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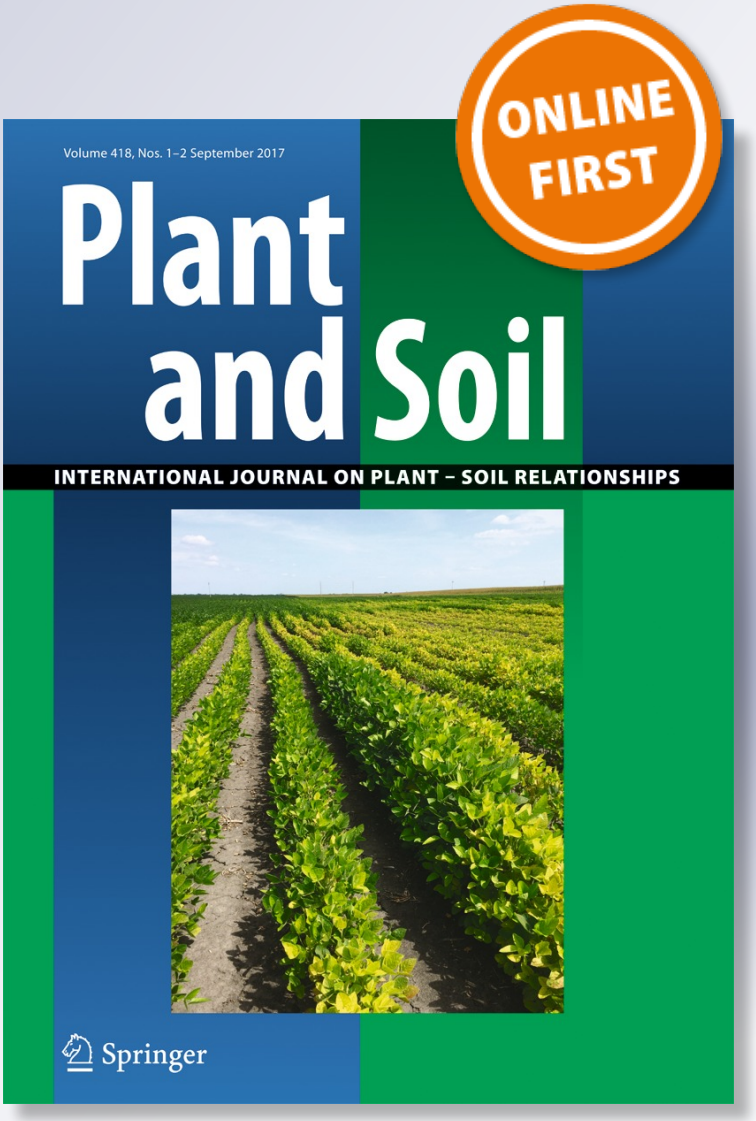

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REGULAR ARTICLE

Nitrogen cycling in tropical Atlantic Forest differing in exposure to urban atmospheric nitrogen deposition

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Abstract

Background and aims Inorganic nitrogen (N)—ammonium (NH_4^+-N) and nitrate (NO_3^--N)—deposition to tropical forests near urban areas frequently exceeds 5-10 kg ha^{-1} yr^{-1}, surpassing critical loads for many forest types. We hypothesized that throughfall N fluxes to Atlantic Forest and effects on soil N cycling and availability would increase with proximity to a megacity (population ~12 M) on Brazil's Atlantic Coast.

Methods We quantified N in rainfall and throughfall, soil nutrient status and N transformations, and relative N availability in three Atlantic Forest sites: an oceanic site ~100 km southwest, a coastal site in, and an inland site ~50 km northeast and downwind from Rio de Janeiro megacity.

Results Annual throughfall N flux did not increase with proximity to the megacity but increased along an ocean (7.6 ± 0.3 kg ha^{-1}) to coast (8.7 ± 1.5 kg ha^{-1}) to inland (14 ± 2.5 kg ha^{-1}) gradient. Potential net N mineralization and nitrification rates did not differ among forests. However, NO_3:NH_4 and resin bag NO_3^- accumulation in soil were highest at the high-N site.

Conclusions Our results suggest that elevated rainfall and throughfall N increase relative N availability and potential NO_3^- leaching losses from Atlantic Forest soils downwind urban areas.

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Keywords Brazil · Net mineralization and nitrification · Nitrogen deposition · Ion-exchange resins · Throughfall

Introduction

Rising atmospheric nitrogen (N) pollution in cities worldwide is contributing to the creation of urban N deposition hotspots (Fenn et al. 2003; Du et al. 2015). Transportation is a major source of nitrogen oxides to urban atmospheres (Baker et al. 2001), while waste, fertilizers, and industrial and fossil fuel combustion are major sources of ammonia (Sutton et al. 2013). Both nitrogen oxides and ammonia are primary pollutants

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that can react with other atmospheric constituents to form secondary pollutants, including nitric acid and N aerosols (e.g., ammonium sulfate; Weathers et al. 2006a). Eventually, these and other N species can be deposited to plant canopies in precipitation (wet and fog deposition) or as dry deposition (particles and gases; Weathers and Ponette-González 2011). Nitrogen is also actively cycled within vegetation canopies, such that deposited N may be absorbed, adsorbed, or assimilated by plants (i.e., uptake), or released into solution upon interaction with water (i.e., leaching; Ponette-González et al. 2010). Throughfall (water that falls from the canopy to the forest floor) thus integrates N from atmospheric deposition and canopy-exchange processes and serves as a good measure of N flux to the soil (Ponette-González et al. 2016).

Compared to other urban ecosystems (e.g., urban grasslands), trees and forests are vulnerable to elevated N deposition (Tulloss and Cadenasso 2015) because of their high leaf area and surface roughness, which increase the scavenging of N-containing atmospheric particles and gases (Slinn 1982). Within the vicinity of cities, ammonium (NH_4^+) and nitrate (NO_3^-) throughfall fluxes can be as much as eightfold higher than in forests less influenced by urban air pollution (Fenn and Bytnerowicz 1993). Gradient studies show that bulk and throughfall inorganic N concentrations and fluxes generally decline with increasing distance from the urban core (Lovett et al. 2000; Rao et al. 2014; Du et al. 2015; de Souza et al. 2015), although this finding is not universal. Working along an urban-suburban-rural gradient, Fang et al. (2011) found that NH_4^+ and NO_3^- fluxes to forest soils were highest at a suburban site downwind of a major urban/industrial area.

