

Nitrogen additions mobilize soil base cations in two tropical forests

Daniela F. Cusack · Jordan Macy ·
William H. McDowell

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Abstract Rates of atmospheric nitrogen (N) deposition are increasing rapidly in tropical regions, which are projected to receive some of the greatest deposition levels globally in the coming decades. Tropical forests on highly weathered soils generally have high N availability, so added N is not likely to stimulate plant growth. Instead, N addition to these soils may rapidly alter the availability of other scarcer nutrients like base cations, via displacement from soil exchange sites and mobilization into solution. We hypothesized that: (1.) Addition of mineral N to highly weathered tropical soils rapidly mobilizes base cations into solution, with increasing fertilization effects

over time. (2.) Nitrogen fertilization reduces cation availability on soil exchange sites, because of increased mobilization and loss down the soil profile. We assessed the short-term (1–2 year) and mid-term (4–5 year) effects of N fertilization on base cation mobilization to 40 cm depths in two distinct tropical forests. Over the first 5 years of the experiment, fertilization significantly increased calcium, magnesium, and potassium concentrations in soil solution, as well as all dissolved N chemical species. There was an increasing fertilization effect over time for all solutes across soil depths, suggestive of downward leaching. Comparing the two forests, there was no difference in the magnitude or timing of the fertilization effect on base cation mobilization, although dissolved N concentrations increased most rapidly in the upper elevation forest, where background dissolved N was also higher. Surprisingly, salt-extractable base cations also increased for fertilized versus control soils. Our results suggest that addition of mineral N to tropical forests on highly weathered soils is highly likely to mobilize base cations into solution, with subsequent leaching down the soil profile. These results imply that N deposition in tropical forests on highly weathered soils may exacerbate cation scarcity in these ecosystems, and could negatively affect long-term plant growth.

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Present Address:

D. F. Cusack (✉)
Department of Geography, University of California, Los Angeles, 1255 Bunche Hall, Box 951524, Los Angeles, CA 90095, USA
e-mail: dcusack@geog.ucla.edu

J. Macy · W. H. McDowell
Department of Natural Resources and the Environment,
University of New Hampshire, 56 College Road, Durham,
NH 03824, USA

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Introduction

Nitrogen (N) deposition is one of the most ubiquitous anthropogenic disturbances to natural ecosystems, and some of the fastest rates of increase are in tropical regions. For example, average rates of atmospheric N deposition in tropical Latin America are projected to exceed 25 kg-N/ha-year by 2050, and N deposition rates in tropical forests near major cities already exceed 50 kg-N/ha-year (Fang et al. 2011; Galloway et al. 2004). Increased N deposition results from fossil fuel combustion, industrial activity, and agricultural fertilizer (Krusche et al. 2003; Lara et al. 2001; Martinelli et al. 2006), and can acidify soils, stimulate leaching of mineral nutrients, and negatively affect water quality (Groffman et al. 2009; Lara et al. 2001; Matson et al. 1999; McDonnell et al. 1997; Pouyat et al. 1995). In both temperate and tropical sites, urban-proximate forests often have higher soil mineral N levels, mineralization rates, and N leaching relative to rural reference sites (Cusack 2013; Groffman et al. 2009; White and McDonnell 1988; Zhu and Carreiro 1999). In addition to changing ecosystem N cycling, elevated N deposition also has the potential to alter the availability of other nutrients via biological and physical processes.

For example, addition of mineral N to soils may affect the availability of exchangeable nutrient cations via a suite of mechanisms. First, elevated concentrations of NH_4^+ in soil solution can directly exchange for positively charged ions on soil surfaces. Second, increased NH_4^+ can lead to elevated nitrification and/or plant uptake, both of which release protons into soil solution (Van Miegroet and Cole 1984). Added protons can then also exchange for positively charged ions on soil surfaces. This type of soil acidification is likely to be especially important for cation mobilization in highly weathered tropical soils, which are typically already acidic and poorly buffered (Sanchez and Logan 1992). Finally, excess NO_3^- is highly mobile in soils and readily leaches out with positively charged ions (Gundersen et al. 2006; Johnson and Reuss 1984). Mobilization of cations and anions from soil surfaces into solution may increase their availability to plants in the short-term, but chronic N additions are likely to lead to cation leaching losses in the long-term (Mitchell and Smethurst 2008).

Nitrogen fertilization effects on nutrient availability in temperate and northern ecosystem have received

much attention in recent years (Aber et al. 1989; Dijkstra et al. 2004; Gundersen et al. 1998; Magill et al. 1997; Nadelhoffer et al. 1995; Pennings et al. 2005). Over decadal timescales, numerous studies have shown that N fertilization and acid deposition can lead to declines in soil extractable cations (Hogberg et al. 2006; Huntington 2005; Saarsalmi and Malkonen 2001), reduced foliar cation concentrations (Elvir et al. 2005; Minocha et al. 2000), and watershed-scale cation export (Fernandez et al. 2003), although some sites show no change in cation cycling (Ingerslev et al. 2001; Nilsen 2001; Nohrstedt 2001; Yanai et al. 1999). Overall, a meta-analysis of 107 primarily temperate and northern sites showed that N additions generally increase mobilization of exchangeable base cations into soil solution and stream water, with parallel declines in soil extractable cations (Lucas et al. 2011). Often, these effects of added N on cation leaching are delayed for decades in temperate sites, because increased plant uptake initially removes added N from soils (Currie et al. 1999; Hogberg et al. 2006).

Nitrogen deposition effects on tropical forests have received far less attention, despite the likelihood of more rapid and drastic negative effects in these ecosystems (Matson et al. 1999). In contrast to most temperate sites, humid tropical forests on highly weathered soils are highly acidic, poorly buffered, and relatively high in soil N availability (Martinelli et al. 1999; Sanchez and Logan 1992). Because soils in many humid tropical forests are already N-rich, plant growth does not generally respond to N fertilization (Cusack et al. 2011; Harrington et al. 2001; Kaspari et al. 2008; Mirmanto et al. 1999; Ostertag 2001). Thus, plant uptake is unlikely to remove added N from soils, so effects on base cation mobility are likely to be faster and larger than in N-poor sites. Indeed, the three tropical Chinese sites included in the above meta-analysis showed greater cation mobilization with N fertilization compared to temperate and boreal ecosystems (Lu et al. 2009; Lucas et al. 2011). Because highly weathered soils are already poor in rock-derived nutrients (Walker and Syers 1976), mobilization and loss of cations from humid tropical forests are likely to have rapid negative consequences for plant productivity.

We assessed N fertilization effects on nutrient cation and anion dynamics in two tropical rainforests. We included lower and upper elevation forests in Puerto Rico that are both relatively N-rich, and where

plant growth has not responded to N fertilization. (Cusack et al. 2011). Nutrient cycling in both forests is generally not at steady-state because of the frequent occurrence of severe tropical storms and hurricanes (Heartsill-Scalley et al. 2010; Scatena et al. 1993; Silver et al. 1996). Despite significant similarities, background soil N levels, climate and soil type vary between the two sites (McGroddy and Silver 2000). Both forests were included to assess heterogeneity in base cation responses to N addition in different tropical forests.

We hypothesized that: (1.) Nitrogen fertilization in highly weathered tropical soils rapidly mobilizes base cations into soil solution, because of cation displacement by NH_4^+ and soil acidification. We expected that chronic N fertilization would increase dissolved N concentrations in soil solution at both sites, and we predicted an increasing fertilization effect on cation mobility over time. (2.) Nitrogen fertilization reduces cation availability on soil exchange sites, because of increased mobilization and leaching losses down the soil profile. We predicted that increased cation mobility with N addition would be apparent both in surface soil and beneath the main rooting zone, suggestive of leaching. Comparing the two forest types, we expected that differences in background N availability would be linked to the magnitude of the fertilization effect.

Methods

Study site

This study was conducted in the Luquillo Experimental Forest (LEF, Lat. $+18.3^\circ$, Long. -65.8°), an NSF-sponsored Long Term Ecological Research (LTER) and Critical Zone Observatory (CZO) site in north-eastern Puerto Rico (Harris et al. 2012; McDowell et al. 2012). This study was conducted in two distinct tropical forests at lower and upper elevations in the LEF (site maps shown in McDowell et al. 1992). The lower elevation site is a wet tropical rainforest (Holdridge et al. 1971) located in the Bisley Experimental Watersheds, where long-term monitoring of streams, throughfall and rainfall is underway (Heartsill-Scalley et al. 2007; Scatena et al. 1993). Long-term mean annual rainfall in the Bisley Watersheds is 3500 mm/year (Garcia-Montino et al. 1996; Heartsill-

Scalley et al. 2007), and plots for this study were located at 260 masl. The upper elevation site is a lower montane forest (Holdridge et al. 1971), characterized by abundant epiphytes and cloud influence (Bruijnzeel 2001) in the Icacos watershed (McDowell et al. 1992). Mean annual rainfall at the upper elevation site is 4300 mm/year (McDowell and Asbury 1994), and plots were located at 640 masl. The two forests differ in tree species composition and structure, with Tabonuco-type forest in the lower elevation (21-m canopies), and Colorado-type forest in the upper elevation (10-m canopies) (Brokaw and Grear 1991). The average daily temperature is 23°C in the lower elevation site, and 21°C in the upper elevation forests.

In general, the LEF experiences little temporal variability in monthly rainfall and mean daily temperature (McDowell et al. 2012). However, the severity of tropical storms varies throughout the year, with a hurricane season from August to November that has frequent small storm events (monthly to annually) and less frequent large tropical storms (multi-decadal). Large storms and hurricanes can alter above- and belowground nutrient pools on the scale of weeks to decades (Heartsill-Scalley et al. 2010; Scatena et al. 1993; Silver et al. 1996). Both of the sites used here have experienced frequent hurricanes, with ten named tropical storms since 1988. The largest of these was Hurricane Hugo (category 4) in 1989, followed by Hurricane Georges in 1998 (category 4), both of which caused crown damage and uprooting (Heartsill-Scalley et al. 2007). Smaller hurricanes and tropical storms passed through the area in 1999 and 2000 before the first fertilization event in this study, with the next hurricane occurring in 2007 after the final measurements presented here (NOAA 2012). Thus, the study spans a recovery period after several major storms and hurricanes, and does not include the occurrence of any new major storm disturbances.

