Nitrogen deposition contributes to soil acidification in tropical ecosystems

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Abstract

Elevated anthropogenic nitrogen (N) deposition has greatly altered terrestrial ecosystem functioning, threatening ecosystem health via acidification and eutrophication in temperate and boreal forests across the northern hemisphere. However, response of forest soil acidification to N deposition has been less studied in humid tropics compared to other forest types. This study was designed to explore impacts of long-term N deposition on soil acidification processes in tropical forests. We have established a long-term N-deposition experiment in an N-rich lowland tropical forest of Southern China since 2002 with N addition as NH_4NO_3 of 0, 50, 100 and 150 kg N ha^{-1} yr^{-1}. We measured soil acidification status and element leaching in soil drainage solution after 6-year N addition. Results showed that our study site has been experiencing serious soil acidification and was quite acid-sensitive showing high acidification ($pH_{(H2O)}$<4.0), negative water-extracted acid neutralizing capacity (ANC) and low base saturation (BS,< 8%) throughout soil profiles. Long-term N addition significantly accelerated soil acidification, leading to depleted base cations and decreased BS, and further lowered ANC. However, N addition did not alter exchangeable Al^{3+}, but increased cation exchange capacity (CEC). Nitrogen addition-induced increase in SOC is suggested to contribute to both higher CEC and lower pH. We further found that increased N addition greatly decreased soil solution pH at 20 cm depth, but not at 40 cm. Furthermore, there was no evidence that Al^{3+} was leaching out from the deeper soils. These unique responses in tropical climate likely resulted from: exchangeable H^+ dominating changes of soil cation pool, an exhausted base cation pool, N-addition stimulating SOC production, and N saturation. Our results suggest that long-term N addition can contribute measurably to soil acidification, and that shortage of Ca and Mg should receive more attention than soil exchangeable Al in tropical forests with elevated N deposition in the future.

Keywords: acid neutralizing capacity, acidification, aluminum, calcium, cation exchange capacity, nitrogen addition, nitrogen deposition, nitrogen saturation, soil buffering capacity, tropical forest

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Introduction

Anthropogenic acid deposition, resulting from increased emissions of SO_2 from fossil-fuel combustion and NO_x from high-energy combustion and agricultural fertilization has greatly modified global biogeochemical cycles of nitrogen (N) and sulfur (S) (Vitousek *et al.*, 1997) and has resulted in acidification of the biosphere (Galloway, 2001; Bouwman *et al.*, 2002; Hicks *et al.*, 2008). Soil acidification has been recognized as a major environmental issue in many temperate and boreal regions (Likens *et al.*, 1996; Yang *et al.*, 2012), causing declines in terrestrial biodiversity (Bobbink *et al.*, 2010; Lu *et al.*, 2010; Chen *et al.*, 2013)and forest productivity (Högberg *et al.*, 2006), and threatening ecosys-

tem health (Bouwman *et al.*, 2002; Krupa, 2003; Burns *et al.*, 2008).

Although SO_2 emissions have declined across Europe and eastern North America since the 1990s (Oulehle *et al.*, 2011) and in China since 2005 (Fang *et al.*, 2013), the contribution of anthropogenic N to acid deposition has been an increasing concern, with human activities accelerating the globalization of N deposition, which increases at a mean global rate of 105 Tg N yr^{-1} (Galloway *et al.*, 2004; Dentener *et al.*, 2006). Currently, 11% of the world's natural vegetation receives N deposition in excess of 10 kg N ha^{-1} yr^{-1} (Dentener *et al.*, 2006; Pardo *et al.*, 2011). Continuous atmospheric N deposition to terrestrial ecosystems can lead to pronounced soil acidification (Van Breemen *et al.*, 1984), resulting in a net decrease in soil pH and acid neutralization capacity (ANC) of the soils (Larssen & Carmichael, 2000; Hédl *et al.*, 2011). Soils typically go through a transition of different buffering ranges during acidification

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accompanied by weathering and release of different elements (Ulrich, 1986; Bowman *et al.*, 2008). Although soils are buffered by bicarbonate in the pH range above 6.5, cation exchange between H^+ and base cations (Ca^{2+}, Mg^{2+}, K^+, and Na^+) is the main buffering mechanism for acid soils in the pH range 4.2–5.0. Once base cations have been exhausted, aluminum (Al) is mobilized from soils, with soil pH buffered by Al compounds at low pH (<4.2). These processes are well demonstrated in temperate regions, especially in Europe and North America (Krug & Frink, 1983; Boxman *et al.*, 2008; Gruba *et al.*, 2013), where atmospheric N deposition commonly exceeds the critical loads of ecosystems, leading to N saturation (Aber *et al.*, 1998; Fenn *et al.*, 2006; Thimonier *et al.*, 2010; Pardo *et al.*, 2011). Accordingly, acid deposition generally causes persistent declines in soil base cation pool (or base saturation, BS), leaching of sulfate and nitrate ions and Al, and acidification of soils and surface waters; meanwhile, elevated Al mobilization with its toxicity to soil biota is a common characteristic in acidified soil (Dise *et al.*, 2001; Edwards *et al.*, 2002; Driscoll *et al.*, 2003; Högberg *et al.*, 2006; Warby *et al.*, 2009).

Our understanding of how N deposition affects soil acidification is based largely on work in temperate ecosystems of the North Hemisphere (Aber *et al.*, 1998; Krusche *et al.*, 2003; Boxman *et al.*, 2008; Lu *et al.*, 2009). Comparable data are generally lacking for tropical regions, where soil acidification is typically recognized as a major pedogenetic process that occurs when precipitation exceeds evapotranspiration (von Uexkull & Mutert, 1995; Larssen *et al.*, 1999). Nitrogen cycling in tropical systems is different from those of temperate, because tropical forest ecosystems are often N-rich (or N-saturated), with high soil N availability, rapid rates of N cycling, and the lack of N limitation to NPP (Matson *et al.*, 1999; Wright *et al.*, 2011; Brookshire *et al.*, 2012). Thus, N deposition is less likely to increase primary productivity of tropical ecosystems, but may alter other aspects of the N cycle (Townsend *et al.*, 1996). Meanwhile, many tropical soils are poorly buffered against acid deposition because they are highly weathered with low base cation pools (Sollins *et al.*, 1988; Matson *et al.*, 1999). As a result, conclusions based on studies conducted in temperate regions are of little relevance for the tropics under elevated N deposition.

