with improved sanitation and the economic and ecological values of clean beaches should warrant these investments.

Control of atmospheric emissions

Balancing N fluxes for pollution control through reforestation and improved sanitation undoubtedly represent a challenge in developing tropical islands.

However, controlling N emissions will be equally important if forests are to continue sequestering N. The increased wet deposition of inorganic N observed in the Luquillo Experimental Forest in Puerto Rico (Figure 4) and the predicted inverse relationship between primary productivity in N-limited tropical forests and N deposition (Matson et al. 1999) suggests that N emissions to the atmosphere may alter the ability of tropical forests to retain N.

In 1999, the Commonwealth Government of Puerto Rico set a strategic plan to reduce by year 2010 the emissions of greenhouse gases by 10% of the 1990 emission level of 30.9 million tons of CO_2 equivalents; a net reduction of 10.4 million tons of CO_2 equivalents. The plan calls for improved efficiency in the energy sector with implementation of alternative energy sources (other than crude oil) such as Ocean Thermal Energy Conversion (OTEC), solar, wind, and natural gas. Also, the plan includes changes in transportation to favor the use of cars with increased fuel efficiency, reduction in traveled miles, and the use of mass transportation such as urban trains. Finally, reforestation and recycling of household wastes will be promoted under the plan. These plans represent an important effort to control emissions of greenhouse gases with benefits at the local and global scales. The observed increase in N wet deposition in the Luquillo Experimental Forest (Figure 5) suggests that local or regional emissions may already affect relatively pristine tropical forests.

Conclusions and recommendations

Quantifying N dynamics on the island of Puerto Rico is essential to protecting economically and ecologically valuable coastal resources that are threatened by increased N inputs. Our analysis indicates that there are serious gaps in understanding of N inputs, transformations (denitrification) and temporal trends that limit the ability of managers to deal with issues of coastal eutrophication. The most important gaps are: (a) those associated with atmospheric N deposition, (b) N fixation in natural and human-dominated landscapes, and (c) denitrification in both terrestrial and aquatic portions of the landscape. Each of these is a quantitatively significant process that affects N delivery to the coast, but both the spatial variability and trends over time of these processes are largely unknown.

A more comprehensive quantification of atmospheric N deposition for the island is central to a better understanding of Puerto Rico's N budget. The presence of only one wet deposition measurement station at a relatively pristine site and the absence of systematic dry deposition measurements provide only limited quantitative information about one of the major N inputs to the island. Given the significant increase of N wet deposition during the last 18 years ($\sim$1.44 kg N ha^{-1} $year^{-1}$) at a station that is relatively unaffected by pollution from the SJMA, it is imperative that atmospheric deposition (wet + dry) is monitored in parts of Puerto Rico that are receptors of urban pollution. N deposition rates in these areas are expected to be comparable to moderately polluted urban regions in the temperate latitudes and changes over time are probably much greater than those measured in the Luquillo Mountains of Northeastern Puerto Rico. Additional information on N inputs to forested lands due to N fixation would also be useful. Past estimates of N fixation range from 8 to 16 kg ha^{-1} $year^{-1}$ (McDowell and Asbury 1994), and rates in suburban and lowland forests are unknown. Conversion of agricultural lands to forest and urban development may have offsetting effects on landscape-scale N inputs due to N fixation, with higher rates in secondary forests offsetting the lower rates in urban areas.

Denitrification is a particularly important process for environmental management because it removes N from soils, streams and rivers and returns it the atmosphere as N_2. Moreover, denitrification is a process that either consumes or produces N_2O and NO, which are both environmentally relevant trace gases. The rates of denitrification in terrestrial and aquatic ecosystems are poorly constrained for the island of Puerto Rico, but are thought to be quantitatively significant in forests (Erickson et al. 2001; Mosier et al. 1998; McSwiney et al. 2001), at the land–water interface (McDowell et al. 1996; McDowell 2001; Chestnut and McDowell 2000), and perhaps in the channels of streams and rivers (Peterson et al. 2001). The warm, wet conditions in much of Puerto Rico, together with the high rates of primary productivity, make the potential for denitrification particularly large in the riparian zone of streams and rivers (McDowell 2003). A particularly important area of research will be to assess landscape-scale rates of denitrification under two contrasting scenarios – on-site disposal of human waste (septic systems) vs. centralized sewage treatment. With on-site disposal, there may be greater potential for denitrification, but there is less control over the quality and effectiveness of the treatment systems and hence greater potential for spatial variability in rates of N delivery to surface waters. With centralized sewage treatment plants, riparian denitrification no longer occurs, and instead N is introduced directly into surface waters, where denitrification may also be occurring. Assessing the environmental costs and benefits of both treatment approaches will be critical to protecting water quality as decisions are made about whether outmoded on-site systems are refurbished, or replaced with centralized sewage treatment plants.

In conclusion, Puerto Rico exemplifies how increased population, coupled with changes in land use and increased industrial development has affected the N dynamics in a tropical Caribbean island. In the future, the development of a comprehensive monitoring network that assesses inputs and outputs of N is needed in Puerto Rico. At the whole-island scale, measures of N imported in food and feed are required. For other fluxes, a watershed approach should be taken in which a few representative sites with varying land uses and some historical data on water quality are studied long-term to determine how trends of N export in rivers relates to changes in inputs and land use in the study watersheds. A particularly important aspect of watershed N dynamics would be to document the magnitude of denitrification in terrestrial and aquatic environments. Understanding the controls on denitrification might provide extremely useful tools for reducing non-point sources of N to coastal waters. Such information will allow a predictive understanding of the N budget under scenarios of climate and land use changes under tropical island conditions.

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