Nitrogen-addition plots in each forest type were established in 2000 at sites described by McDowell et al. (1992), and fertilization began in January 2002. Three 20×20 m fertilized plots were paired spatially with three control plots in each forest to control for slope and topography, for a total of 12 plots ($n = 3$). The buffers between plots were at least 10 m, with fertilized plots located to avoid runoff into control plots. Starting in 2002, 50 kg N/ha/year were added using a hand-held broadcaster, applied in two annual doses of NH_4NO_3 . Background rates of wet N

deposition are still relatively low in Puerto Rico (3.9 kg N/ha/year), but have more than doubled in the past decades (NADP/NTN 2013). The rate of 50 kg N/ha/year is similar to the highest levels projected for the Latin American tropics in the coming decades (Dentener et al. 2006), and is similar to highs of ~40 kg-N/ha-year measured in the San Juan, Puerto Rico metropolitan area (IITF, unpublished data).

Parent material in the lower elevation is basaltic volcanic material, and in the upper elevation is quartz diorite. Soils in both sites are deep with clay-rich B horizons. The most recent USDA-NRCS survey determined that the volcanoclastic rocks weather into Oxisols, and the quartz diorite rock weathers into Inceptisols (Beinroth 1982; Huffaker 2002). Soils at both sites are rich in variable-charged clays, with pH-dependent net charge, and relatively low levels of exchangeable nutrient cations (Fox 1982). The upper elevation Inceptisols are characterized by lower bulk soil N concentrations compared with the lower elevation Oxisols (Cusack et al. 2009). Nonetheless, soil N in both forests is relatively high and plant productivity has not responded to added N in either site (Cusack et al. 2011). Upper elevation soils also have relatively lower soil redox potential (Silver et al. 1999), and higher bulk soil phosphorous (P) (McGroddy and Silver 2000) compared with the lower elevation sites.

Sample collection

Pre-treatment samples were collected from 2000 to 2001, and post-treatment samples were collected in two periods to assess immediate fertilization effects during years 1–2 (2002–2003), and intermediate effects during years 4–5 (2005–2006). Soil solution was collected using Prenart sand-point super-quartz tension lysimeters (Prenart Equipment ApS, Denmark) installed 5, 20, and 40 cm deep in the soil profile. The 5 and 20 cm depth lysimeters were initially installed in 2000 for pre-fertilization measurements, and the 40 cm lysimeters were installed in 2003. Samples were collected starting in 2000 after allowing lysimeters to equilibrate for 2 weeks, after which lysimeter solution chemistry was checked for short-term directional drift to confirm the absence of an artefact effect of insertion. Soil solution was collected approximately monthly, with 17 collections each for 2000–2001 and 2002–2003, and 15 collections for 2005–2006. For each sampling point, soil

solution from paired treatment and control plots was collected on the same day. Lysimeters were placed under 80 cb tension, and solution was collected in 500 ml acid-washed glass bottles within 2 days. Samples were filtered immediately through ashed (450 °C for 4–6 h) Whatman GF/F filters (nominal pore size 0.7 µm) into polyethylene (HDPE) sample bottles, frozen, and shipped with blanks to the University of New Hampshire for chemical analyses. A total of 1525 lysimeter samples were collected for the study.

Soils samples for nutrient analysis were collected in 2006 with a 2.5 cm diameter corer from 0–10, 10–20, 20–30, and 30–40 cm depths. These depths was previously shown to have significant changes in soil C, N and pH with N fertilization at these sites, with the largest effect at 0–10 cm (Cusack et al. 2011). Three 10 m transects were established within the core area of each 20 × 20 m plot, along which soils were collected at five randomly selected locations and then pooled by transect, giving three spatially representative sub-samples per plot. Pre-treatment soils were collected in 2002 from 0 to 30 cm depth using a similar spatial sampling approach within plots. Fresh soils were subsampled for extractable mineral N analyses (see below), and then air dried and ground using a mortar and pestle for subsequent analyses.

Chemical analyses

Soil solution samples were analyzed for total dissolved N (TDN), dissolved organic N (DON), NO_3^- , NH_4^+ , calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), sodium (Na^+), sulfate (SO_4^{2-}), chloride (Cl^-), and soluble reactive phosphorus (PO_4^{3-}). Total dissolved N, including organic and mineral N, was measured using a Shimadzu TOC analyzer (Shimadzu Corporation, MD) and an NOx analyzer (Antek Instruments, Inc., Houston, TX) as described in (Merriam et al. 1996) during the early years of the study, and later was measured with a Shimadzu TOCV with N Detection Module. Dissolved organic nitrogen was measured as the difference between TDN and inorganic nitrogen. Cations and anions were measured using ion chromatography, with Dionex membrane suppression for anions, and an unsuppressed isocratic method with nitric acid mobile phase for cations. Phosphate was measured using a Westco SmartChem robotic discrete analyzer using ammonium molybdate.

Ammonium was measured on the same instrument using phenol hypochlorite. The pH of soil solution was measured in the field for each lysimeter using a portable digital pH meter.

Soil salt-extractable ions were measured for pre-treatment (2002) and post-treatment (2006) differences between treatments and forests. Salt-extractable nutrients included Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Mn^{2+} , Zn^{2+} , Al , Fe , Cl^- , SO_4^{3-} and PO_4^{3-} , which are reported here as mg/kg-dry-soil. Exchangeable cations were extracted using a 1 M NH_4Cl salt extraction in 10:1 ratios of solution:soil, shaken for 15 min, and filtered following standard protocols (Blume et al. 1990). Cation elemental analysis was done on an ICP Perkin-Elmer Optima DV 3000 series. Exchangeable Cl^- and SO_4^{3-} were similarly extracted using deionized water in a 10:1 ratio of solution:soil, and anion analysis was done on an ion chromatograph Dionex 600DX with a 14A anion column. Phosphorus was extracted using a standard Bray P method (Bray and Kurtz 1945; Frank et al. 1998), and PO_4^{3-} was measured using a Lachat QuikChem AE flow injection autoanalyzer. Soil pH was measured using a 2:1 (v:v) ratio of water:soil. Effective cation exchange capacity (CECe) was calculated as the summed charges of extractable Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+ and is reported as $\text{cmol}^+\text{charge/kg-soil}$. Extractable ions, soil pH and CECe were measured at the University of Vermont Agricultural and Environmental Testing Laboratory using standard quality assurance/quality control methods (Ross et al. 2015).

Soil salt-extractable NH_4^+ and NO_3^- were measured on fresh soils from 0–10 cm depth using 2 M potassium chloride (KCl) on the day of collection in Puerto Rico to minimize storage effects on mineral N pools (Turner and Romero 2009) as described in Cusack (2013). Frozen extracts were shipped for analysis to the University of California – Los Angeles. Extractable NH_4^+ and NO_3^- were analyzed using standard colorimetric techniques in 96-well plates (Doane and Horwath 2003; Rhine et al. 1998). Analyses included standard curves, check standards, and four analytical replicates per sample. Mineral N levels were measured on a BioTek Instruments Inc., Synergy HT absorbance spectrometer.

To assess total nutrient content of soils from each site, we used a standard acid digestion for soils from 0 to 10 cm depth. This measure was used primarily to determine baseline differences in nutrient status

between the two forests and among treatment plots. Samples were digested with concentrated HNO_3 , 30 percent H_2O_2 and concentrated HCl at the USFS IITF lab in Puerto Rico, in a modification of the digestion method recommended by (Luh Huang and Schulte 1985). Total-acid extraction values of Ca, Mg, K, Na, and P were determined. The subsequent elemental analysis was performed utilizing a Spectro Plasma Emission Spectrometer (model Spectro Ciros CCD-ICP). The certified reference material Montana Soil (NIST-2711) was analyzed to verify the completeness of elemental recovery. Subsamples dried at 105 °C were used for moisture correction.

Statistical analyses

To assess the effect of N fertilization on nutrient cation mobilization through the soil profile and over time (**H1**), soil solution data were analyzed in three ways. First, we calculated average “fertilization effect” ratios for pre-fertilization time points, years 1–2, and years 4–5 using $\log(\text{fertilization}:\text{control})$ for paired plots at each depth. Using this ratio, values significantly >0 signify a positive fertilization effect, which was assessed for each data point. The magnitude of the fertilization effect was then compared across the three time points, across soil depths, and between the two forests using ANOVA.

Second, for a more comprehensive analysis of the extensive temporal data collected, we analyzed repeated measures of each solute using repeated measures multivariate analysis of variance (MANOVA), including all biannual time points. For this analysis, pre-treatment solute values were averaged to obtain one starting level (i.e., $t = 0$) for each plot. Each chemical solute was assessed as a response factor, and predictive factors included time, forest type, soil depth, fertilization treatment, and all interactions. Where there were significant interactions, post hoc analyses were conducted to assess differences among treatments, forest types, and/or depths using ANOVA or paired t-tests were appropriate to take advantage of the paired-plot design. Dissolved N species and solution pH were also tested as direct predictors of cation concentrations using multiple regressions across all data for individual lysimeters.

Third, to confirm that pre-existing biases between control and fertilized plots were not driving our

results, we assessed temporal shifts within fertilized plots for pre-treatment versus post-treatment data (years 4–5) using paired t-tests. We conducted a similar comparison for control plots to assess background temporal trends in soil solution chemistry.

Finally, to assess the fertilization effect on soil cation availability (**H2**), we conducted ANOVA for salt-extractable nutrients for years 4–5 using forest type, depth, and treatment as factors. We performed similar analyses on pre-treatment extraction chemistry to assess pre-existing biases among plots. Acid-digestible total nutrients were assessed similarly to compare total nutrient status among sites.

For all analyses, biannual time point data were calculated as averages of all collections during that 6-month period, and included 1–10 measurements (variability due to precipitation and soil water availability), resulting in three pre-fertilization and seven post-fertilization biannual time points. Analyses were performed using 10.0.0 JMP software (SAS Institute Inc. 2015). Data were averaged by plot ($n = 3$), and were log transformed where necessary to meet assumptions of normality. Statistical significance was determined as $p < 0.05$, and trends are reported as $p < 0.1$. Data are reported as the mean \pm one standard error.