Although tropical forests in major urban/industrial areas, including Mexico City and São Paulo, receive wet N deposition rates of similar or greater magnitude (e.g., Forti et al. 2005; REDDA 2017) than critical load limits for many temperate forests (5-10 kg ha^{-1} yr^{-1}, Pardo et al. 2011), N deposition effects on tropical forests are comparatively less well understood than in temperate regions (Matson et al. 1999; Galloway et al. 2008; Allen et al. 2011). Further, predicted ecosystem responses to N deposition in tropical systems stem largely from controlled fertilization studies (but see Fenn et al. 1999; Cusack 2013) conducted in locations not in immediate proximity to urban centers (Corre et al. 2010; Homeier et al. 2012; Fisher et al. 2013). These studies indicate that N deposition effects on N cycling and loss in tropical forests may vary considerably as a result of soil age, soil nutrient status, and soil mineralogy; duration and level of N deposition; and the form of N added (Lohse and Matson 2005). Similar to temperate forests, young N-limited tropical forests may retain considerable N from atmospheric deposition in biomass and soils before losses to the atmosphere and surface and groundwater occur (Hall and Matson 2003; Lohse and Matson 2005). Conversely, elevated and/or chronic N inputs to N-rich forests may result in rapid and greater N losses via leaching and/or to atmosphere (Hall and Matson 2003; Lohse and Matson 2005).

Whether, when, and to what extent tropical forests respond similarly to urban N deposition remains unclear. Even in cities, ambient wet N deposition is generally much lower than typical application rates used in fertilization studies (>75 kg N ha^{-1} yr^{-1}; Bejarano-Castillo et al. 2015). Moreover, cities experience warmer soil temperatures than surrounding rural areas due to the urban heat island effect (Edmondson et al. 2016), and thus N transformations are likely to be faster in urban soils.

We examined the influence of throughfall inorganic N (NH_4^+-N + NO_3^--N) fluxes on several indicators of N cycling and availability in tropical Atlantic Forest differing in exposure to atmospheric N deposition from the Metropolitan Region of Rio de Janeiro (hereafter megacity of Rio de Janeiro; population ~12 M). We hypothesized that the coastal forest located in the city core would exhibit: (i) increased throughfall N fluxes as a result of higher dry/fog deposition (Fenn et al. 1999; Lovett et al. 2000) and canopy leaching (Homeier et al. 2012); and (ii) faster soil N transformation rates (Niu et al. 2016) due to elevated N fluxes, improved substrate quality (Corre et al. 2010) and warmer soil temperatures (Breuer et al. 2002). We expected that throughfall N and soil N transformation rates would be comparatively lower in oceanic and inland forests more distant from the megacity, resulting in lower relative N availability.

Materials and methods

Atlantic Forest sites

Now reduced to ~12% of its original extension, Brazil's Atlantic Forest is highly fragmented; forest fragments are generally small (<50 ha; Ribeiro et al. 2009), and many are in, near, or downwind of rapidly growing

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cities. Impacts of N deposition on Atlantic Forest are of concern because of this biome's exceptional biodiversity (Phoenix et al. 2006) and role in water supply to downstream populations.

In this study, three tropical Atlantic Forest sites were selected within protected areas in and near the megacity of Rio de Janeiro (Fig. 1, Table 1). Sampling sites were chosen at 700-800 m elevation on south-facing slopes to control for aspect and elevation, factors that strongly influence atmospheric deposition rates in montane landscapes (Weathers et al. 2006b). These sampling sites are underlain by granite and gneiss (Vieira and Gramani 2015) and dominated by Cambisols (EMBRAPA 2008; INEA 2010; Ministerio do Meio Ambiente 2008).

The oceanic site is within Ilha Grande State Park, an island off the coast of Rio de Janeiro State ~100 km southwest of the megacity of Rio de Janeiro (Fig. 1). Mean annual rainfall is ~1500 mm and mean annual temperature is ~23°C. The park contains a mosaic of montane dense ombrophilous forest in varying stages of succession (de Oliveira 2002). Based on vegetation monitoring conducted by da Rosa (2013) near the study site, forest basal area is 43 m^2 ha^{-1}, mean tree height is 11 m, and stem density is 1847 individuals ha^{-1}. Families with the highest species richness include Myrtaceae, Rubiaceae, Fabaceae, Lauraceae, and Sapotaceae. In 2002, wet N deposition at the oceanic site was 4.8 kg ha^{-1} yr^{-1} (de Souza et al. 2006).

The coastal urban site is situated in Tijuca National Park, within the megacity ~7 km from the Atlantic Ocean and surrounded by urban land. Mean annual rainfall is ~1517 mm (Alerta Rio 2017). Mean monthly temperatures range 19-25°C (Silveira and Coelho Netto 1999). On south-facing slopes between ~600-700 m, the canopy of this montane dense ombrophilous forest is 9 m tall and stem density is 2256 individuals ha^{-1} (de Oliveira et al. 1995). Approximately 50% of the species belong to the Myrtaceae, Lauraceae, Fabaceae, Rubiaceae, Euphorbiaceae and Meliaceae families. Inorganic N deposition along the coast was >5 kg N ha^{-1} yr^{-1} in 1988-1989 (de Mello 2001) and 7.4 kg N ha^{-1} yr^{-1} in 2008-2009 (de Souza et al. 2015).

The inland site is within Serra dos Órgãos National Park, ~50 km northeast and downwind of the megacity