The purpose of this study was to experimentally test how long-term N deposition affects soil acidification process in a tropical forest. In 2002, we established long-term N deposition research plots in a typical N-rich lowland tropical mature forest at Dinghushan Biosphere Reserve of Southern China, where atmospheric N deposition rates are commonly above 19 kg N ha^{-1} yr^{-1} (Mo *et al.*, 2006; Lü & Tian, 2007; Lu *et al.*,

2010, 2013). In fact, long-term records have shown a significant decrease in soil pH at this reserve over the past three decades (Fig. 1), but reasons remain unclear. Here, we hypothesize that: (i) tropical forests are vulnerable to excess inputs of N, with N additions decreasing soil buffering capacity and accelerating soil acidification; and (ii) because of their highly weathered nature, tropical forest soils will be more sensitive to N additions than those from temperate forests, as seen in changes in acidity of soil and soil solution, soil exchangeable cations, BS, CEC. and cation leaching dynamics.

Materials and methods

Study Site

We carried out our study at Dinghushan Biosphere Reserve (DBR), an UNESCO/MAB site located in the middle of Guangdong Province in southern China (112°10′ E, 23°10′ N). The reserve covers an area of 1155 ha within the subtropical/tropical moist forest life zone. The monsoon climate of this site averages 1927 mm precipitation per years with approximately 75% occurring between March and August, and 6% between December and February. Relative humidity averages 80% throughout the year. Mean annual temperature is 21.0 °C, ranging from mean coldest in January (12.6 °C) and hottest in July (28.0 °C). Dinghushan Biosphere Reserve has experienced high rates of atmospheric N deposition (21–38 kg N ha^{-1} yr^{-1} as inorganic N in bulk precipitation) since 1990's (Huang *et al.*, 1994; Lu *et al.*, 2013 and references there). In 2009–2010, total

$$Y = 54.42 - 0.025X$$
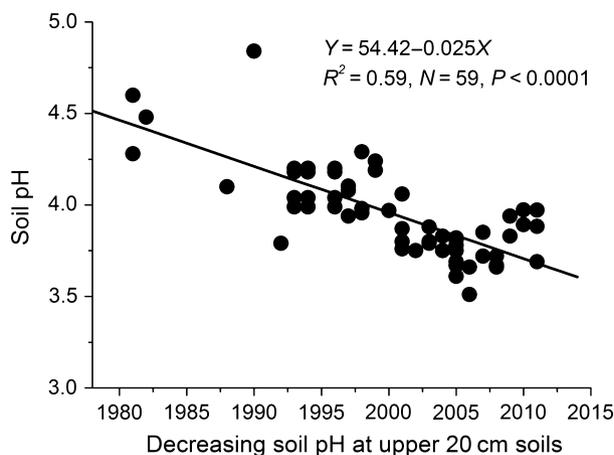$$R^2 = 0.59, N = 59, P < 0.0001$$

Fig. 1 Soil $pH_{(water)}$ changing trend at upper 20 cm soils during the last three decades in the lowland tropical forest (monsoon evergreen broadleaf forest) of Dinghushan Biosphere Reserve in Southern China. *Note*: The data set used here was compiled from the published papers, which focused on the same forest to this study. The upper 20 cm of the mineral soil (below the forest floor) was sampled. Method for determination of soil pH is the same as this study, using the national standard of China (GB7859-87). These published papers are listed in Data S2.

wet N deposition was 34.4 kg N ha^{-1} yr^{-1}, with 18.2 kg ha^{-1} dissolved inorganic N (7.7 kg ha^{-1} NO$_3^-$-N and 10.5 kg ha^{-1} NH$_4^+$-N, respectively) and 16.2 kg ha^{-1} dissolved organic N (calculated as differences between total dissolved N and dissolved inorganic N), respectively (Lu *et al.*, 2013); total wet S deposition was 32.6 kg S ha^{-1} yr^{-1}(2009 July–2010 June; Xiankai Lu, unpublished data).

We established the research site in the monsoon evergreen broadleaf forest in 2002 between 250 and 300 m above sea level. According to ^{14}C measurement, forest stands have been protected from direct human disturbance for >400 years (Shen *et al.*, 1999). These support a rich assemblage of plant species, most of which are evergreen tree species native to the tropics and subtropics. These include *Castanopsis chinensis* Hance, *Schima superba* Chardn. & Champ., *Cryptocarya chinensis* (Hance) Hemsl., *Cryptocarya concinna* Hance, *Machilus chinensis* (Champ. Ex Benth.) Hemsl., and *Syzygium rehderianum* Merr. & Perry. Canopy closure is typically above 95% (Lu *et al.*, 2010). Soils are oxisols (lateritic red earths) formed from sandstone approximately 30 to 70 cm in depth.

Experimental treatments

Nitrogen addition experiments were initiated in July 2003, with four N addition rates used: Control (0 N added), Low-N (50 kg N ha^{-1} yr^{-1}), Medium-N (100 kg N ha^{-1} yr^{-1}) and High-N (150 kg N ha^{-1} yr^{-1}). A buffer strip of at least 10-m width surrounded each of 12 10-m × 20-m plots, with plots and treatments replicated in triplicate and randomly located within the study area. Monthly applications of NH$_4$NO$_3$ solution were added by hand to the forest floor of these plots as 12 equal applications over the whole year. Fertilizer was weighed and mixed with 20 l of water, with solution added via backpack sprayer below the canopy. Two passes were made across each plot to ensure an even distribution of fertilizer. Control plots received an equivalent volume of deionized water.

Field soil sampling and laboratory analysis

Soil samples were collected in August 2009 with a 5-cm-diameter corer at 10 cm depth intervals down to 40 cm depths, where bedrocks exist widely. For the 0–10 cm soils, the cores were taken beneath the loose litter layer (Oi) and were comprised of Oe and Oa horizon plus mineral soil to a total depth of 10 cm. The corer was then driven to a depth of 20 cm to collect the sample from the 10–20 cm depth. By using this method, the 20–30 cm and 30–40 cm soils were collected, respectively. Three randomly selected locations were sampled in each plot. Altogether, there were three subsamples for each layer per plot. In the laboratory, soils from each subsample were sieved (2 mm) to remove roots and stones, and mixed thoroughly by hand for subsequent chemical analysis. We analyzed each subsample separately. We got an average value from the data of three subsamples, and then had a further statistical analysis.