Results

Fertilization effects on dissolved nitrogen in soil solution

Fertilization effect ratios for dissolved N species were significantly different from zero in both forests by years 1–2, except NH_4^+ which was not significantly different from zero in the upper elevation forest until years 4–5. The magnitude of the fertilization effect also increased significantly over time in both forests, with larger fertilization effect ratios in years 4–5 versus years 1–2 for nearly all N solutes (Fig. 1). Comparing different chemical species of N, the fertilization effect was significantly larger for NO_3^- than for NH_4^+ or TDN (Fig. 1). For example, for years 4–5 at the 5 cm depth, average TDN increased up to 190 \times in fertilized versus control plots for the lower elevation forest, and 90 \times in the upper elevation forest (Table 1a). At the same time, NO_3^- was 415 \times higher in fertilized versus control plots for the lower elevation

forest, and 64 \times higher for the upper elevation forest (Table 1a). There was no difference in the magnitude of the fertilization effect between the two forest types or across depths.

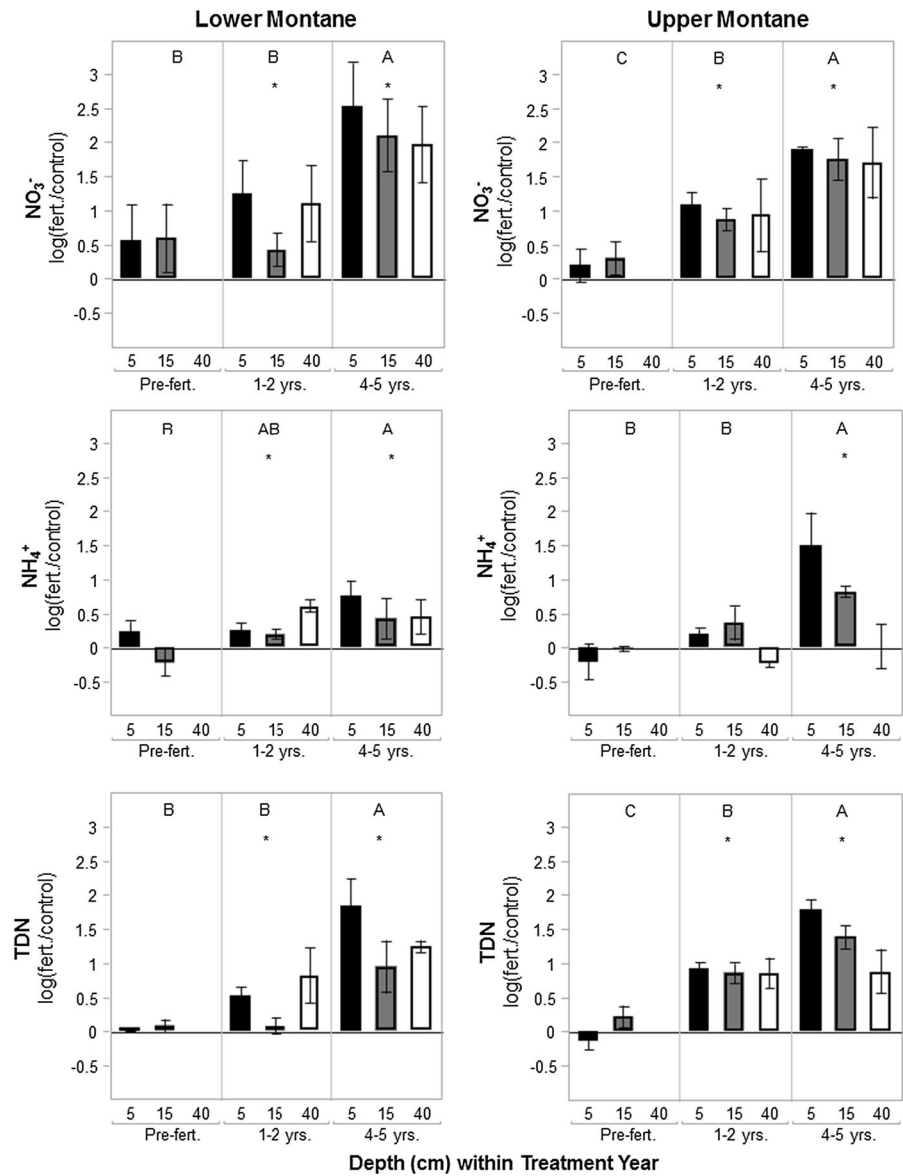
Results from repeated measures MANOVA showed that N fertilization and time were significant predictors of all N solutes across sampling points, with concentrations of TDN, NO_3^- , NH_4^+ , and DON elevated in fertilized plots and increasing over time (Fig. 2; Table 2). Forest type was a significant factor in analysis of TDN, NO_3^- , NH_4^+ , and DON, with higher background values in the upper versus lower elevation forest (Fig. 2).

All MANOVA showed significant two-, three- and/or four-way interactions among time, forest type, depth, and/or fertilization treatment (Table 2). These types of interactions are common in repeated measures analyses, and do not detract from the overall significance of the main effects (i.e., fertilization treatment). The most common significant interactions included time, because differences among treatments or depths invariably were not significant for some time points. Three-way interactions with forest type results when fertilized plots were significantly different in only one forest type for a given time period. An interaction between depth and fertilization treatment was also common, because there were significant declines with depth in control plots of both forests for TDN, DON, NH_4^+ , and NO_3^- , but no declines with depth in fertilized plots (Fig. 2; Table 1a). Thus, fertilization appears to have both increased N solute levels, and overwhelmed background depth gradients.

Comparing pre-fertilization data with years 4–5 within fertilized plots, all N solutes increased significantly in both forest types following fertilization (Table 1a). For example, TDN increased $\sim 120\times$ in the lower elevation forest and $\sim 50\times$ in the upper elevation forest, whereas other forms of N increased by factors of 3–15 \times (Table 1a).

In addition to temporal variability at the biannual scale (Fig. 2), there was substantial fine-scale spatial and temporal variability in solute chemistry. For example, individual lysimeters in fertilized plots showed increasing variability over the course of the experiment, whereas lysimeters in control plots maintained similar levels of variability (Fig. 3). Also, there were no short-term directional shifts during the early months of the experiment, confirming the lack of an artefact effect of initial lysimeter

Fig. 1 Fertilization effect ratios are shown for dissolved N levels for a lower and an upper elevation tropical forest. Capital letters show temporal shifts from pre- to post-fertilization sampling dates using Tukey HSD test ($p < 0.05$). Asterisk signifies an overall significant fertilization effect for a given time point (difference from 0). The magnitude of the fertilization effect was not significantly different between the two forest types for any dissolved N species, and there was no significant effect of soil depth



insertion (Fig. 3). Very high variability was particularly apparent for NH₄⁺ in the upper elevation forest during years 4–5 of the experiment (Table 1a). This reflected occasionally very high NH₄⁺ values that occurred in three different lysimeters on 7 different collection dates across the three fertilization plots in this forest type. Despite this significant short-term and small-scale variability, the broader

trends of increasing fertilization effect over time were still apparent for individual lysimeters.

Fertilization effects on nutrient cations in soil solution

Similar to results for dissolved N, a significant fertilization effect was quickly apparent by years 1–2

Table 1 Soil solution chemistry is shown for N fertilized (Fert.) and control (Cont.) plots in two tropical forest types at a lower elevation and an upper elevation site**1(a)**

Forest Type	Depth cm	Year of Fert.	Fert Trt	TDN mg N/L ^{A, B, C}	DON mg N/L ^{A, B}	NO ₃ ⁻ mg N/L ^{A, B}	NH ₄ ⁺ μg N/L ^{A, B, C}
Lower Elev.	5	Pre	Cont.	^{E, f, g} 0.26 ± 0.05	^{f, h} 0.21 ± 0.05	^{E, f, h} 0.03 ± 0.02	^{D, g} 37.6 ± 6.6
			Fert.	0.28 ± 0.04	0.19 ± 0.04	0.04 ± 0.02	54.4 ± 1.4
		1-2	Cont.	0.34 ± 0.11	0.20 ± 0.06	0.22 ± 0.07	47.5 ± 8.4
			Fert.	1.1 ± 0.21	0.18 ± 0.01	1.14 ± 0.10	127 ± 61.7
		4-5	Cont.	0.19 ± 0.05	0.07 ± 0.01	0.1 ± 0.03	42.5 ± 22.4
			Fert.	36.3 ± 21.4	0.25 ± 0.07	41.5 ± 29.2	274 ± 125
	20	Pre	Cont.	0.17 ± 0.03	0.13 ± 0.01	0.02 ± 0.02	44.5 ± 2.9
			Fert.	0.18 ± 0.003	0.1 ± 0.01	0.1 ± 0.02	33.9 ± 13.2
		1-2	Cont.	0.29 ± 0.08	0.37 ± 0.18	0.32 ± 0.05	39.5 ± 4.4
			Fert.	0.33 ± 0.06	0.12 ± 0.04	0.23 ± 0.04	68.2 ± 2.5
		4-5	Cont.	0.24 ± 0.1	0.05 ± 0.01	0.1 ± 0.04	43.0 ± 15.1
			Fert.	3.6 ± 3.0	0.1 ± 0.08	4.7 ± 4.2	177 ± 99.7
40	1-2	Cont.	^{e, F} 0.22 ± 0.14	^f 0.08	^{e, f} 0.16 ± 0.14	^f 27.5 ± 11.3	
		Fert.	1.07 ± 0.36	0.10	0.92 ± 0.38	138 ± 84.3	
	4-5	Cont.	0.1 ± 0.03	0.03 ± 0.01	0.1 ± 0.04	13.7 ± 2.3	
		Fert.	2.1 ± 0.1	0.06 ± 0.01	1.4 ± 0.5	171 ± 87.1	
Upper Elev.	5	Pre	Cont.	^{E, f, g, H} 0.77 ± 0.05	^{e, H} 0.26 ± 0.07	^{E, F, G} 0.5 ± 0.1	^e 63.4 ± 12.6
			Fert.	0.89 ± 0.19	0.20 ± 0.03	0.8 ± 0.2	50.6 ± 17.8
		1-2	Cont.	0.39 ± 0.06	0.18 ± 0.01	0.23 ± 0.03	76.6 ± 10.3
			Fert.	4.72 ± 0.33	0.96 ± 0.41	3.81 ± 0.52	216 ± 62.7
		4-5	Cont.	0.46 ± 0.11	0.08 ± 0.01	0.2 ± 0.1	77.2 ± 36.0
			Fert.	42.5 ± 17.6	0.88 ± 0.48	12.7 ± 3.4	4803 ± 3651
	20	Pre	Cont.	^{e, F, G} 0.83 ± 0.3	^{F, G, H} 0.22 ± 0.04	^{e, F, G} 0.7 ± 0.3	^{e, f, g, h} 30.3 ± 2.7
			Fert.	1.7 ± 0.83	0.24 ± 0.07	1.5 ± 0.8	30.1 ± 2.1
		1-2	Cont.	0.35 ± 0.12	0.17 ± 0.07	0.33 ± 0.12	30.4 ± 2.1
			Fert.	3.08 ± 1.38	0.51 ± 0.25	2.89 ± 1.37	119 ± 46.9
		4-5	Cont.	0.22 ± 0.08	0.08 ± 0.03	0.1 ± 0.04	22.5 ± 4.7
			Fert.	6.0 ± 0.79	0.65 ± 0.09	4.7 ± 0.5	310 ± 113
40	1-2	Cont.	^e 0.34 ± 0.13	0.18 ± 0.06	^e 0.77 ± 0.69	34.1 ± 8.8	
		Fert.	2.49 ± 0.80	0.72 ± 0.49	2.21 ± 0.66	20.1 ± 4.5	
	4-5	Cont.	0.29 ± 0.13	0.08 ± 0.01	0.1 ± 0.1	36.5 ± 3.9	
		Fert.	3.4 ± 2.4	1.39 ± 1.24	2.8 ± 2.0	49.0 ± 27.7	