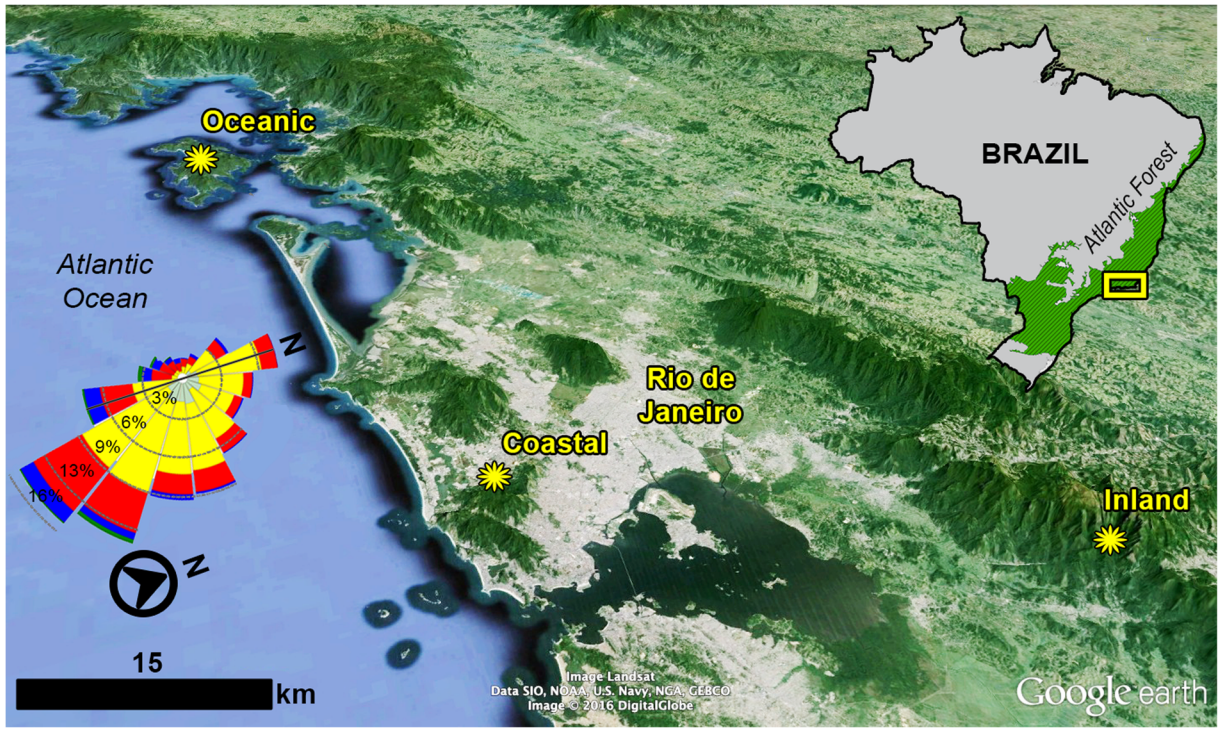

Fig. 1 Location of oceanic, coastal urban, and inland tropical Atlantic Forest sites in and near the megacity of Rio de Janeiro. Inset: Brazil with potential distribution of Atlantic Forest (green) and Rio de Janeiro State (yellow box) in southeastern Brazil. Wind rose for 2005-2010 (Rio de Janeiro Santos Dumont airport)) shows prevailing southerly winds. Wind rose and north arrow are both aligned north. Wind speeds are from 0.5-2 m/s (light green), 2-3 m/s (yellow), 3-4 m/s (red), 4-5 m/s (blue), and ≥5 m/s (dark green)

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Table 1 Characteristics of three tropical Atlantic Forest sites in and near the megacity of Rio de Janeiro, southeastern Brazil

	Oceanic	Coastal	Inland
Site (date established)	Ilha Grande State Park (1971)	Tijuca National Park (1961)	Serra dos Órgãos National Park (1939)
Coordinates	23°9'20"S, 44°11'38"W	22°57'3"S, 43°17'45"W	22°29'08"S, 43°01'2"W
Location	~100 km southwest of Rio de Janeiro	In Rio de Janeiro	~50 km northeast of Rio de Janeiro
Elevation (m asl)	800	800	700
Distance to coast (km)	3	7	53
Rainfall during study period (mm)	1555	1137	2539
Mean annual rainfall (mm)	1500[a]	1517[b]	2774[c]

[a,c] Fiderj (1961-1990)

[b] Alerta Rio (1997-2016)

of Rio de Janeiro in the Serra do Mar Mountain Range. Mean annual rainfall is ~2774 mm. The park contains secondary as well as mature montane dense ombrophilous forest on steep mountain slopes (C. Cronemberger, *personal communication*). Near the sampling site, basal area is 38 m^2 ha^{-1}, mean canopy height is 10 m, and stem density is 2007 individuals ha^{-1} (Fonseca 2009). Approximately 50% of the species are from the Lauraceae, Fabaceae, Euphorbiaceae, Meliaceae, Myrtaceae, and Sapindaceae families. Inorganic N deposition at the inland site ranged from 12 to 8 kg ha^{-1} yr^{-1} between 2004 and 2009, respectively (Rodrigues et al. 2007; de Souza et al. 2015).

Rainfall data

Hourly rainfall data for the study period (15-Jul-2013 to 15-Jul-2014) were obtained from meteorological stations closest to each of the sites (Table 1). Data were obtained for Paratí and Teresopolis stations (7 and 54 km from the oceanic and inland sites, respectively; INMET 2017) and for Tijuca station, 8 km from the coastal urban site (Alerta Rio 2017).

Bulk N deposition and throughfall N fluxes

We measured inorganic N (NH_4^+-N + NO_3^--N) in bulk rainfall and throughfall from 15-Jul-2013 to 15-Jul-2014 using mixed bed anion and cation exchange resins, a technique developed for measuring the flux of these ions in rain- and throughfall over large spatial scales (Fenn et al. 2002; Simkin et al. 2004). Samplers consisted of a 20-cm diameter plastic high-density polyethylene funnel (324 m^2) connected to flexible Tygon tubing, a plastic connector, and a disposable chromatograph column filled with Amberlite IRN150 mixed bed resin (after Simkin et al. 2004). Resin was prepared by mixing dry resin beads with double deionized water to create a slurry. The 1 mm thick filter at the bottom of each chromatograph column was replaced with a 3 mm thick 30-μ pore-size filter to reduce clogging. Columns were then filled with 20 mL of resin slurry and refrigerated. All other sampler components were rinsed, soaked overnight, and rinsed again with deionized water before deployment.

These funnel samplers collect and drain water through the ion-exchange resin column, where ions in water adhere to charged resin surfaces. The main advantage of this method over traditional aqueous sampling is that ionic bonds between ions in the sample and resin exchange sites result in greater chemical stability than ions in solution (Simkin et al. 2004). Thus, ion-exchange resin samples can remain in situ for weeks to months before columns need to be replaced. We employed this method given the 150 km linear distance between, and the remote location, of the three study sites (Fig. 1).

Similar to Rao et al. (2014), we deployed five collectors at each of the study sites. Three throughfall collectors were established within a 200 m^2 area under continuous closed canopy forest, a minimum of 5 m apart, and ~1 m from the bole of individual trees (~20-40 cm diameter at breast height). Samplers were mounted on PVC pipe and installed 1 m aboveground. A polywool filter was inserted into the neck of each funnel to prevent debris and insects from inhibiting water flow and entering the sample column. Nitrogen in throughfall was not used to estimate total (wet + dry +

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fog) atmospheric N deposition because of canopy-exchange processes (i.e., uptake and leaching), but was used to measure N flux to the forest floor.

Two identical bulk collectors were established in clearings near each of the forest sites. Bulk collectors capture rainwater that has not interacted with tree canopies but, because they remain open between sampling periods, also capture some coarse dry particles (>2 μm) heavy enough to settle on the collectors. Bulk collectors were used to measure rainfall N deposition.

Funnels and ion-exchange resin columns were simultaneously set and removed at the three sampling sites in July 2013 and July 2014, respectively. Resin columns were collected every 4-10 weeks during 48-hour rain free periods, for 11 sampling periods at the oceanic and coastal urban sites and six sampling periods at the inland site. All resin columns were replaced in late March during the transition from the wet (October to March) to the dry (April to September) season. After each sample collection, funnels were rinsed with deionized water in the field and new columns and collector components were attached along with new polywool filters. Samples were refrigerated until chemical analyses could be performed.

Relative N availability

Buried resin bags were used as an indicator of relative N availability in soil solution (Binkley 1984). Nylon stockings cut to ~7.5 cm lengths were packed with 10 grams of Amberlite IRN150 mixed bed resin and closed using a ziptie. Within a 2 m radius of each throughfall collector, one resin bag was buried 10-15 cm deep. A metal bar was gently inserted into the soil at an angle and the resin bag lowered into place. Resin bags were attached to fishing line and a yellow stake, which remained at the surface (Lovett et al. 2004). Resin bags were collected concomitantly with throughfall samples in September 2013, January 2014, March 2014, and July 2014, for four collection periods per site. To minimize soil disturbance, the location of each resin bag was noted upon removal, and the new resin bag buried >30 cm from the previous location.