Soil pH was measured with a glass electrode using a 1 : 2.5 soil–water suspension. Exchangeable cations (H$^+$, K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}) and water-soluble ions (K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, NH$_4^+$, NO$_3^-$, SO$_4^{2-}$, F$^-$, Cl$^-$) were extracted with 0.1 mol l^{-1} BaCl$_2$ (50 : 1, solution : soil) and deionized water (5 : 1, water : soil), respectively. After centrifugation and filtration through 0.45 μm cellulose–acetate filters, the filtrates were analyzed for cations and anions. Exchangeable H$^+$ and Al^{3+} were determined by NaOH neutralization titration after BaCl$_2$ extraction. Cations of K$^+$, Na$^+$, Ca^{2+}, Mg^{2+} and Fe^{3+} were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, Waltham, MA, USA.). Water-soluble inorganic nitrogen (NH$_4^+$-N and NO$_3^-$-N) was measured using a Lachat QC8000 Flow Injection Analyzer. Anions of SO$_4^{2-}$, F$^-$ and Cl$^-$ were determined using Dionex DX-120 Ion-Chromatography. Total soil organic carbon (SOC) was measured by dichromate oxidation before titration with Fe^{2+} solution. Subsamples of soil were oven-dried at 105 °C to a constant weight (at least 24 h) to allow reporting soil results on an oven-dry basis.

Field water sampling and laboratory analysis

We collected soil solution from all plots at 20 and 40 cm soil depth in the studied forest. At 20 cm soil depth, two replicate zero-tension tray lysimeters (755 cm^2 per tray) per plot were installed in April/May 2003 3–4 months before the experiment. Each lysimeter was connected to a 10 l bottle using site slope to facilitate water flow and sampling. At 40 cm soil depth, two acid-washed ceramic suction cup lysimeters (except in one of the medium-N plots due to its shallow soil and rocky substrate) were installed per plot to sample percolating water. The applied suction was −50 kPa, and water sample was collected about 24 h later.

Water samples were taken from May 2009 to July 2010. We took soil solution samples after each rain event (especially for heavy rainstorm events). Altogether, there were thirty-six samplings: three samplings/month in May–July, October and December, 2009, and May and July, 2010; two samplings/month in August and September, 2009, and January–April, and June, 2010; and one sampling in November, 2009. For all soil solution samples, water volume was recorded and combined into one for the same soil layer within a plot on the date of collection. Water collectors were washed with distilled water immediately after each collection. All water samples were filtered through 0.45 mm micron filters within 24–48 h of collection in the laboratory, and later stored in plastic bottles at 4 °C until later chemical analysis. Concentrations of NH$_4^+$-N, NO$_3^-$-N, K$^+$, Na$^+$, Ca^{2+}, Mg^{2+}, Al^{3+} and Fe^{3+} and water pH (before filtration) were determined for each sample date as described above.

Data analyses

Acid neutralizing capacity was calculated as the difference between sum of water-soluble base cations and sum of water-soluble acid anions on an equivalent basis (Vogt *et al.*, 2006); that is, water-extracted ANC = [2(Ca^{2+}) + 2(Mg^{2+}) + (K$^+$) + (Na$^+$) + (NH$_4^+$)]– [2(SO$_4^{2-}$) + (NO$_3^-$) + (Cl$^-$) + (F$^-$)]. ANC was used in this study because ion-exchange occurs at the

interface between mineral and solution and ANC of waters is commonly used to quantify the sensitivity of drainage water to acidification (Sullivan *et al.*, 1989; Hemond, 1990; Neal *et al.*, 1999). Soil cation exchange capacity (CEC) was calculated as sum of exchangeable cations (i.e., K^+, Na^+, Ca^{2+}, Mg^{2+}, H^+, Al^{3+}, Fe^{3+}) on an equivalent basis. Fraction of Al and base cations (i.e., K^+, Na^+, Ca^{2+}, Mg^{2+}) in CEC were calculated as soil Al saturation and soil base saturation (BS), respectively (Mulder & Stein, 1994). We also calculated the relative composition of soil exchangeable cations, expressed as percentage charge of total CEC. To investigate how solubility of Al responded to elevated N addition in the acid forest soils, we estimated the activities of Al in soil solutions, using the methods developed in acid forest soils (Mulder & Stein, 1994; Gruba & Mulder, 2008). The activities of free Al were calculated from the concentrations of Al and DOC (published data in Lu *et al.*, 2013) and solution pH, after ionic strength (fixed at 0.001 mol l^{-1}) and temperature (at 25 °C) correction using Visual MINTEQ (http://vminteq.lwr.kth.se/download/; verified on 13 June, 2014).

Repeated measures analysis of variance (ANOVA) was performed to examine the effects of N treatments on the leaching dynamics (monthly average) of soil solution chemistry (i.e., concentrations of NH_4^+-N, NO_3^--N, Al^{3+}, Ca^{2+}, Mg^{2+}, and pH) during the study period. One-way ANOVA with Fisher LSD (Least-significant difference) multiple range test was employed to identify N-treatment effects on soil exchangeable cations, BS, CEC, soil pH, SOC, and ANC. A paired *t*-test was applied to the differences of these parameters between soil depths. We used Pearson correlation analysis to address the relationships between soil solution cations (Ca, Mg and Al) and inorganic N, pH, and N-treatment levels at 20 cm and 40 cm soil depth. We conducted the planned contrast analysis to test differences between Control plots and N-treatment plots. Linear regression analysis was also used to examine the relationships between CEC and SOC in soils, and relationships between the solubility of Al and solution pH in soil solutions. Because concentrations of Al^{3+} were below detection in most solution samples at 40 cm soil depth, we only focused on the activities of Al^{3+} at 20 cm soil depth. All analyses were conducted using SPSS 14.0 for Windows® (SPSS, Chicago, IL, USA), with significant differences set with $P < 0.05$, unless otherwise stated.