Table 1 continued

1(b)

Forest Type	Depth cm	Year of Fert.	Fert Trt	Ca ²⁺ mg Ca/L ^{A, B}	Mg ²⁺ mg Mg/L ^{A, C}	Na ⁺ mg Na/L	K ⁺ mg K/L ^A	Cl ⁻ mg Cl/L	SO ₄ ²⁻ mg S/L ^{A, B}	PO ₄ ³⁻ μg P/L ^B		
Lower Elev.	5	Pre	Cont.	^{E, f, g, H} 0.7 ± 0.1	^{f, g} 1.0 ± 0.3	^{f, H} 5.9 ± 0.9	0.2 ± 0.02	^h 10.8 ± 2.0	^g 0.4 ± 0.1	3.5 ± 2.1		
			Fert.	1.3 ± 0.5	0.8 ± 0.3	5.3 ± 1.2	0.1 ± 0.03	7.9 ± 3.8	0.8 ± 0.3	3.8 ± 1.6		
		1-2	Cont.	0.6 ± 0.1	1.2 ± 0.3	6.8 ± 1.4	0.3 ± 0.1	13.0 ± 3.2	0.3 ± 0.01	1.8 ± 0.1		
			Fert.	2.1 ± 0.5	1.2 ± 0.2	5.4 ± 1.0	0.2 ± 0.03	9.6 ± 3.3	0.5 ± 0.2	2.8 ± 0.7		
		4-5	Cont.	0.4 ± 0.1	0.6 ± 0.1	3.9 ± 0.3	0.2 ± 0.2	7.0 ± 0.3	0.5 ± 0.1	5.0 ± 0.7		
			Fert.	11.7 ± 5.0	4.8 ± 1.8	5.3 ± 0.8	1.0 ± 0.8	4.8 ± 1.4	0.4 ± 0.2	3.5 ± 1.9		
	20	Pre	Cont.	^{f, h} 0.7 ± 0.2	^{D, h} 1.1 ± 0.2	^H 6.0 ± 0.8	0.2 ± 0.03	^h 11.2 ± 2.6	0.4 ± 0.1	9.3 ± 6.3		
			Fert.	1.0 ± 0.2	0.9 ± 0.1	4.5 ± 0.7	0.3 ± 0.2	6.3 ± 2.8	0.7 ± 0.4	2.0 ± 0.1		
		1-2	Cont.	0.7 ± 0.3	0.9 ± 0.2	5.6 ± 0.6	0.2 ± 0.03	10.0 ± 2.3	0.5 ± 0.1	2.2 ± 0.4		
			Fert.	1.1 ± 0.05	1.2 ± 0.3	6.4 ± 2.2	0.3 ± 0.1	11.6 ± 6.5	0.5 ± 0.3	2.8 ± 0.9		
		4-5	Cont.	0.4 ± 0.2	0.6 ± 0.1	4.0 ± 0.3	0.1 ± 0.1	7.0 ± 1.1	0.2 ± 0.1	2.8 ± 2.0		
			Fert.	2.4 ± 0.8	2.6 ± 1.7	6.2 ± 1.9	0.3 ± 0.1	7.1 ± 1.7	0.3 ± 0.1	5.8 ± 2.8		
	40	1-2	Cont.	^{e, F} 0.4 ± 0.1	^F 0.7 ± 0.2	5.8 ± 1.0	^{e, F} 0.6 ± 0.1	8.7 ± 1.8	^e 0.2 ± 0.1	1.8 ± 0.8		
			Fert.	1.4 ± 0.4	1.2 ± 0.3	5.4 ± 0.9	0.8 ± 0.1	7.9 ± 1.5	0.4 ± 0.1	4.0 ± 1.9		
		4-5	Cont.	0.3 ± 0.2	0.7 ± 0.2	4.8 ± 0.5	0.1 ± 0.04	7.9 ± 0.6	0.2 ± 0.1	4.3 ± 1.7		
			Fert.	1.7 ± 0.5	1.4 ± 0.1	4.4 ± 0.7	0.4 ± 0.1	6.6 ± 1.3	0.5 ± 0.1	4.3 ± 1.7		
		Upper Elev.	5	Pre	Cont.	^{c, h} 0.3 ± 0.1	^{d, e, f, g, h} 0.7 ± 0.1	3.9 ± 0.1	0.2 ± 0.02	6.3 ± 0.3	^{D, g, h} 0.6 ± 0.02	1.3 ± 0.1
					Fert.	0.9 ± 0.3	0.9 ± 0.1	4.2 ± 0.2	0.3 ± 0.3	7.1 ± 0.6	0.8 ± 0.1	1.7 ± 0.1
1-2	Cont.			0.2 ± 0.01	0.7 ± 0.01	4.9 ± 0.2	0.2 ± 0.04	9.7 ± 0.4	0.4 ± 0.1	1.3 ± 0.1		
	Fert.			1.7 ± 0.6	1.9 ± 0.4	6.2 ± 0.5	0.7 ± 0.5	9.5 ± 1.1	0.6 ± 0.1	1.6 ± 0.2		
4-5	Cont.			0.2 ± 0.03	0.6 ± 0.1	3.0 ± 0.3	0.1 ± 0.1	6.0 ± 0.5	0.7 ± 0.04	1.8 ± 0.6		
	Fert.			3.8 ± 2.8	2.3 ± 0.7	4.6 ± 0.4	0.5 ± 0.1	6.3 ± 1.4	0.7 ± 0.1	2.1 ± 0.2		
20	Pre		Cont.	^h 0.4 ± 0.1	^{e, f, g, H} 0.6 ± 0.1	3.4 ± 0.6	0.1 ± 0.02	6.2 ± 1.1	^{e, D, G} 0.7 ± 0.1	^G 1.3 ± 0.2		
			Fert.	0.5 ± 0.1	0.7 ± 0.1	3.8 ± 0.3	0.4 ± 0.3	6.9 ± 0.5	0.9 ± 0.1	1.1 ± 0.1		
	1-2		Cont.	0.2 ± 0.02	0.6 ± 0.2	4.1 ± 0.9	0.1 ± 0.02	9.0 ± 1.4	0.4 ± 0.03	1.7 ± 0.1		
			Fert.	0.6 ± 0.2	1.1 ± 0.2	5.3 ± 0.6	0.5 ± 0.4	8.4 ± 1.4	0.6 ± 0.1	1.7 ± 0.6		
	4-5		Cont.	0.2 ± 0.04	0.5 ± 0.1	3.7 ± 0.4	0.2 ± 0.1	7.7 ± 0.7	0.5 ± 0.1	3.4 ± 1.4		
			Fert.	1.9 ± 1.5	1.3 ± 0.3	3.8 ± 0.4	0.2 ± 0.1	5.9 ± 1.2	0.6 ± 0.1	2.5 ± 0.3		
40	1-2	Cont.	0.6 ± 0.3	^{e, f} 0.6 ± 0.1	3.4 ± 0.4	0.2 ± 0.03	6.4 ± 0.5	0.5 ± 0.1	1.8 ± 0.2			
		Fert.	0.7 ± 0.1	0.9 ± 0.1	4.4 ± 1.6	0.3 ± 0.1	7.2 ± 1.5	1.1 ± 0.4	1.4 ± 0.3			
	4-5	Cont.	0.6 ± 0.5	0.5 ± 0.2	3.7 ± 0.2	0.1 ± 0.01	7.3 ± 0.6	0.6 ± 0.1	1.8 ± 0.1			
		Fert.	1.1 ± 0.3	0.8 ± 0.2	5.0 ± 0.6	0.1 ± 0.04	8.2 ± 0.4	1.0 ± 0.4	2.5 ± 0.4			

Average values are shown for three distinct sampling time periods: (1) prior to the onset of fertilization, (2) during years 1–2 of the experiment, and (3) during years 4–5 of the experiment. Values for fertilized plots are bolded for ease of comparison. Letters in column headings give overall significant effects over time (i.e. repeated measures) of N fertilization treatment, forest type, and depths (A–C). Letters within boxes of data grouped by depth give significant differences between control and fertilized plots for specific time points (D–F), or differences for pre-treatment versus post-treatment time points within fertilization plots (G–H). Upper case letters denote p < 0.05, lower case denote p < 0.1. Mean ± one standard error are shown (n = 3)

^A Overall significant effect of fertilization for post-treatment measures using ANOVA

^B Overall significant effect of forest type using ANOVA

^C Overall significant effect of depth using ANOVA

^{D, d} Significant difference between control versus fertilized plot averages pre-fertilization treatment (i.e. pre-existing trend)

^{E, e} Significant difference between control versus fertilized plot averages for years 1-2 post-treatment (e.g. treatment effect)

^{F, f} Significant difference between control versus fertilized plot averages for years 4-5 post-treatment (e.g. treatment effect)

^{G, g} Significant difference in fertilized plots for pre-fertilization versus 4-5 year time point (e.g. change in treatment plots after onset of fertilization)

^{H, h} Significant difference in control plots for pre-fertilization versus 4-5 year time point (i.e., background temporal trend in control plots)

for most base cations (Fig. 4). The magnitude of the fertilization effect on cation concentrations increased over time, with the largest effect during years 4–5 for most cations (Fig. 4). Only dissolved K^+ appeared to peak in the years immediately following fertilization in the upper elevation forest, with a diminishing fertilization effect by years 4–5 (Table 1b). These results support our first hypothesis that N fertilization would positively affect cation mobilization, with an increased effect over time. We also saw no effect of soil depth on the magnitude of the fertilization effect, which supports our prediction that cation mobilization would promote leaching through the soil profile. We did not see a significant difference in the magnitude of the fertilization effect between the two forest types.