Rainfall, throughfall, and resin bag sample extraction and analysis

Approximately 10% of samples were lost to branch falls and funnel clogging. Forty-nine bulk (20 at the oceanic and coastal, 9 at the inland), 74 throughfall (31 at the oceanic and coastal, 12 at the inland), 21 blank precipitation samples, 30 resin bags (6 at the oceanic, 12 at the coastal and inland), and 12 blank resin bags were collected and shipped to the University of North Texas Ecosystem Geography Laboratory for sample preparation and extraction.

Samples and blanks were extracted following the methods of Fenn et al. (2002) and Simkin et al. (2004). Samples were extracted three times with 2 *M* KCl solution. Immediately following extraction, samples were refrigerated at 4°C and then shipped to the Cary Institute of Ecosystem studies where NH_4^+-N and NO_3^--N were measured using a QuickChem Flow Injection Analyzer +8000 Series (Lachat Instruments, Loveland, Colorado). The detection limit of this method is 0.02 mg L^{-1}. External check samples (QC-ERA), two standards as unknown samples, and four replicate samples were included with each instrument run, and a matrix spike analysis was run, for quality assurance-quality control (after Weathers et al. 2006b). Two bulk deposition samples with high NH_4^+-N values and no visible evidence of contamination were re-analyzed. The values did not change and thus samples were included in the analysis. However, we report bulk deposition with and without outliers for comparison. Values below detection limit were set to half the detection limit for data handling (Wetherbee et al. 2005).

Soil temperature, soil nutrient pools, and soil C and N transformations

At each site, one iButton temperature logger (Maxim DS1922) was buried 10-15 cm deep next to each throughfall collector. Temperature was recorded every 90 minutes. In May 2013, 10 composite soil samples were collected at each site from the top 15 cm of the soil along a 1 km south-facing transect. At each sampling point, a 1 m^2 plot was established and four samples were collected from the corners of the plot. Samples were combined and mixed in black plastic bags, refrigerated at 4ºC, and shipped to the Soil Biogeochemistry Lab at the Ecosystem Research and Sustainability Institute, National Autonomous University of Mexico. Soil pH was measured in deionized water (soil:solution ratio, 1:2 w/v) with a pH meter equipped with a glass electrode (Corning Co.). Total carbon (C) was measured by combustion and coulometric detection (Huffman 1977) on a

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total carbon analyzer (UIC CM5012). Soil samples were digested in a mixture of concentrated H_2SO_4, H_2O_2 (30%) and K_2SO_4 plus $CuSO_4$ at 360 °C. Subsequently, total N was determined using the macro-Kjeldahl method (Bremner 1996), while total P was determined using the molybdate colorimetric method following ascorbic acid reduction (Murphy and Riley 1962). Soil available NH_4^+-N and NO_3^--N were extracted from 10 grams of fresh soil with 2 *M* KCl (Binkley and Hart 1989). Ammonium-N, NO_3^--N, and P were determined colorimetrically on a Braun+Luebbe 3 Autoanalyzer (Norderstedt, Germany).

Potential net C mineralization rate (microbial respiration) was measured following the method of Coleman et al. (1977). Forty grams of fresh soil were placed in a 5 cm diameter PVC tube with a 0.15 mm mesh fitted to the bottom. Samples were incubated in individual hermetic jars for 14 days, in darkness at 25°C in a constant temperature growth chamber. Soil was wetted periodically with deionized water to maintain field capacity. The CO_2-C evolved was collected in traps containing 10 mL 2M NaOH and was determined after adding 5 mL of 2.5 M $BaCl_2$ and phenolphthalein by titrating with 2 M HCl. After incubation, samples were analyzed for NH_4^+-N and NO_3^--N concentrations (see above). Potential net N mineralization was calculated as the difference between NH_4^+-N plus NO_3^--N concentrations prior to and following incubations. Net ammonification was calculated as the net change in extractable NH_4^+-N and net nitrification as the net change in NO_3^--N (Binkley and Hart 1989). Data were expressed on an oven-dry soil mass basis.

Flux calculations and statistical analysis

Bulk and throughfall N concentrations were converted to fluxes (kg ha^{-1} period $^{-1}$; collector surface area = 324 cm^2). Bulk deposition and throughfall fluxes of NH_4^+-N, NO_3^--N, and inorganic N (NH_4^+-N + NO_3^--N) were summed per collector for wet and dry seasons separately. To account for lost samples, wet and dry season values were divided by the number of days sampled and scaled to the season by multiplying by 183 days. Wet and dry season values for each collector were summed to obtain annual bulk deposition and throughfall fluxes. Annual values were also normalized (i.e., divided) by rainfall amount to assess the relative effect of urban exposure on these variables.

To examine the influence of forest canopies on throughfall flux, net throughfall flux (NTF) was calculated:

$$NTF = TF - BD$$

where TF is throughfall and BD is bulk deposition (kg ha^{-1} $time^{-1}$). Net throughfall integrates dry/fog deposition and canopy-exchange processes. Positive NTF values (NTF > 0, N in throughfall > N in bulk deposition) indicate greater N inputs from dry/fog deposition and canopy exchange than uptake in the canopy (i.e., net input of N to the soil). Negative NTF values (NTF < 0, N in throughfall < N in bulk deposition) indicate net N uptake by the canopy.

Resin bag N concentrations were converted to N accumulation rates (μg g^{-1} resin $period^{-1}$) by incorporating resin weight. Resin bag NH_4^+-N, NO_3^--N, and inorganic N were handled in the same way as bulk N deposition and throughfall N fluxes. Accumulation rates were summed for each collector and season. These values were then divided by the number of days sampled in each season and multiplied by 183 days to obtain seasonal rates. Annual accumulation was calculated as the sum of wet and dry season accumulations. Annual rates were also normalized by rainfall.

All variables were tested for normality using the Shapiro-Wilk test. Variables with non-normal distributions were square-root or log-transformed where necessary to meet assumptions of normality and homogeneity of variance. Linear mixed models were used to examine the effect of site, season, and site by season interaction on throughfall N fluxes, resin bag accumulation rates, and soil temperature. Site and season were fixed effects while sampling location was a random effect in the models. Post hoc comparisons were conducted using Tukey's HSD when significant differences between means were detected. One-way ANOVA with Tukey's HSD was used to determine whether there were significant differences in soil nutrient pools and transformations among the sites. Pearson's correlations were employed to examine relationships between rainfall amount, throughfall N fluxes, and resin bag accumulation rates; and between soil nutrient pools and transformations across sites. For data that could not easily be transformed, non-parametric Spearman's rho was used. Significance was set at $p < 0.1$. Statistical analyses were performed in JMP v.12.