Results

Soil pH and water-extracted acid neutralizing capacity (ANC)

Soil pH was commonly less than 4.0 in all plots, and increased significantly with increased soil depth (Fig. 2a). Nitrogen additions decreased soil pH, and the decreases were significant under the Medium-N and High-N treatments in the upper 0–30 cm depth. ANC was typically negative (<-0.3 m molc kg^{-1}) across all plots for any soil layer (Fig. 2b). Nitrogen additions further decreased ANC in all soil layers; these decreases

were significant under High-N treatments at 0–10 cm soil, and under the Medium-N and High-N treatments at 10–30 cm soil depth.

Soil exchangeable cations

In control plots, concentrations of soil exchangeable cations decreased significantly with depth (Fig. 3). For the given soil layer, elevated N additions significantly increased soil exchangeable H^+, especially for the upper three layers (Fig. 3a), but decreased soil exchangeable Ca^{2+} and Mg^{2+} in all layers (Fig. 3c and d). However, N treatments generally had no significant effects on soil exchangeable Al^{3+}, K^+ and Na^+ at any soil layer (Fig. 3b, e and f).

Al^{3+} and H^+ accounted for more than 90% of total exchangeable cations, with the dominant component being Al^{3+}, comprising about 60–90% of the total (Fig. 4). Base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) accounted for less than 10% of total exchangeable cations, and Fe^{3+} accounted for less than 1% of the total along the soil profiles. However, elevated N additions significantly increased the relative proportion of H^+, which had become the second-most important exchangeable cation, while relative proportion of Al^{3+} decreased greatly, especially in the upper layers (Fig. 4). Meanwhile, relative proportion of base cations
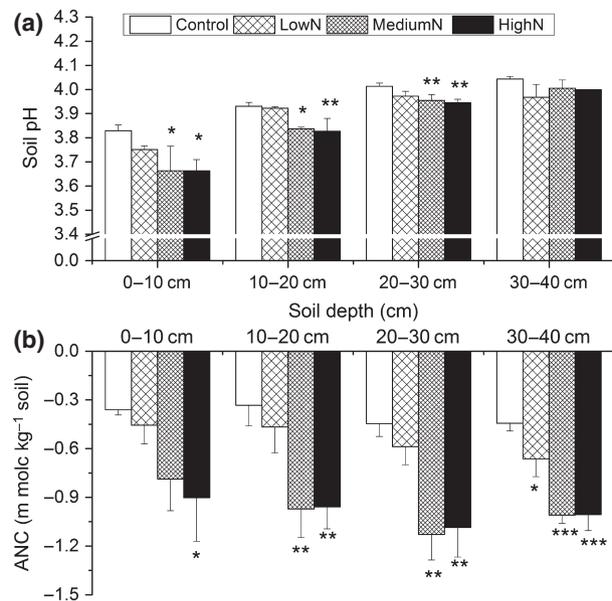

Fig. 2 Responses of soil pH and water-extracted acid neutralizing capacity (ANC) to long-term N addition in the lowland tropical forest of Southern China. *Note*: Error bar means standard error; Asterisks (*), (**) and (***) indicate that there are significant differences at $P < 0.1$, $P < 0.05$ and $P < 0.01$ levels between N treatments and the Controls, respectively.
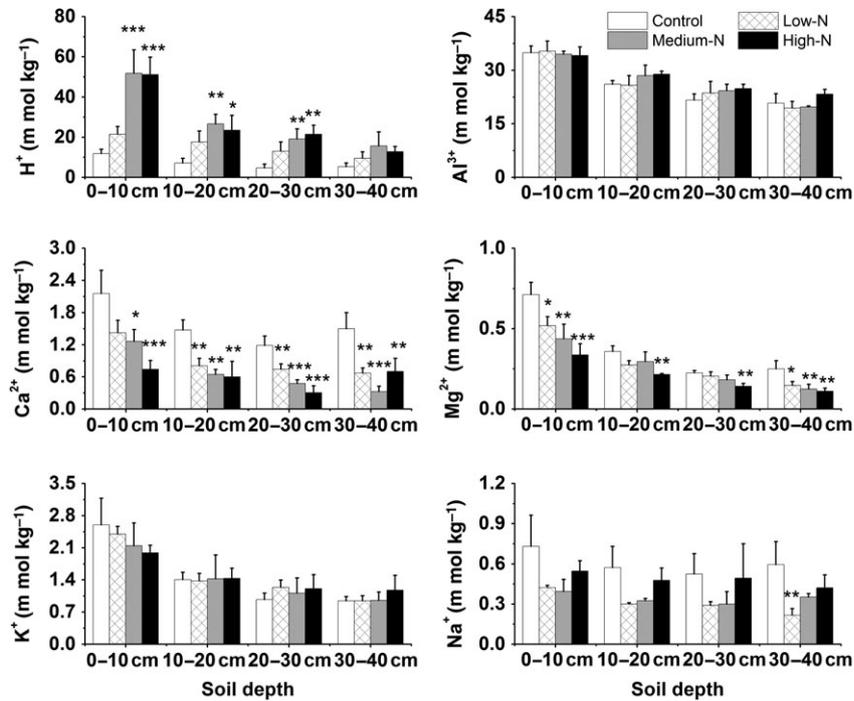
Fig. 3 Responses of soil exchangeable cations to long-term N addition in the lowland tropical forest of Southern China. Asterisks (*), (**) and (***) indicate that there are significant differences at $P < 0.1$, $P < 0.05$ and $P < 0.01$ levels between N treatments and the Controls, respectively.

decreased significantly in N-treatment plots at any soil layer.