Comparing different cations, the magnitude of the fertilization effect on Ca^{2+} mobilization was significantly larger than for Mg^{2+} or summed base cations [$Ca^{2+} + Mg^{2+} + K^+$] (Fig. 4). For example, Mg^{2+} concentrations were 5–10 \times higher in fertilized versus control plots, whereas Ca^{2+} concentrations were 30 \times higher in fertilized versus control plots for the lower elevation forest (Table 1b).

Results from repeated measures MANOVA confirm that N fertilization and time were significant factors for predicting biannual averages of Ca^{2+} , Mg^{2+} (Fig. 5; Table 2), and K^+ in soil solution (Table 1b). Forest type was a significant factor in analysis of Ca^{2+} , PO_4^{3-} , and SO_4^{2-} , with greater background SO_4^{2-} in the upper elevation forest, and greater Ca^{2+} and PO_4^{3-} in the lower elevation forest (Table 1b). Similar to results for dissolved N, all MANOVA analyses of cations had significant two-, three- and/or four-way interactions among time, forest type, depth, and/or fertilization treatment (Table 2). However, background depth profiles were less apparent for individual cations, so interactions between fertilization treatment and depth were not as common. Among cations and anions, only Mg^{2+} declined significantly with depth overall (Table 1b). Thus, N fertilization increased cation concentrations relatively evenly across the three depths.

Comparing pre-fertilization data with years 4–5 within fertilized plots, Mg^{2+} and Ca^{2+} increased significantly in both forest types following fertilization, with 3–10 \times increases across both forests (Table 1b).

Strong small-scale variability in dissolved cation concentrations at the individual lysimeter scale were

Fig. 2 Dissolved N levels are shown in soil solution for two tropical forests at three depths in control (*black*) and fertilized (*white*) plots. Data are shown for **a** total dissolved N (TDN), **b** total organic N (DON), **c** nitrate (NO_3^-), and **d** ammonium (NH_4^+). An increasing fertilization effect over time is apparent, as well as background declines for all N concentrations. Note different scales for the two forest types in B, C and D. Each point represents averaged biannual data (mean \pm standard error, $n = 3$ plots) for 2 years prior to fertilization (points –3 to 0), 2 years immediately post fertilization (points 1–4), and for years four and five (points 8–10)

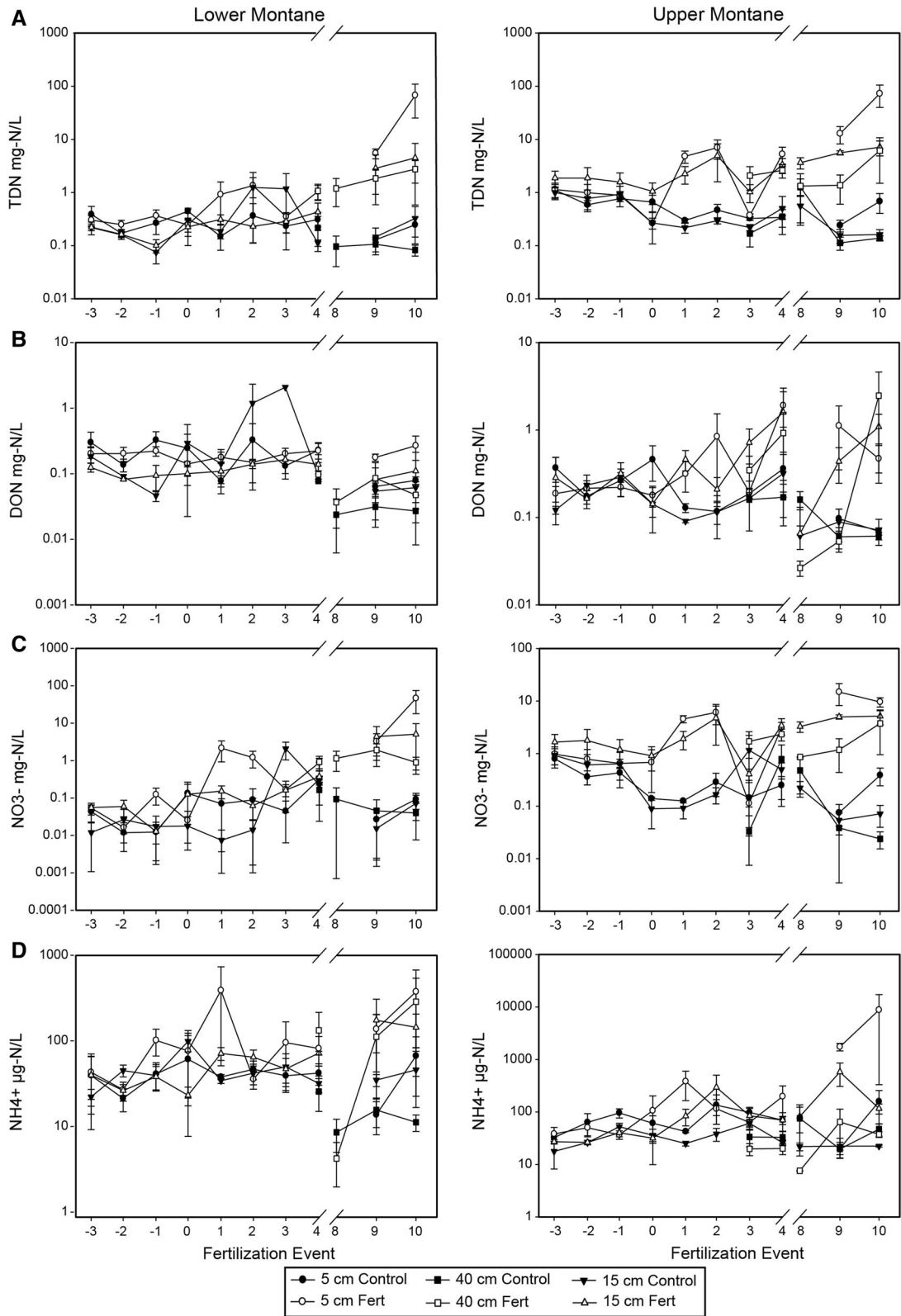
very similar to those for dissolved N, and tended to mirror N variability within a given lysimeter (Fig. 3).

Relationships among N, pH, and cations in solution

There were significant correlations among dissolved N species, cations, and solution pH. Across forest types and depths, NO_3^- was the strongest single predictor of Ca^{2+} and Mg^{2+} ($R^2 = 0.53$ and 0.49 respectively, $n = 1303$), and weakly but significantly correlated with K^+ concentrations ($R^2 = 0.18$, $n = 1303$). Soil TDN, DON, NO_3^- , NH_4^+ , and SO_4^{2-} were negatively correlated with soil solution pH ($R^2 = 0.22$, 0.25 , 0.14 , 0.29 , and 0.21 , respectively, $n = 36$), whereas PO_4^{3-} was positively correlated with solution pH ($R^2 = 0.21$, $n = 34$). Soil solution pH varied significantly between forest types during years 4–5 of the experiment, with a significant interaction between forest type and fertilization treatment, and no difference by depth (Table 3). Depth-averaged soil solution pH was significantly lower in fertilized versus control plots for the upper elevation forest (4.1 ± 0.1 vs. 4.5 ± 0.1 , respectively), but there was no significant effect on pH in the lower elevation forest (4.7 ± 0.1 control, vs. 4.9 ± 0.3 fertilized).

Background trends for soil solutes

In addition to the significant fertilization effects on N solutes and cation mobilization, there were long-term background trends in soil solution chemistry. Control plots showed significant declines over the 7-year study period for concentrations of TDN, DON, NO_3^- , Mg^{2+} , Ca^{2+} , Na^+ , Cl^- , and SO_4^{2-} in both forest types for multiple depths (Table 1a, b), indicating that background conditions were not at



steady state. For example, dissolved N species within control plots declined by factors of 0.2–3× from pre-fertilization to years 4–5 of the experiment, and background Ca^{2+} and Mg^{2+} declined 0.3–2× (Table 1b). Thus, the fertilization effect reported here is not an effect over a steady baseline, but rather occurred in non-steady-state conditions. Accordingly, there were more significant differences in solute levels for control versus fertilized plots by years 4–5, than there were significant fertilization effects over time within plots.

Soil exchangeable ions and total nutrients

Exchangeable ions, CECe and soil pH showed significant effects of nitrogen fertilization and forest type for post-treatment 2006 soils, with few effects of soil depth to 40 cm. As expected, N fertilization had a significant positive effect on NH_4^+ , and a marginal positive effect on extractable NO_3^- ($p = 0.07$, Table 4). Surprisingly, N fertilization also had a significant positive effect on salt-extractable Ca^{2+} , K^+ , Mn^{2+} , Cl^- and CECe (Table 5). This does not support H2, nor our prediction that NH_4^+ sorption would displace and therefore decrease exchangeable nutrient cations. Forest type was a significant factor for most exchangeable ions, with greater levels of CECe, pH, Ca^{2+} , K^+ , Mg^{2+} , Mn^{2+} , and Cl^- in the lower elevation forest; the upper elevation forest had significantly higher levels of Al, Fe, and Bray P (Table 5). Several extractable ions declined significantly with depth across forest types and fertilization treatments, including K^+ , Na^+ , Fe, Zn^{2+} , and Cl^- (Table 5). There were no significant interactions among factors for any of these analyses.