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Results

Bulk N deposition

The oceanic and coastal urban forests received similar rates of bulk inorganic N deposition (6.8 ± 0.17 and 6.2 ± 0.21 kg ha^{-1} yr^{-1}, respectively), with NH_4^+-N and NO_3^--N each comprising ~50% of the inorganic N deposited (Fig. 2a). At the inland site, bulk N deposition was 17 ± 1.7 kg ha^{-1} yr^{-1} (14 ± 1.6 kg ha^{-1} yr^{-1} with two outliers excluded) and was dominated by NH_4^+-N. When bulk deposition was normalized by rainfall amount to assess the relative effect of urban exposure on N deposition, bulk NH_4^+-N and NO_3^--N were highest at the inland and coastal urban sites, respectively (Table 2).

Seasonality (season = wet or dry) in rainfall and bulk deposition was most pronounced at the oceanic and inland sites, with ~60-65% of rainfall, NH_4^+-N, and NO_3^--N deposited during the wet season. At the coastal urban site, nearly equal proportions of rain and NO_3^--N were deposited during both seasons; 58% of NH_4^+-N was deposited during the wet season.

Throughfall N fluxes

Site had a significant effect on annual throughfall NH_4^+-N ($p < 0.01$) flux to the forest floor. Throughfall fluxes were higher at the inland site downwind from the megacity of Rio de Janeiro compared to the oceanic ($p < 0.01$) and coastal urban ($p < 0.05$) sites (Fig. 2b). Season ($p < 0.0001$) and site by season ($p < 0.01$) also had significant effects in the model. Mean wet season throughfall fluxes were more than twofold greater (6.5 ± 0.24 kg ha^{-1}) at the inland than at the coastal urban (2.4 ± 0.50 kg ha^{-1}; $p < 0.0001$) and oceanic sites (3.1 ± 0.22 kg ha^{-1}; $p < 0.01$; Fig. 3a). Mean dry season throughfall NH_4^+-N fluxes were 0.96 ± 0.05 kg ha^{-1} at the oceanic, 2.2 ± 0.47 kg ha^{-1} at the coastal urban, and 2.9 ± 0.45 kg ha^{-1} at the inland site; only differences between the inland and oceanic site were significant ($p < 0.01$). Unlike NH_4^+-N, below-canopy NO_3^--N fluxes did not differ among sites ($p = 0.79$; Fig. 2b) or between seasons ($p = 0.11$), and there was no site by season interaction ($p = 0.29$; Fig. 3b). Annual throughfall inorganic N flux increased along the ocean (7.6 ± 0.30 kg ha^{-1}) to coast (8.7 ± 1.5 kg ha^{-1}) to inland (14 ± 2.5 kg ha^{-1}) gradient and was highest at the inland site ($p < 0.05$, $p < 0.1$).

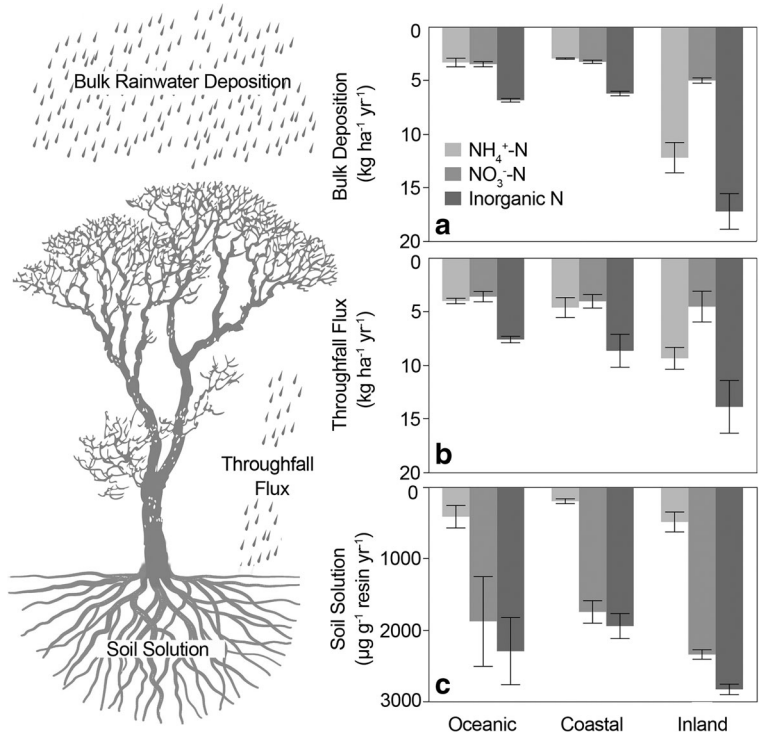

Fig. 2 Ammonium-N (NH_4^+-N), nitrate-N (NO_3^--N), and inorganic nitrogen (NH_4^+-N + NO_3^--N, N) in **a** bulk deposition (kg ha^{-1} yr^{-1}); **b** throughfall (kg ha^{-1} yr^{-1}); and **c** soil solution (µg g^{-1} resin yr^{-1}) measured from 15-Jul-2013 to 15-Jul-2014 in three tropical Atlantic Forest sites southwest (oceanic), in (coastal), and downwind (inland) of the megacity of Rio de Janeiro, southeastern Brazil

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Table 2 Normalized annual ammonium (NH_4^+-N), nitrate (NO_3^--N), and inorganic N (NH_4^+-N + NO_3^--N) fluxes (g mm^{-1} ha^{-1}) in bulk deposition and throughfall, and accumulation rates on resin bags in soil solution (μg mm^{-1} g^{-1} resin) in three tropical Atlantic Forest sites in and near the megacity of Rio de Janeiro, southeastern Brazil. Fluxes and rates may not sum due to rounding

	Oceanic	Coastal	Inland
Bulk NH_4^+-N	2.15 ± 0.26	2.61 ± 0.05	4.81 ± 0.56
Bulk NO_3^--N	2.25 ± 0.15	2.88 ± 0.13	1.98 ± 0.10
Inorganic N	4.40 ± 0.11	5.49 ± 0.19	6.79 ± 0.66
Throughfall NH_4^+-N	2.58 ± 0.16^c	4.07 ± 0.82^a	3.69 ± 0.40^{ab}
Throughfall NO_3^--N	2.32 ± 0.31^b	3.55 ± 0.56^a	1.79 ± 0.57^b
Throughfall inorganic N	4.90 ± 0.19^b	7.62 ± 1.35^a	5.48 ± 0.97^b
Soil solution NH_4^+-N	0.27 ± 0.1^a	0.17 ± 0.03^a	0.19 ± 0.06^a
Soil solution NO_3^--N	1.21 ± 0.4^a	1.54 ± 0.14^a	0.92 ± 0.03^a
Soil solution inorganic N	1.48 ± 0.3^a	1.71 ± 0.15^a	1.12 ± 0.03^a

Different letters indicate statistically significant differences in soil properties among forest sites ($p < 0.1$)

Season ($p < 0.0001$) and site by season ($p < 0.01$) had significant effects on throughfall inorganic N as well. During the wet season, the inland site received more inorganic N in throughfall than the coastal urban site ($p < 0.1$), but dry season differences among sites were not significant (Fig. 3c).