Soil BS was typically less than 8% at all soil layers. The decreases in base cations (Ca^{2+} and Mg^{2+}) significantly lowered soil BS with N additions at any soil layer (Fig. 5a). At 0–10 cm layer, for example, BS was 7%, 6%, 5% and 5% in the Control, Low-N, and Medium-N and High-N treatments, respectively. However, soil CEC increased greatly at 0-10 cm layer in response to Medium-N and High-N treatments (Fig. 5b). For the deeper soil layers, the increase in CEC was generally not significant. Linear regression analysis revealed
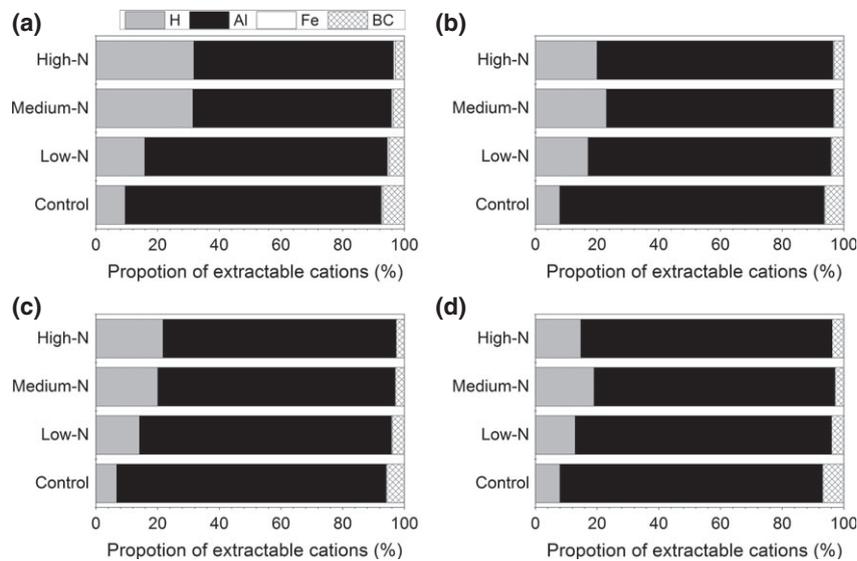

Fig. 4 Effects of long-term N additions on relative composition of soil exchangeable cations (percentage charge of total CEC) in 0–10 cm (a), 10–20 cm (b), 20–30 cm (c) and 30–40 cm (d) soils. *Note*: BC, the total base cations of K^+, Na^+, Ca^{2+} and Mg^{2+}.

significant relationships between CEC and SOC across all plots along whole soil profiles (Fig. 6).

Leaching dynamics of ions and pH in soil solutions

In all plots, concentrations of NO_3^--N generally showed increasing trends from 20 cm soil depth to 40 cm soil depth during the study period (Fig. 7a, b). At 20 cm solutions, repeated measures ANOVA revealed that N additions significantly increased concentrations of NO_3^--N at $P = 0.09$ level. At 40 cm solutions, concentrations of NO_3^--N in N-treatment plots were generally higher than that of the Controls, and there were significant interactions between treatment and time (months) on NO_3^--N ($P = 0.01$).

Concentrations of NH_4^+-N (commonly less than 1 mg N/L as mean values for the whole period) were much lower than those of NO_3^--N at both 20 and 40 cm soil depth (Fig. 7c, d). In contrast to the response of concentrations of NO_3^--N, no significant response was found for NH_4^+-N concentrations to N addition across all plots and sampling times. This is further confirmed by the result of repeated measures ANOVA ($P = 0.31$ and 0.38 at 20 and 40 cm depth, respectively).

Soil solution pH showed significant difference between 20 and 40 cm soil depth at all plots (Fig. 7e, f). Solution pH at 20 cm was near to that of the upper 0–
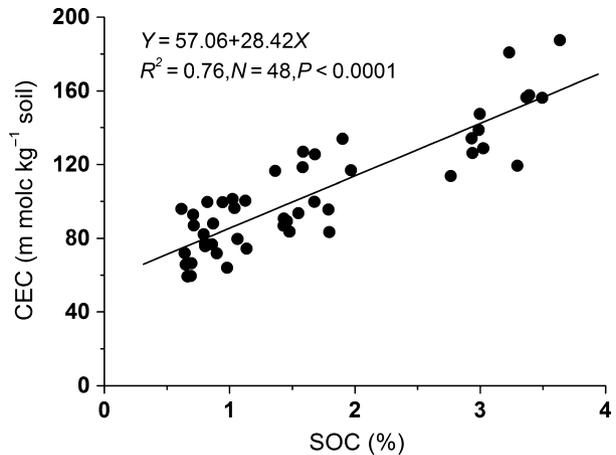
Fig. 6 Relationships between soil cation exchange capacity (CEC) and soil organic carbon (SOC) across all plots along the whole soil profiles from 0–40 cm depth.

20 cm soils, but solution pH at 40 cm increased greatly and was significantly higher than soil pH at any layer. Repeated measures ANOVA showed that N addition significantly ($P < 0.001$) decreased soil solution pH at 20 cm soil depth, whereas soil solution pH at 40 cm depth showed a slight but no significant increasing trend with elevated N addition.

Concentrations of Al^{3+} differed greatly depending on soil depth, with significant higher values at 20 cm depth (Fig. 7g, h). Repeated measures ANOVA showed that N addition significantly increased the concentrations of Al^{3+} at 20 cm soil solutions ($P = 0.001$), while there were no significant N-treatment effects at 40 cm. There was significant negative relationship between Al activity and solution pH (Fig. 8).

In contrast to Al^{3+}, concentrations of Ca^{2+} increased significantly along the soil depth (Fig. 7i, j). For example, concentrations of Ca^{2+} ranged from 20–350 µmol l^{-1} at 20 cm soil solutions, but ranged from 500–1500 µmol l^{-1} at 40 cm. There were decreasing trends at 20 cm soil solutions, but increasing trends in 40 cm soil solutions with elevated N addition. Repeated measures ANOVA showed there were significant interactions between treatment and time at both 20 and 40 cm soil solutions ($P < 0.001$ and $P = 0.04$, respectively).

With the increase of soil depth, concentrations of Mg^{2+} also increased greatly (Fig. 7k, l). Contrary to Ca^{2+}, N additions increased Mg^{2+} at 20 cm soil solution, and repeated measures ANOVA revealed there were significant interactions between treatment and time ($P < 0.001$). At 40 cm solution, N additions significantly increased concentrations of Mg^{2+}, especially in High-N plots. Repeated measures ANOVA confirmed the great
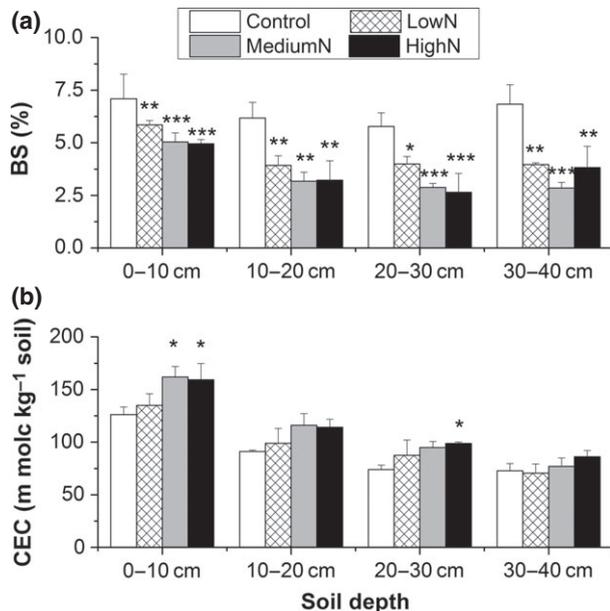