Similar measures for exchangeable nutrient using 2002 soils showed no significant pre-treatment biases for cations between fertilization and control plots in either forest, although there was higher CECe and SO_4^{2-} in fertilization plots (see Appendix Table 6). Pre-treatment exchangeable ions were significantly different between the two forest types, with higher levels of CECe, exchangeable Ca^{2+} , Mg^{2+} , K^+ , and Na^+ in the lower elevation forest, and higher levels of Fe in the upper elevation forest (see Appendix Table 6).

Total acid-digestible soil nutrient levels for 2006 were generally significantly greater for the lower elevation forest versus the upper elevation forest (Table 4). There were no differences for fertilized versus control plots in either forest except for total P, which was higher in fertilized plots.

Discussion

Our results support the hypothesis that N addition to N-rich tropical soils rapidly increases cation mobilization into soil solution. We saw particularly strong responses for Ca^{2+} and Mg^{2+} , followed by K^+ . If nutrients are lost, N additions may ultimately negatively affect plant growth, as has been observed in boreal and temperate forests (Lucas et al. 2011). In contrast, plant uptake and retention of newly mobilized nutrients could stimulate plant growth and increase cation cycling rates, at least in the short term, if these nutrients are limiting. A previous study at these sites found significant declines in fine root biomass from 0 to 10 cm (Cusack et al. 2011), which suggests a response to increased nutrient availability. However, this previous study found no increase in plant productivity with N fertilization, indicating that any possible alleviation of cation scarcity was not sufficient to increase plant growth. At the same time, the consistent fertilization effect we observed across depths to 40 cm is suggestive of downward leaching and ultimately cation losses, since the majority of fine roots in these forests are in the top 20 cm of soil (Lugo 1992). Thus, it seems that root uptake of base cations in surface soils was not sufficient to retain newly mobilized cations.

In addition to cation mobilization, we saw a surprising increase in soil extractable cations and CECe with N fertilization. This result, which was driven by increases in extractable Ca^{2+} and K^+ , was contrary to our second hypothesis that N fertilization would deplete exchangeable cations in soils. We did see increased soil extractable NH_4^+ with fertilization, which suggested active exchange of added N for other positively charged ions from soil surfaces, but this did not translate into cation depletion on exchange sites. Similar to our results, a study in three tropical southern

Table 2 Results for repeated measures MANOVA tests are presented for each solute. Factors in each analysis included fertilization treatment (fert), forest type (for), and soil depth (depth)

Parameter F (p value)	TDN	DON	NO ₃ ⁻	NH ₄ ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	PO ₄ ³⁻
Fertilization	12.3 (<0.01)*	6.8 (0.02)*	2.5 (<0.01)*	2.6 (0.1)	8.4 (<0.01)*	12.6 (<0.01)*	2.7 (0.1)	0.3 (0.6)
Forest type	2.5 (0.1)	0.6 (0.4)	0.1 (0.2)	2.3 (0.1)	1.2 (0.3)	0.4 (0.5)	0.8 (0.4)	10.2 (<0.01)*
Soil depth	4.2 (0.06)	0.1 (0.8)	0.5 (0.02)*	1.2 (0.2)	2.2 (0.2)	6.8 (0.02)*	0.01 (0.9)	1.9 (0.1)
Time	16 (<0.01)*	3.5 (0.03)*	3.3 (0.03)*	5.0 (<0.01)*	31 (<0.01)*	7.6 (<0.01)*	6.2 (<0.01)*	2.0 (0.1)
Significant interactions	Fert × depth; time × fert	Fert × for; time × fert	Depth × fert; time × fert; time × for; time × fert × for; time × for × depth;	Time × fert; time × for; time × depth; time × fert × for × depth; time × fert × for; time × for × depth; time × depth × fert	Time × fert; time × for; time × depth; time × fert × for × depth; time × fert × for; time × for × depth; time × depth × fert	Time × fert; time × depth; time × fert × for	Time × for; time × depth	Time × for
Overall model Wilks' lambda (p)	0.001 (<0.01)*	0.02 (0.02)*	0.002 (<0.01)*	0.005 (<0.01)*	0.003 (<0.01)*	0.004 (<0.01)*	0.1 (0.01)*	0.25 (0.05)*

Eight biannual time points were included as the repeated measure, with t = 0 calculated using average baseline data (i.e., pre-fertilization). F and p values are presented for each factor. All significant interactions are listed (p < 0.05). Wilks' Lambda and p values for each complete model are listed. Only solutes where the overall model was significant are shown

* Denotes significance of factors or overall tests (p < 0.05)

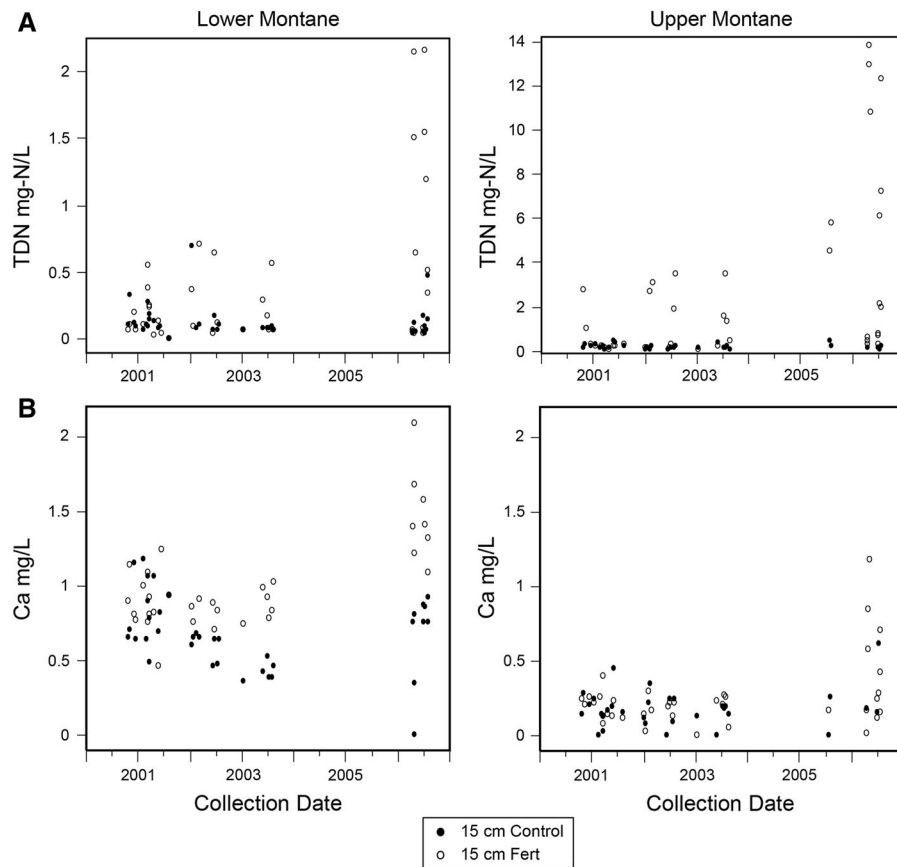


Fig. 3 Fine-scale temporal data are shown for **a** total dissolved N (TDN), and **b** calcium (Ca^{2+}) in representative lysimeters at 15 cm depth in a lower and an upper elevation tropical forest. Data prior to 2002 represent baseline data before the onset of an N fertilization treatment. Approximately 40 data points are shown for a single lysimeter in a fertilized plot (*open circles*) in

each forest, and a lysimeter in a paired control plot (*closed circles*). Data from both forest types show significant temporal variability at this scale. Nonetheless, these data exemplify the clear increasing trend over time for both TDN and Ca^{2+} in the fertilized versus control plots after the onset of fertilization (2002) in both tropical forest types

China forest types also found an overall positive effect of N fertilization on mobilized cations, soil extractable cations, and CECe after 6 years of fertilization (Lu et al. 2009, 2011). Unlike our results, soil extractable Al and Mn^{2+} had the most consistent positive responses to N fertilization in the Chinese study, while extractable Ca^{2+} and Mg^{2+} responses were more variable and tended to decline in a mature forest site. The authors suggested that elevated soil organic matter (SOM) pools with N fertilization were responsible for increased CECe, since SOM supplies cations to soils. At the Puerto Rico sites, N fertilization also increased SOM over

the first 5 years of the experiment, with the majority of added OM in the mineral-sorbed soil fraction (Cusack et al. 2011). An alternate explanation for the increase in available soil cations across these tropical studies is that N fertilization promoted weathering of soil minerals, leading to more exchangeable ions. This types of weathering effect on cation production was observed in a temperate forest with CO_2 fertilization, which increased carbonic acid in soil solution (Jackson et al. 2009; Oh et al. 2007). However, accelerated weathering requires significant increases in acidity, which we did not observe. Also, the amount of weatherable