When throughfall fluxes were normalized by annual rainfall, a different spatial pattern emerged (Table 2). Per mm of rainfall, the coastal urban site received more NO_3^--N and inorganic N in throughfall compared to the inland ($p < 0.01$, $p < 0.05$) and oceanic sites ($p < 0.05$, $p < 0.01$). Normalized throughfall NH_4^+-N fluxes were highest at the coastal urban, lowest at the oceanic, and intermediate between the two at the inland site.

Net throughfall N fluxes

The direction and magnitude of net throughfall N fluxes differed among the sites. At the oceanic and coastal sites, throughfall NH_4^+-N was greater than bulk NH_4^+-N deposition, resulting in positive net NH_4^+-N fluxes (Fig. 4). In contrast, negative and lower ($p < 0.1$) net throughfall NH_4^+-N fluxes were measured at the inland site. Net throughfall NO_3^--N fluxes were similar and close to zero at all sites. Overall, annual net inorganic throughfall N flux was negligible at the oceanic site (0.78 ± 0.30 kg ha^{-1} yr^{-1}; Fig. 4), whereas at the coastal urban site net N flux was 2.4 ± 1.5 kg^{-1} ha^{-1} yr^1, indicating higher rates of dry/fog deposition and/or canopy leaching. The inland forest canopy retained 3.3 ± 2.5 kg N ha^{-1} yr^{-1} (0.0047 ± 2.5 kg N ha^{-1} yr^{-1}; two outliers excluded) even though bulk N deposition was higher at this site.

Resin bag N accumulation rates

Resin bag NH_4^+-N accumulation rates were more than twofold higher at the inland (489 ± 140 μg g^{-1} resin yr^{-1}) and oceanic sites (415 ± 158 μg g^{-1} resin yr^{-1}) compared to the coastal urban site (198 ± 33 μg g^{-1} resin yr^{-1}; Fig. 2c), but differences were not significant ($p = 0.13$). Season and site by season interaction effects were not detected. Nitrate-N comprised >75% of resin bag N at all sites. Resin bag NO_3^--N was higher at the inland (2343 ± 66 μg g^{-1} resin yr^{-1}) than at the coastal urban site (1750 ± 158 μg g^{-1} resin yr^{-1}, $p < 0.05$) and similar to that measured at the oceanic site (1882 ± 627 μg g^{-1} resin yr^{-1}). Mean wet season accumulation rates were lower than those measured during the dry season ($p < 0.1$). Resin bags captured 848 ± 44, 719 ± 67, and 1034 ± 115 μg NO_3^--N g^{-1} resin during the wet season, and 1071 ± 338, 1032 ± 224, and 1309 ± 65 μg g^{-1} resin during the dry season at the oceanic, coastal urban, and inland sites, respectively. In total, resin bag inorganic N was significantly higher at the inland than at the coastal urban site ($p < 0.01$), while the oceanic site was intermediate between the two. Differences between seasons were not detected nor were there interaction effects.

Annual resin bag accumulation rates increased with increasing rainfall for NH_4^+-N and inorganic N ($\rho = 0.82$, $p < 0.05$). During the wet season, rainfall was positively correlated with resin bag NO_3^--N ($\rho = 0.82$,

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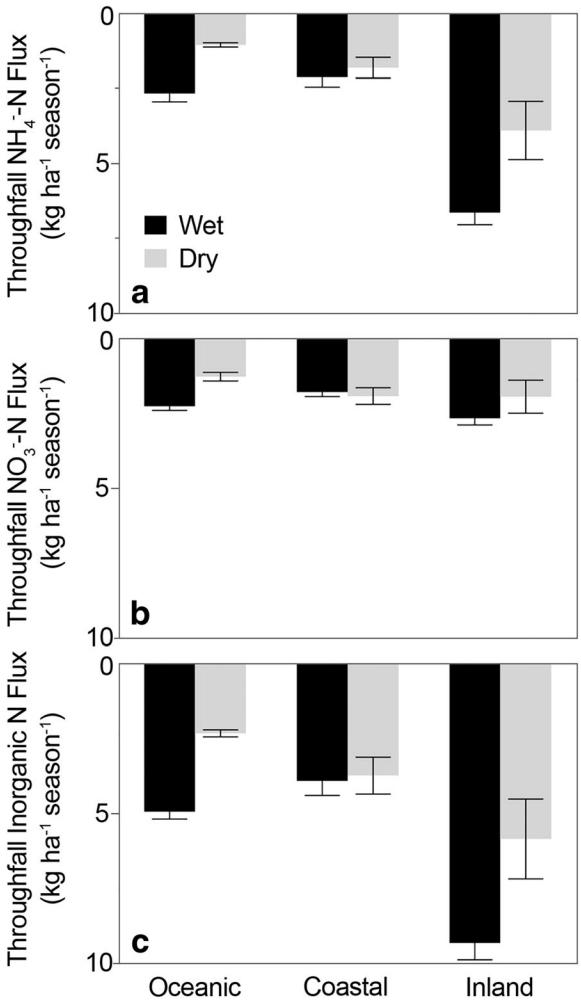

Fig. 3 **a** Ammonium-N (NH_4^+-N), **b** nitrate-N (NO_3^--N), and **c** inorganic nitrogen (NH_4^+-N + NO_3^--N, N) in throughfall (kg ha^{-1} season^{-1}) during wet (October to March) and dry (November to April) seasons measured from 15-Jul-2013 to 15-Jul-2014 in three tropical Atlantic Forest sites southwest (oceanic), in (coastal), and downwind (inland) of the megacity of Rio de Janeiro, southeastern Brazil

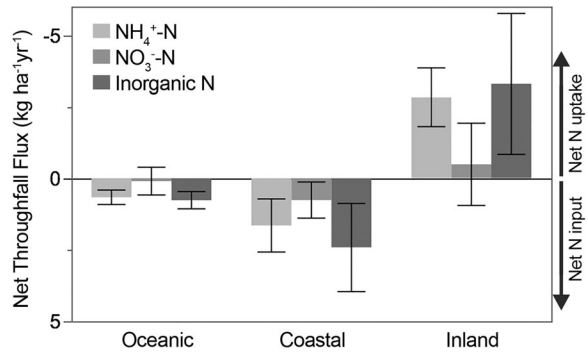

Fig. 4 Net throughfall ammonium-N (NH_4^+-N), nitrate-N (NO_3^--N), and inorganic N (NH_4^+-N + NO_3^--N) fluxes (kg ha^{-1} yr^{-1}) in three tropical Atlantic Forest sites southwest (oceanic), in (coastal), and downwind (inland) of the megacity of Rio de Janeiro, southeastern Brazil. Negative net throughfall values indicate net N uptake by the canopy and positive net throughfall values indicate net N input to the soil

$p < 0.05$) and inorganic N ($\rho = 0.76$, $p < 0.05$). There were also positive correlations between throughfall NH_4^+-N and resin bag NH_4^+-N ($\rho = 0.71$, $p < 0.1$), and between throughfall NO_3^--N and resin bag NO_3^--N ($\rho = 0.79$, $p < 0.05$). No correlations were detected between rainfall, throughfall N fluxes, and resin N accumulation during the dry season.