Fig. 5 Responses of soil base saturation (BS, (a) and cation exchange capacity (CEC, (b) to elevated N addition in the lowland tropical forest of Southern China. Asterisks (*), (**) and (***) indicate that there are significant differences at $P < 0.1$, $P < 0.05$ and $P < 0.01$ levels between N treatments and the Controls, respectively.
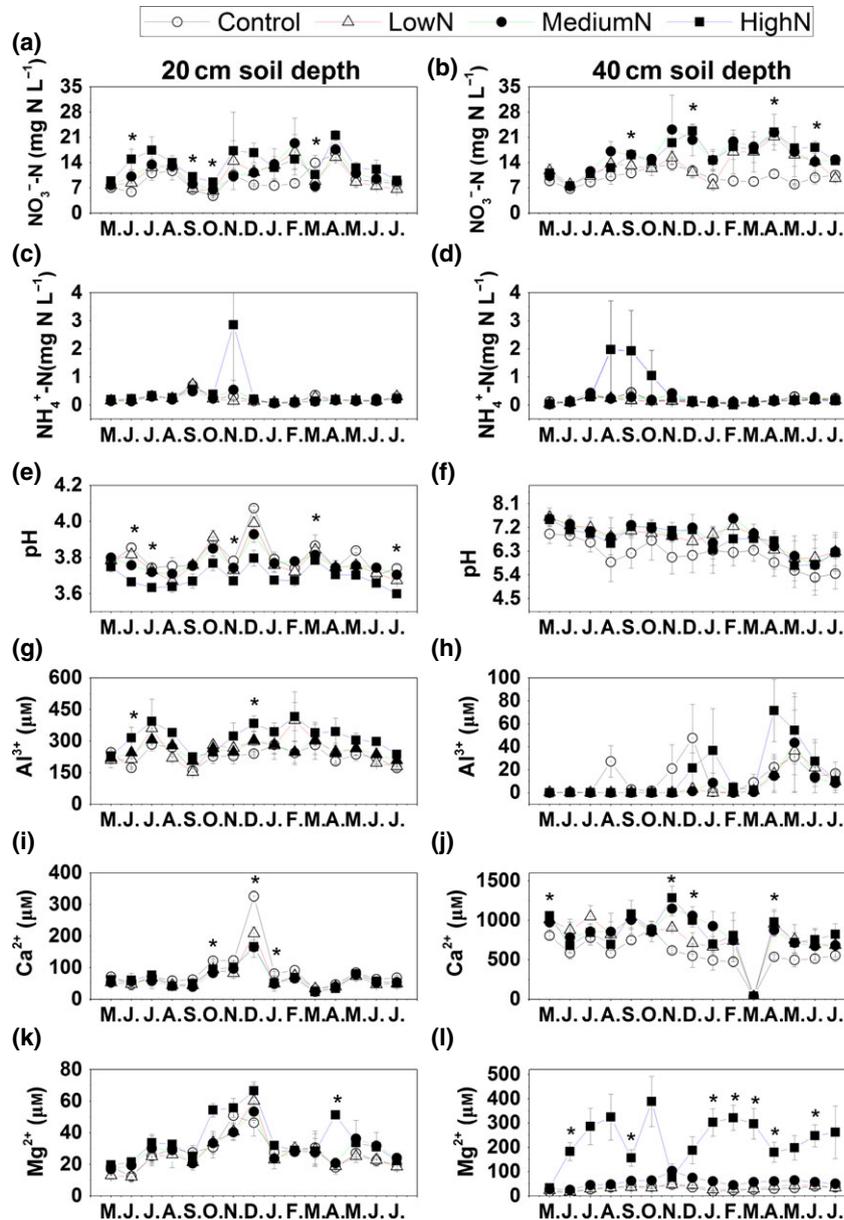
Fig. 7 Responses of NO_3^--N (a, b), NH_4^+-N (c, d), pH(e, f), Al^{3+}(g, h), Ca^{2+} (i, j) and Mg^{2+} (k, l) dynamics to long-term N addition in soil solutions at 20 cm (left panel) and 40 cm (right panel) soil depth. Water samples were taken from May 2009 to July 2010. Asterisks (*) indicates that there are significant differences at $P < 0.05$ levels between N treatments and the Controls using planned contrast analysis.

N-treatment effects and interactions between treatment and time ($P = 0.078$ and $P < 0.001$, respectively).

Pearson correlation analysis (Table 1) showed that Ca^{2+} concentrations were significantly and negatively ($P < 0.05$) related to N treatment, but positively ($P < 0.001$) correlated with solution pH at 20 cm soil depth; at 40 cm depth, concentrations of Ca^{2+} were positively ($P < 0.001$) related with N treatment, NO_3^-, and pH, but not for NH_4^+. Mg^{2+} concentrations were significantly and positively related to N treatments and inorganic N and pH at both 20 and

40 cm, except for pH at 40 cm depth. There were significantly positive relationships between Al and N treatments and NO_3^-, but negatively with pH at 20 cm soil solution.