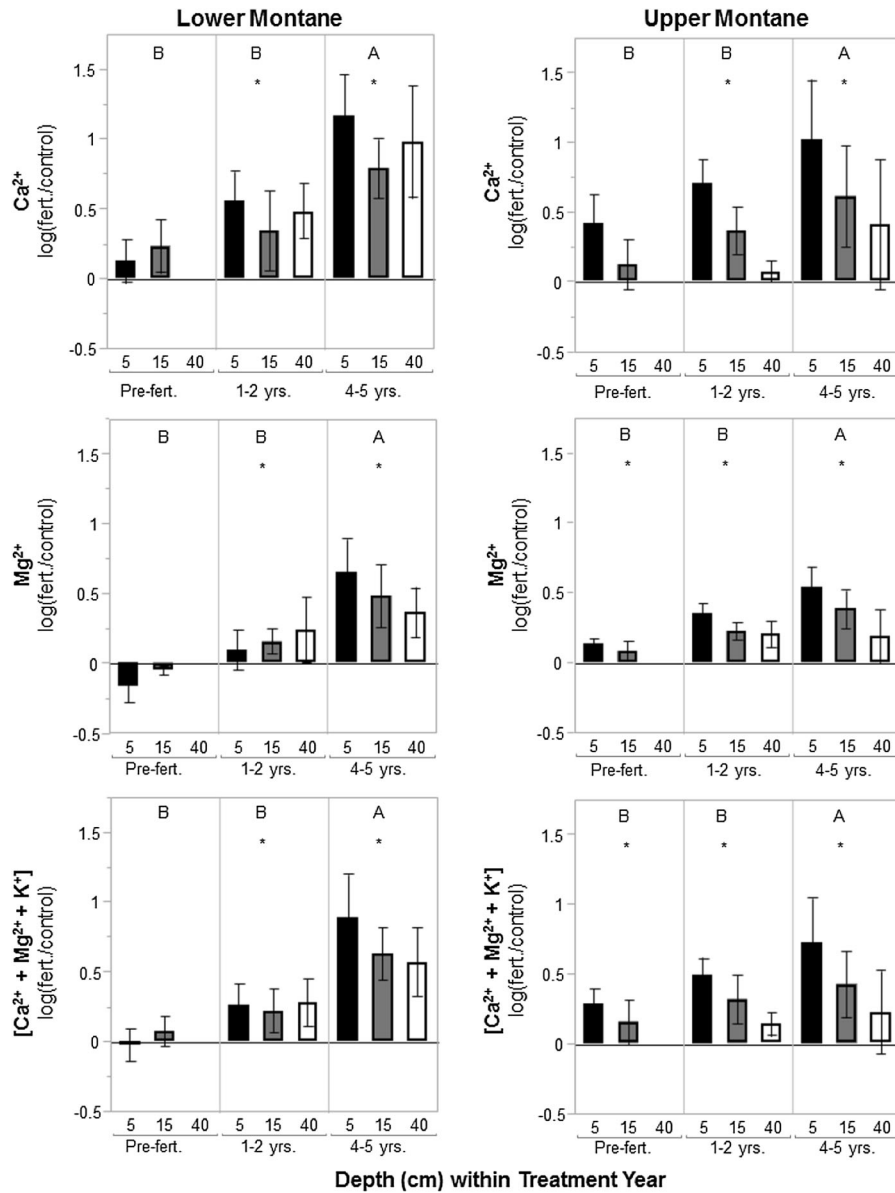


Fig. 4 Fertilization effect ratios are shown for dissolved cations for a lower and an upper elevation forest. Capital letters show significant temporal differences from pre- to post-fertilization sampling dates using Tukey HSD test ($p < 0.05$). Asterisk signifies an overall significant fertilization effect for a

given time point (different from 0, $p < 0.05$). The magnitude of the fertilization effect was not significantly different between the two forest types for base cations, and there was no significant difference by soil depth

minerals in surface soils at these Puerto Rican sites is minimal (Jones et al. 1982). Still, our measures of bulk soil pH were coarse-scale, and may have missed more subtle changes in organic acid dynamics, which can promote weathering (Jones et al.

2003). In summary, the increase in extractable soil cations observed in these Puerto Rican forests with N fertilization most likely resulted from previously documented increases in mineral-associated OM pools.

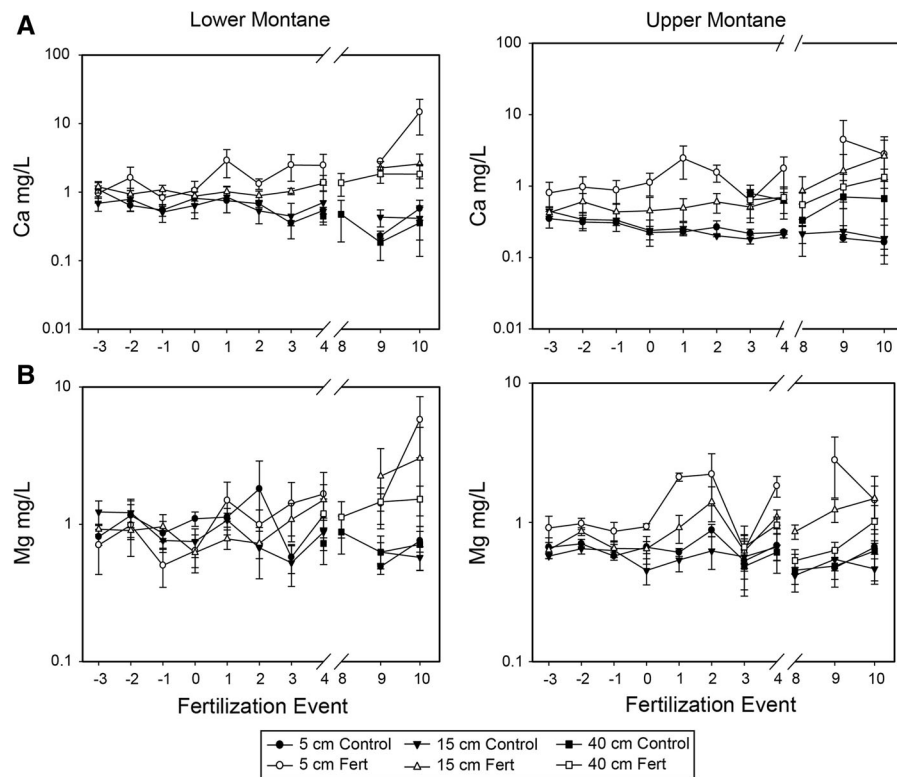


Fig. 5 Cation levels are shown in soil solution for two tropical forests at three depths in control (*black*) and fertilized (*white*) plots. Data are shown for **a** calcium (Ca^{2+}), and **b** magnesium (Mg^{2+}). An increasing fertilization effect over time is apparent, as well as background declines for all N concentrations. Each

point represents averaged biannual data (mean \pm standard error, $n = 3$ plots) for 2 years prior to fertilization (points -3 to 0), 2 years immediately post fertilization (points $1-4$), and for years four and five (points $8-10$)

Comparing different mineral N species, we observed much greater increases in solute NO_3^- versus NH_4^+ concentrations, and significant increases in soil exchangeable NH_4^+ but not in extractable NO_3^- . Together, the increase in soil exchangeable NH_4^+ and the increase in soil solution NO_3^- likely provide the main mechanism for cation mobilization through the soil profile. Added NH_4^+ appears to have exchanged with base cations on mineral surfaces, whereas NO_3^- remained in solution and leached down the soil profile with mobilized cations. A similar effect of NH_4^+ displacement of base cations on soil surfaces has been observed across 14 European forests with varying climates (Matschonat and Matzner 1996). Another mechanism for potential cation mobilization with N addition is the acidification effect described above, particularly with the high background nitrification rates at these sites, where nitrification accounts for the fate of $>50\%$ of NH_4^+ (Templer et al.

2008). Increased acidity was the apparent driver of cation mobilization with N fertilization in a humid tropical Panamanian forest on highly weathered soils (Turner et al. 2013). Again, we did not observe increased soil acidity, although soil solution acidity did increase in the upper elevation forest. Thus, it seems that direct exchange of NH_4^+ for cations on mineral surfaces is likely the dominant mechanism driving cation mobilization at these sites.

Comparing forest types, we expected the fertilization effect on cation mobilization to be greater in the forest with relatively higher background N levels. However, we did not see a difference in the magnitude of the fertilization effect on solution N or cations across these two humid tropical forests. Unlike our results, an N fertilization study in three subtropical forest types on highly weathered soils in China documented a greater effect of N fertilization

Table 3 Soil solution pH is given for years 4–5 in N fertilization (Fert.) and control (Cont.) plots for a lower elevation and an upper elevation tropical forest across three depths

Forest type	Depth (cm)	Fert. Trt. ^{A,B}	pH of soil solution
Lower Elev.	5	Cont.	4.9 ± 0.2
		Fert.	4.7 ± 0.3
	20	Cont.	4.4 ± 0.04
		Fert.	4.9 ± 0.3
	40	Cont.	4.9 ± 0.2
		Fert.	5.0 ± 0.1
Upper Elev.	5	Cont.	4.6 ± 0.1
		Fert.	3.9 ± 0.2
	20	Cont.	4.4 ± 0.1
		Fert.	4.1 ± 0.1
	40	Cont.	4.5 ± 0.2
		Fert.	4.2 ± 0.1

Mean ± one standard error are shown (n = 3, p < 0.05)

^A Significant interaction between N fertilization and forest type (N fertilization significant in upper elevation forest only)

^B Significant effect of forest type

Table 4 Salt-extractable mineral N and acid-digestion “total” nutrient content for soils from 0 to 10 cm depth in N fertilization (Fert.) and control (Cont.) plots for a lower elevation and an upper elevation tropical forest year 5 of the experiment

Forest	Fertilization treatment	NH ₄ ⁺ (mg-N/kg) ^A	NO ₃ ⁻ (mg-N/kg) ^a	Total Ca (mg/g) ^B	Total Mg (mg/g) ^B	Total Na (mg/g) ^B	Total K (mg/g) ^B	Total S (mg/g)	Total P (mg/g) ^B
Lower Elev.	Cont.	2.62 ± 0.43	0.26 ± 0.04	0.66 ± 0.08	0.96 ± 0.29	0.10 ± 0.02	0.24 ± 0.03	0.46 ± 0.10	0.38 ± 0.06
	Fert.	3.62 ± 0.75	1.13 ± 0.48	0.96 ± 0.28	2.27 ± 0.76	0.11 ± 0.01	0.48 ± 0.17	0.52 ± 0.05	0.54 ± 0.01
Upper Elev.	Cont.	1.92 ± 0.25	0.26 ± 0.05	0.19 ± 0.01	0.19 ± 0.02	0.06 ± 0.01	0.12 ± 0.01	0.32 ± 0.04	0.15 ± 0.02
	Fert.	3.12 ± 0.57	0.47 ± 0.18	0.21 ± 0.02	0.19 ± 0.03	0.06 ± 0.01	0.12 ± 0.02	0.39 ± 0.09	0.17 ± 0.03

^{A, a} Significant effect of N fertilization

^B Significant effect of forest type

Letters show significant effects of N fertilization treatment, forest type, and/or soil depths across repeated measures (A-C in column headings, n = 3, p < 0.05). Upper case letters denote p < 0.05, lower case denote p < 0.1. Mean ± one standard error are shown

on cation mobilization in the forest with the highest background soil N (Lu et al. 2009). Here, however, differences in N availability between the two sites were not entirely clear. We found that soil solution dissolved N levels were greater in the upper elevation forests versus the lower elevation forest, while a previous study showed that bulk soil N concentrations were greater in the lower elevation forest. This discrepancy between bulk soil N and dissolved N in solution may be related to soil hydrology at the two sites, with poorer drainage, higher clay content, and greater anaerobiosis at the lower elevation forest (McDowell et al. 1992), which could have retained more of the added N in shallow

soil solution (Lohse and Matson 2005), and promoted greater off-gassing of dissolved N in anaerobic conditions (Liptzin et al. 2011). Despite these differences in soil N dynamics and other ecosystem characteristics, both of these humid tropical forests responded to N fertilization with similar timing and magnitude.