Soil nutrient pools

Soil pH was acidic (approximately 4) and did not differ significantly among the Atlantic forest sites (Table 3). Soil total C concentrations were more than twofold lower at the coastal urban and inland compared to the oceanic site ($p < 0.01$), while total N concentrations were lowest at the coastal urban site ($p < 0.05$). The oceanic site had a higher C:N mass ratio (21) than the coastal urban and inland sites (13 and 14, respectively, $p < 0.05$; Table 3). Low total P was measured in the oceanic and coastal urban forest soils, while concentrations were threefold to fourfold higher at the inland site ($p < 0.001$). The soil C:P mass ratio was highest at the oceanic (254), intermediate at the coastal urban (121), and lowest at the inland site (45).

Both the size of the soil inorganic N pool and the relative importance of NH_4^+-N declined from the ocean-inland, while soil NO_3^--N pools increased slightly (Table 3). At the oceanic site, the soil extractable NH_4^+-N pool was large and represented 83% of inorganic N. Ammonium-N also dominated the inorganic N pool at the coastal urban site, while the NH_4^+-N pool was significantly lower ($p < 0.05$) and comprised 45% of the inorganic N at the inland site.

Soil temperature, potential net C mineralization and N transformation rates

Mean daily soil temperatures ranged from 14-23°C during the study period, with higher temperatures during the wet (20 ± 0.060°C) compared to the dry (17 ± 0.051°C) season ($p < 0.0001$). Soil temperatures were higher in the coastal urban forest (19 ± 0.12°C)

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Table 3 Soil nutrient pools, potential net carbon (C) mineralization, soil nitrogen (N) transformation rates, and other soil characteristics (mean ± SE) in three tropical Atlantic Forest sites in and near the megacity of Rio de Janeiro, southeastern Brazil

	Oceanic	Coastal	Inland
Soil pH	4.4 ± 0.07[a]	4.4 ± 0.14[a]	4.4 ± 0.06[a]
Total C (mg g^{-1} dwt)	101 ± 8.8[a]	38 ± 4.9[b]	49 ± 3.3[b]
Total N (mg g^{-1} dwt)	4.9 ± 0.42[a]	2.8 ± 0.26[b]	3.5 ± 0.18[a]
Total P (mg g^{-1} dwt)	0.41 ± 0.040[a]	0.33 ± 0.025[a]	1.3 ± 0.18[b]
C:N (mass)	21 ± 0.61[a]	13 ± 0.88[b]	14 ± 0.78[b]
C:P (mass)	254 ± 14[a]	121 ± 19[b]	45 ± 7.8[c]
NH_4^+-N (μg g^{-1} dwt)	28 ± 6.5[a]	15 ± 5.4[ab]	7.5 ± 2.7[b]
NO_3^--N (μg g^{-1} dwt)	5.9 ± 0.96[a]	7.3 ± 1.2[a]	9.1 ± 1.5[a]
Inorganic N (NH_4^+-N + NO_3^--N)	34 ± 5.9[a]	22 ± 6.3[b]	17 ± 3.0[b]
Median NO_3^-:NH_4^+ (IQR)	0.33 ± 0.68[a]	0.53 ± 2.2[ab]	1.8 ± 1.1[b]
Net C mineralization (μg g^{-1} dwt d^{-1})	42 ± 6.0[a]	28 ± 4.9[ab]	24 ± 2.6[b]
Net N mineralization (μg g^{-1} dwt d^{-1})	0.17 ± 0.33[a]	0.29 ± 0.35[a]	0.32 ± 0.27[a]
Net ammonification (μg g^{-1} dwt d^{-1})	-0.31 ± 0.19[a]	-0.81 ± 0.38[a]	-0.33 ± 0.12[a]
Net nitrification (μg g^{-1} dwt d^{-1})	0.48 ± 0.21[a]	1.1 ± 0.50[a]	0.64 ± 0.26[a]
Mean daily soil temperature (°C)	18 ± 1.1[a]	19 ± 0.12[b]	18 ± 0.11[a]

Different letters indicate statistically significant differences in soil properties among forest sites ($p < 0.1$)

compared to the oceanic (18 ± 0.11°C) and inland forest sites (18 ± 0.11°C; $p < 0.0001$).

Potential net C mineralization rates were nearly two-fold lower at the inland ($p < 0.05$) than at the oceanic site and intermediate between the two at the coastal urban site (Table 3). Unlike soil C mineralization, there were no differences in mean soil N transformation rates. Overall, net N mineralization rates were low, ranging from 0.17-0.32 μg N g^{-1} d^{-1}. Net ammonification was close to zero or negative at all sites, indicating either net immobilization of NH_4^+ or rapid conversion to NO_3^-. Net nitrification was nearly always positive.

There was a significant positive correlation between total soil C and potential net C mineralization across the entire data set ($r = 0.62$, $p < 0.001$). There were no significant correlations between soil variables and either net nitrification or net N mineralization. Net ammonification, on the other hand, was significantly negatively correlated with initial NH_4^+-N pools across the entire data set ($\rho = -0.56$, $p < 0.01$).

Discussion

Nitrogen pollution from major urban areas is among the many threats facing Brazil's Atlantic Forest (Phoenix et al. 2006). Yet, relatively little information exists on the ecosystem consequences of N deposition in this highly diverse tropical ecosystem (but see Forti et al. 2007; Ranzini et al. 2007). We measured N deposition to and effects on Atlantic Forest soils at three sites spanning a 150 km linear distance in and near the megacity of Rio de Janeiro.

Hotspots of N flux to Atlantic Forest

Particulate and gaseous N can constitute a significant fraction (~50%) of inorganic N deposition to tropical forest canopies near urban areas of southeast Brazil (Allen et al. 2011). Enhanced N fluxes to soil and subsequent root uptake can also accelerate N leaching losses from plant canopies (Homeier et al. 2012). Thus, relative to bulk N deposition, throughfall N typically increases with proximity to urban emissions sources (i.e., greater net throughfall fluxes; Lovett et al. 2000; Du et al. 2015; Tulloss and Cadenasso 2015). Consistent with these studies, we measured a peak in net throughfall N flux at the coastal urban site, indicating greater dry/fog deposition and/or canopy leaching than canopy retention of N (Fig. 4).

However, contrary to expectation, throughfall N fluxes to the Atlantic Forest sites did not increase with proximity to the megacity, but along an ocean-coast-inland gradient. This is likely, in part, due to prevailing

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southerly winds that result from a continuous sea-land breeze (de Souza et al. 2015) coupled with the location of the coastal urban forest relative to urban and industrial sources (Fig. 1), which are concentrated between Tijuca massif and Serra dos Órgãos. Indeed, our findings suggest that the considerable below-canopy flux of N measured at the inland site (14 kg ha^{-1} yr^{-1}) was the result of both elevated rainfall amount (Table 1) and NH_4^+ concentrations (Table 2). Working in the megacity of Rio de Janeiro, de Souza et al. (2015) measured higher bulk rainfall NH_4^+ than NO_3^- concentrations at a peri-urban site upwind of our inland forest as well as in rainfall and throughfall at a nearby lower montane forest. They suggested that emissions from urban sewage and cattle pastures were potential major sources of NH_4^+ in precipitation.