Discussion

Acidification characteristics of tropical forest soil

Results indicate that these tropical forest soils are highly acidified (Fig. 2) with related low base cation
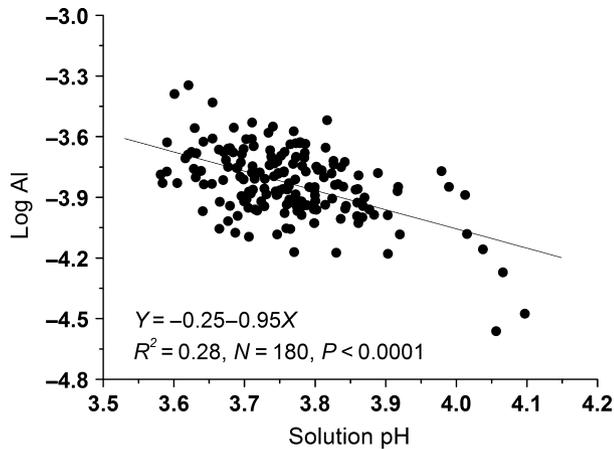
Fig. 8 Relationships between the activities of Al and pH in the solutions at 20 cm soil depth across all plots during the study period.

content and exchangeable Al^{3+} predominating soil cation exchange sites throughout the profile (Figs 3 and 4). These conditions are common in tropical forest ecosystems (Krusche *et al.*, 2003; Vogt *et al.*, 2006; Quesada *et al.*, 2010), and contrast sharply with most temperate ecosystems, wherein exchangeable base cations generally dominate soil cation pools (Fernandez *et al.*, 2003; Watmough & Dillon, 2003; Högberg *et al.*, 2006). It is further notable that H^+, rather than base cations, co-dominated soil cation pool with Al^{3+}. The reaction of soil minerals with H^+ may release base cations to soil solution, which are leachable from soil as a result of charge balance with acid anions, as soil solution drains from the watershed (Tomlinson, 2003). Considering that H^+ concentration in soil water is buffered by Al^{3+} dissolution, the concentration of Al^{3+} increases exponentially with decreasing pH. Consequently, dissolved Al^{3+} competes more effectively with exchangeable base cations, because of higher adsorption affinities of Al^{3+} to colloidal particles than base cations. Hence, a high leaching potential for base cations can occur, when strong acids derived from acid deposition enter the soil solution (Tomlinson, 2003).

There are two main geographical regions of acid soils (defined as soils with pH <5.5 in their surface layers) in the world: the northern belt, with cold, humid temperate climate, and the southern tropical belt, with warmer, humid conditions (von Uexküll & Mutert, 1995). Acid soils from northern belt also show comparable soil acidification characteristics with our study (Skyllberg *et al.*, 2001; Johnson, 2002; Gruba *et al.*, 2013). The sharpest contrast, however, between these belts is that the southern tropical belt is dominated by Ultisols and Oxisols and highly weathered, and supplies less base cations than many younger, glaciated temperate soils (von Uexküll & Mutert, 1995; Soil Survey Staff, 1999). Furthermore, the humid tropical climate with high rainfall and temperature favors rapid dissolution and leaching of weatherable minerals. As such, resultant soils are poor in base cations and rich in kaolinitic clays and sesquioxides, which possess pH-dependent charges.

We further found the dominance of K^+ among exchangeable soil base cations at this site (Fig. 3), indicating the leaching of Ca^{2+} and Mg^{2+} by selective weathering (Ca>Na>Mg>K; after Likens & Bormann, 1994). Base cation budgets show that all cations except K^+ tend toward entire depletion (see Data S1 and Table S1). High weathering rates and strong leaching of base cations should reduce the pool of base cations and consequently soil ANC. However, because of greater output of base cations via stream flow, the atmospheric input of base cations (plus weathering supply) did not neutralize soil acidity, suggesting eventual exhaustion of soil base cations. The negative ANC (Fig. 2b) and low BS (Fig. 5a) at our site indicates low soil buffering capacity to external acid inputs. Hence, the humid tropics deserve greater attention.

Effects of N addition on soil acidification

Our results show that long-term N addition significantly accelerated soil acidification and depleted soil base cations, similar to large areas of Europe and North

Table 1 Pearson correlation coefficients between concentrations of cations (Ca, Mg and Al) and inorganic N, pH and N treatment (N addition rates) in soil solutions at 20 and 40 cm soil depth in the lowland tropical forest of Southern China

Parameters	20 cm soil solution			40 cm soil solution		
	Ca	Mg	Al	Ca	Mg	Al
N treatment	−0.15*	0.21**	0.34***	0.28***	0.68***	0.04
NH_4^+	0.04	0.15*	0.05	0.03	0.20**	−0.05
NO_3^-	−0.02	0.25***	0.38***	0.24***	0.26***	0.25***
pH	0.51***	0.18*	−0.183*	0.51***	0.10	−0.60***

*Correlation is significant at the 0.05 level (2-tailed); **Correlation is significant at the 0.01 level (2-tailed); ***Correlation is significant at the 0.001 level (2-tailed).

America, where high atmospheric N deposition has been experienced during the last decades (Likens *et al.*, 1996; Fenn *et al.*, 2006; Högberg *et al.*, 2006; Bowman *et al.*, 2008; Lucas *et al.*, 2011). Driscoll *et al.* (2003) suggested that depletion may occur when nutrient cations were displaced from soils by acidic deposition at a rate faster than they can be replenished by slow mineral weathering or deposition of nutrient cations from atmosphere.

Our study site is highly acid-sensitive, so that the depletion of base cations may be attributed to a limited adsorption capacity for N and consequent leaching of NO_3^-, confirmed by decreasing ANC. Earlier studies have shown that our study site is N-saturated, with elevated N addition leading to large loss of NO_3^- (Mo *et al.*, 2006; Fang *et al.*, 2009). Indeed, in this study, significant increases of soil solution NO_3^- fluxes at both 20-cm and 40-cm resulted from N additions (Fig. 7a, b). Ca^{2+} and Mg^{2+} leaching and mobilization with NO_3^- (see Fig 7i–l, Table 1), as the solution drains from the soil, further support this suggestion.

We further found that H^+ concentration and its proportion among soil extractable cations increased significantly for all soil layers under N treatments, which arises from increasing competitiveness of protons relative to base cations for cation exchange sites (Van Breemen *et al.*, 1984). With H^+ remaining in the system, soil acidification continues, and many more base cations will be replaced by H^+ and thus leach out (Schulze, 1989; Edwards *et al.*, 2002; Tomlinson, 2003).