Finally, we observed significant background declines in soil solutes over the six-year study period for most dissolved N species and cations. The background trend may reflect long-term recovery from tropical storm disturbances. For example, immediately following Hurricane Hugo in 1989 stream water N and K⁺ concentrations increased and then took up to

Table 5 Extractable ions, pH and CECe are given for year 5 in N fertilization (Fert.) and control (Cont.) plots for a lower elevation and an upper elevation tropical forest across three depths

Forest Elev.	Depth (cm)	Fert Trt	CECe (cmol +/ kg) ^{A,B}	pH ^B	Ca ²⁺ (mg/kg) ^{A,B}	Mg ²⁺ (mg/kg) ^B	Na ⁺ (mg/kg) ^{A,B,C}	K ⁺ (mg/kg) ^{A,B,C}	Al (mg/kg) ^B	Fe (mg/kg) ^{B,C}	Mn ²⁺ (mg/kg) ^B	Zn ²⁺ (mg/kg) ^C	Cl ⁻ (mg/kg) ^{A,B,C}	SO ₄ ²⁻ (mg/kg)	PO ₄ ³⁻ (mg/kg) ^B
Lower Elev.	0–10	Cont.	5.1 ± 1.6	5.1 ± 0.5	320 ± 169	217 ± 114	26 ± 6	85 ± 22	126 ± 35	22 ± 4	77 ± 66	1.2 ± 0.4	35 ± 11	6.6 ± 2.5	1.4 ± 0.3
	0–10	Fert.	8.1 ± 2.5	5.2 ± 0.3	778 ± 394	333 ± 139	33 ± 6	149 ± 37	84 ± 53	16 ± 7	227 ± 126	0.5 ± 0.03	47 ± 5	5.7 ± 1.5	1.0 ± 0.2
	10–20	Cont.	4.5 ± 1.8	4.9 ± 0.1	267 ± 192	187 ± 109	21 ± 5	63 ± 22	123 ± 15	15 ± 3	81 ± 74	0.8 ± 0.5	21 ± 5	4.7 ± 0.4	1.2 ± 0.3
	10–20	Fert.	6.9 ± 2.4	5.3 ± 0.3	673 ± 355	300 ± 143	28 ± 8	99 ± 28	63 ± 39	14 ± 6	182 ± 89	0.2 ± 0.1	49 ± 11	6.3 ± 1.5	1.0 ± 0.4
	20–30	Cont.	3.5 ± 1.3	4.8 ± 0.2	196 ± 152	140 ± 81	15 ± 3	50 ± 15	110 ± 14	8 ± 4	61 ± 57	0.8 ± 0.3	18 ± 4	5.2 ± 1.5	0.9 ± 0.2
	20–30	Fert.	6.3 ± 2.4	5.3 ± 0.2	607 ± 338	283 ± 124	23 ± 5	80 ± 31	55 ± 28	7 ± 3	189 ± 93	0.3 ± 0.1	20 ± 7	5.5 ± 2.4	0.9 ± 0.2
	30–40	Cont.	3.2 ± 1.1	5.0 ± 0.1	146 ± 101	134 ± 68	14 ± 2	44 ± 9	103 ± 26	12 ± 9	51 ± 48	0.3 ± 0.2	11 ± 4	4.4 ± 0.5	0.8 ± 0.1
	30–40	Fert.	5.9 ± 2.1	5.4 ± 0.3	495 ± 271	292 ± 131	22 ± 5	90 ± 37	64 ± 32	8 ± 2	193 ± 96	0.3 ± 0.1	20 ± 6	6.8 ± 3.2	0.7 ± 0.1
	0–10	Cont.	3.5 ± 0.8	4.4 ± 0.2	77 ± 34	41 ± 6	28 ± 9	55 ± 16	224 ± 75	111 ± 38	4 ± 0.8	1.0 ± 0.5	30 ± 11	9.2 ± 3.1	4.6 ± 3.5
	0–10	Fert.	3.6 ± 1.0	4.4 ± 0.3	76 ± 5	35 ± 6	27 ± 4	49 ± 17	244 ± 84	118 ± 52	4 ± 0.6	1.1 ± 0.5	31 ± 14	7.5 ± 3.0	2.4 ± 0.8
	10–20	Cont.	2.5 ± 0.6	4.5 ± 0.2	47 ± 18	23 ± 2	24 ± 7	35 ± 5	170 ± 56	100 ± 48	3 ± 0.9	0.5 ± 0.2	23 ± 8	7.1 ± 2.6	2.2 ± 1.0
	10–20	Fert.	2.6 ± 0.4	4.5 ± 0.2	39 ± 12	27 ± 6	18 ± 7	39 ± 10	184 ± 40	118 ± 68	4 ± 0.2	0.6 ± 0.2	28 ± 10	6.4 ± 2.3	1.6 ± 0.2
20–30	Cont.	1.7 ± 0.3	4.6 ± 0.2	27 ± 15	15 ± 3	10 ± 1	25 ± 2	116 ± 31	107 ± 43	3 ± 1.1	0.3 ± 0.1	14 ± 3	4.4 ± 1.5	1.7 ± 0.9	
20–30	Fert.	2.5 ± 0.1	4.5 ± 0.1	28 ± 12	20 ± 8	17 ± 10	26 ± 8	182 ± 6	62 ± 7	3 ± 0.7	0.3 ± 0.1	23 ± 13	5.9 ± 1.8	1.2 ± 0.4	
30–40	Cont.	1.6 ± 0.1	4.7 ± 0.1	20 ± 14	11 ± 2	7 ± 0.3	17 ± 4	117 ± 20	12 ± 4	1 ± 0.5	0.4 ± n.d.	7 ± 2	3.8 ± 1.8	1.5 ± 0.7	
30–40	Fert.	2.6 ± 0.9	4.6 ± 0.1	21 ± 13	15 ± 7	7 ± 2	16 ± 1	205 ± 70	22 ± 7	3 ± 0.6	0.3 ± 0.2	11 ± 4	5.9 ± 1.6	0.9 ± 0.3	

Letters show significant effects of N fertilization treatment, forest type, and/or soil depths across repeated measures (A–C in column headings). Mean ± one standard error are shown (n = 3, p < 0.05)

^A Significant effect of N fertilization

^B Significant effect of forest type

^C Significant effect of depth

2 years to return to pre-hurricane levels in the lower-elevation forest (Schaefer et al. 2000). The response trajectory was even more pronounced in high-elevation forest, with return of stream chemistry to baseline conditions taking about a decade (McDowell et al. 2013). Similarly, groundwater solutes at our lower elevation site spiked after the hurricane and gradually declined, with mineral N returning to pre-hurricane levels after 2 years, but most base cations and anions recovering after 3–5.5 years (McDowell et al. 1996). Aboveground nutrient storage in trees immediately declined post-Hugo and recovered within 5 years, but plant species richness and stem densities remained elevated at 15 years post-Hugo, suggesting ongoing longer-term successional processes (Heartsill-Scalley et al. 2010). Our study began 2 years after Hurricane Georges, and on the same year as several smaller storms. Thus, the background declines in soil solution N and base cations observed here were likely in response to those storms, and suggest non-steady state conditions in soil solution chemistry during the period of this study.

Regardless of background conditions and small-scale variability in soil solution nutrient dynamics, this study strongly indicates that we can expect to see rapid cation mobilization and downward leaching in tropical forests with increased N deposition. These results imply that N deposition in tropical forests on highly weathered soils may exacerbate cation scarcity in these ecosystems, and could negatively affect plant productivity over the longer term.

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Appendix

See Table 6.

Table 6 Extractable ions, pH and CECe for pre-treatment soils from 0 to 30 cm depth are shown in N fertilization (Fert.) and control (Cont.) plots for a lower elevation and an upper elevation tropical forest

Forest	Fert	CECe (cmol +/- kg) ^{A, B}	pH	Ca ²⁺ (mg/ kg) ^A	Mg ²⁺ (mg/kg) ^A	Na ⁺ (mg/ kg) ^A	K ⁺ (mg/ kg) ^A	Al (mg/ kg)	Fe (mg/ kg) ^A	Mn ²⁺ (mg/kg)	Zn ²⁺ (mg/kg)	Cl ⁻ (mg/ kg)	SO ₄ ²⁻ (mg/ kg) ^B	PO ₄ ³⁻ (mg/kg)
Lower	Control	4.8 ± 0.5	4.2 ± 0.1	177 ± 107	125 ± 58	43 ± 8	33 ± 6	235 ± 62	34 ± 15	134 ± 127	1.0 ± 0.6	33 ± 3	22 ± 4	4.4 ± 0.7
Elev.	Fert	7.0 ± 1.1	4.5 ± 0.2	579 ± 170	233 ± 90	55 ± 8	52 ± 11	151 ± 62	21 ± 16	298 ± 155	1.3 ± 0.3	37 ± 8	31 ± 2	6.1 ± 1.3
Upper	Control	3.1 ± 0.3	4.1 ± 0.02	76 ± 26	28 ± 6	21 ± 3	22 ± 2	202 ± 14	71 ± 9	5 ± 0.5	0.4 ± 0.1	23 ± 6	20 ± 2	4.4 ± 0.3
Elev.	Fert	3.9 ± 0.5	4.0 ± 0.1	87 ± 27	38 ± 9	24 ± 5	25 ± 6	269 ± 30	87 ± 15	8 ± 2.5	0.6 ± 0.2	25 ± 7	25 ± 4	6.7 ± 1.5

Letters show significant effect of forest type. There were no significant pre-treatment differences between control and fertilized plots. Mean ± one standard error are shown (n = 3, p < 0.05)

^A Significant effect of forest type

^B Significant pre-treatment difference between fertilization and control plots

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