In addition, much of the additional NH_4^+ deposited to the inland site was delivered during a very wet season (1498 mm; Fig. 3). For comparison, wet season rainfall was 606 mm at the coastal urban site, 35% below the historical average of 935 mm for 1997-2016 (Alerta Rio 2017). This low rainfall was due to an extreme drought caused by El Niño that affected southeastern Brazil during the 2014 austral summer (January to March), months that generally experience the highest rainfall volumes (Coelho et al. 2016). The 2014 austral summer was the largest negative precipitation anomaly (relative to mean rainfall for 1981-2010) recorded between 1961 and 2014 (Coelho et al. 2016). At the coastal urban forest we sampled, severe rainfall deficits occurred in January (84% below normal), February (74% below normal), and March (38% below normal). Thus, all else equal (i.e., precipitation concentrations), the coastal urban forest should receive ~33% more N in throughfall, or ~12 kg N ha^{-1}, during a 'typical' water year (1517 mm). Taken together, these results indicate that rainfall may be relatively more important than dry/fog deposition and canopy leaching in controlling the location and magnitude of N deposition hotspots within urban-affected Atlantic and other tropical forests.

Ecosystem responses to high throughfall N flux in an Atlantic Forest hotspot

Although studies often report NO_3^- as the dominant form of N in urban forest throughfall (e.g., Tulloss and Cadenasso 2015), in some urban areas, including the megacity of Rio de Janeiro, NH_4^+ fluxes have been shown to exceed those of NO_3^- (Fang et al. 2011; Rao et al. 2014; de Souza et al. 2015; Du et al. 2015; Decina et al. 2017). Ammonium-N deposited to forest ecosystems can have several possible fates, including canopy or root uptake, microbial uptake, nitrification and subsequent denitrification, and leaching (Templer et al. 2008).

Our results indicate that canopy uptake of NH_4^+ at the high-N, inland site was equivalent to ~20% of incoming NH_4^+ in rainfall (Fig. 4). Canopy NH_4^+ uptake is widespread in tropical and temperate forests, amounting to as much as 61-83% of the NH_4^+ deposited (Clark et al. 1998; Gaige et al. 2007). Experimental studies in which seedlings or canopy components have been misted or sprayed with inorganic N in solution provide evidence of direct NH_4^+ uptake by foliar surfaces (Adriaenssens et al. 2011), epiphytic bryophytes (Clark et al. 2005), and lichens (Lang et al. 1976). Nitrogen-limited microbes living on canopy surfaces may also take up and immobilize NH_4^+ (Vance and Nadkarni 1990). In ecosystems such as the inland forest we studied, where epiphytic material comprises an important fraction of canopy biomass and canopy organic matter provides surfaces for NH_4^+ retention, biotic and abiotic retention may be especially high (Matson et al. 2014). A caveat of this interpretation is that two bulk rainfall and three throughfall samplers were deployed at each of the sites; in a few cases, this resulted in high measurement variability. However, after two outliers were excluded, net throughfall N flux at the inland site was zero, suggesting that either dry deposition and canopy leaching were low, or that canopy consumption of N nearly balanced these processes.

Regardless, high N deposition and throughfall flux at the inland site were associated with greater relative soil N availability, a response documented in various humid tropical systems (reviewed in Cusack et al. 2016). The NO_3:NH_4 ratio, a commonly used index of N availability (Davidson et al. 2007), was more than fivefold higher at the inland than at the oceanic site (Table 3). In Hawaiian montane forest, Lohse and Matson (2005) similarly found that N fertilization led to an increase in soil NO_3^- pools relative to those of NH_4^+. The inland high-N site was also the only forest in which NO_3^- dominated the soil inorganic N pool. Nitrate is the dominant form of N in systems where N availability is very high; reduced competition for NH_4^+ between plants and microbes results in increased NH_4^+ supply to nitrifying communities and, in turn, enhanced NO_3^- production (Schimel and Bennett 2004). The low total soil C

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concentrations (a good correlate of microbial biomass; Paul 2007), soil C:N ratio, and potential net C mineralization rates we measured at the inland site are all consistent with lower relative microbial demand for N.

Laboratory incubations did not reveal differences in potential soil N transformation rates, but NO_3^--N accumulation by resin bags support the notion of accelerated nitrification in the inland forest soils. In situ resin bag estimates of N availability are sensitive to several factors: temperature, soil water status, ion mobility and concentration, and competition from microbes and plant roots (Binkley 1984; Johnson et al. 2005). Positive correlations between wet season rainfall, throughfall NO_3^--N flux, and NO_3^--N accumulated by resin bags indicate that the increase in soil solution NO_3^--N at the inland site was also due to high annual rainfall and throughfall N level.

Because soil water fluxes are a major control on NO_3^- leaching loss from soils in tropical systems (Lohse and Matson 2005), elevated NO_3^- in soil solution may be lost via leaching to deeper soil layers or surface waters (Fang et al. 2011). Ranzini et al. (2007) modeled N deposition effects on N cycling in Brazilian Atlantic Forest and found that as N deposition increased so did nitrification, NO_3^- leaching losses, and denitrification. We did not measure denitrification in this study—an important pathway for N loss in humid tropical systems (Houlton et al. 2006)—but soil N_2O-N fluxes measured at the inland forest indicate that gaseous losses there are small, <0.3 kg ha^{-1} yr^{-1} (Rodrigues and de Mello 2012). This rate is well below the median N_2O flux reported for Atlantic (0.9 kg ha^{-1} yr^{-1}) and Amazonian tropical forests (2.4 kg ha^{-1} yr^{-1}; Meurer et al. 2016) and represents ~2% of the inorganic N flux we measured to the forest floor of the inland site. Thus, extra N may be preferentially lost via hydrologic rather than atmospheric pathways.

Implications and conclusions

Our results have implications for understanding ecosystem responses to urban N deposition in highly diverse, tropical forest regions. Within and downwind of the megacity of Rio de Janeiro, we documented throughfall N fluxes in Atlantic Forest close to or exceeding 10 kg ha^{-1} yr^{-1}. Rainfall strongly influenced the magnitude of throughfall N flux, resulting in higher N fluxes at an inland site downwind of the megacity than in the urban core. Potential soil N transformation rates did not differ among the forests, but field measurements showed that high throughfall N flux increased relative N availability. These findings suggest that high N deposition to urban-affected Atlantic Forest increases the potential for NO_3^- leaching loss from Atlantic Forest soils.

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Author contributions AGPG, KCW, and WZD conceived the study. AGPG, KCW, YP, and PAS designed the sampling and conducted fieldwork. AGPG, YP, and FG analyzed the data. AGPG and YP designed figures and tables. AGPG wrote the manuscript; all authors provided editorial advice.

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