However, we found that long-term N addition did not change soil exchangeable Al^{3+} (Fig. 3b), which is in sharp contrast to results from other studies (Warby *et al.*, 2009; Perry & Amacher, 2012). Chronic acid deposition typically leaches base cations out of soil profile, simultaneously increasing exchangeable Al^{3+} concentrations. Release of Al^{3+} is an important acid buffering process in acid soils (Mulder *et al.*, 1989; Berggren & Mulder, 1995; Larssen *et al.*, 1999). Considering the depletion of base cations from the soil complex under N treatments (Fig. 5a), a consequence of elevated H^+ production (low pH) is the dissolution of Al from soil (Van Breemen *et al.*, 1983; Schulze, 1989; Krusche *et al.*, 2003). To balance the leaching of mobile NO_3^-, more free Al^{3+} was leached out (Fig. 7g, and Fig. 8), whereas N addition had no effects on soil exchangeable Al^{3+}. These findings suggest that soil buffering may be accompanied by a progressive shift in exchangeable cation composition from Al^{3+} to H^+ (Fig. 3a) and Fe^{3+} (Lu *et al.*, 2013), with Al^{3+} being desorbed and progressively mobilized from the exchange surface as the pH falls below 3.8 (Ulrich, 1986).

With the depletion of base cations and increases of acid cation H^+, soil BS decreased sharply in N-treat-

ment plots of this study. Our results showed that BS was typically less than 8% along all soil profiles, which was greatly lower than other sites in tropical zones with low atmospheric N deposition (Krusche *et al.*, 2003; Xu *et al.*, 2012). Research on soil acidification in southern China and SE Asia suggested that 20% of BS could be used as a threshold for estimating acidification damage (Hicks *et al.*, 2008).

Meanwhile, we found that N addition greatly increased soil CEC while decreasing pH. This finding contradicts the positive correlation between pH and CEC typically found in variable-charge soils (Foth & Ellis, 1997; Johnson, 2002). Generally, soil CEC decreases in response to excess N input in temperate ecosystems, considering that protons induced by N addition can occupy cation exchange sites (Ludwig *et al.*, 2001; Tomlinson, 2003). At a long-term N fertility trial in South-Central Wisconsin, USA, Barak *et al.* (1997) found decreases in CEC were accompanied by decreases in BS (mainly caused by decreases in exchangeable Ca^{2+} and Mg^{2+}). Considering that SOC can be the main cation exchanger and the predominant source of soil surface charge (Johnson, 2002; Gruba & Mulder, 2008; Gruba *et al.*, 2013), we suspect that CEC may increase simultaneously with the increase in SOC. Our further finding supports this, showing that there are positive relationships between CEC and SOC across all plots (Fig. 6). Another parallel study from this site also showed the significantly larger contents of SOC in N-treatment plots, and N addition was suggested to contribute to the increased SOC (Lu *et al.*, 2013). Hence, N addition-induced increase in SOC may be an important reason for the increase in CEC. In this study, however, we found the significant increases in acid cation H^+ in N-treatment plots. In most soils, carboxyl groups provide CEC of organic matter by dissociation of H^+, which may decrease soil pH (Foth & Ellis, 1997). Therefore, a greater organic content could contribute to both higher CEC and lower pH in this study.

Responses of soil solution pH and free Al to elevated N additions

Interestingly, soil solution pH showed significantly vertical patterns between 20 and 40 cm soil depth at all plots (Fig. 7e and f). Nitrogen addition only significantly decreased soil solution pH at 20 cm depth, but had no effects at 40 cm depth. At 20 cm, the lower pH could be related more to significantly higher concentrations of Al^{3+} than to Ca^{2+} and Mg^{2+}. Increasing neutralization of H^+ by Al solubility caused Al^{3+} concentrations to increase under elevated N addition, which suggests that Al dissolution is the major acid neutralizing process in upper soils. At 40 cm,

however, increased cation concentrations were dominated by Ca^{2+} and Mg^{2+} (especially for Ca^{2+}) rather than Al^{3+}. Higher leaching losses of NO_3^- were likely responsible for the greater amounts of Ca^{2+} and Mg^{2+}, as accompanying ions, especially under N-treatments plots. These data indicate pronounced acid neutralization through mobility of Ca^{2+} (and some Mg^{2+}), associated with significant immobilization of Al^{3+}, reinforcing the importance of alkaline ion inputs for the acid neutralization of drainage waters in much of south China (e.g., Larssen *et al.*, 2006). In addition, our soils are acidic and noncalcareous soils, such that CaO is commonly less than 0.3% in the whole mineral soils, with the highest at surface soils (Zhang, 2011). Hence, both great mobilization of base cations (Ca^{2+} and Mg^{2+}) to deeper soils and immobilization of Al^{3+} therein may contribute to high soil solution pH at 40 cm. These response patterns in vertical profiles contrast with acid temperate forests in the Netherlands, wherein soil solutions were extremely acidic even at 60 cm depth soil (e.g., soil solution pH values were as low as 4.0), and Al^{3+} was the dominant cation in solution at a charge basis and increased with depth, while concentration of Ca^{2+} was fairly constant with depth (Mulder & Stein, 1994). In addition, we should have a caution that a contamination in lysimeters may be possible in similar studies, so that small amounts of easy-soluble carbonates or silicates seem to increase the solution pH.

We further found a negative relationship between the solubility of Al and solution pH (Fig. 8) at 20 cm equilibrium solution, suggesting that the activities of Al are pH-dependent, consistent with conclusions from studies of highly acid soils in temperate and boreal forests (Gruba & Mulder, 2008; Gruba *et al.*, 2013). Hence, if Al in solutions leached from 0–20 soil layers, it will threaten the health of downstream aquatic ecosystems under high acidic deposition. However, there is relatively little Al mobility at 40 cm soil depth (Fig. 7 g and h) because of potential co-sorption of Al^{3+} and SO_4^{2-} in deeper soil layers (Vogt *et al.*, 2007), and probably the leaching to stream water is limited.

Implications

Although soil acidification has been observed in temperate/boreal regions, studies such as ours in tropical forest soils represent sharp contrasts to these regions, because high weathering rates and associated leaching predisposes such soils to chronic low soil buffering capacity toward extrinsic acid inputs in tropical ecosystems. Soils at our study site were highly acid-sensitive, and long-term N addition significantly accelerated soil acidification, leading to depleting base cations and decreasing BS, which is similar to findings in temperate and boreal ecosystems. However, long-term N addition did not change soil exchangeable Al^{3+}, but significantly increased exchangeable H^+ proportion in soil cation pools and soil CEC. Nitrogen addition-induced increase in SOC is suggested to contribute to both higher CEC and lower pH. We further found that elevated N addition greatly decreased soil solution pH at 20 cm soil depth, but not at 40 cm, where soil solution pH was significantly higher than that at 20 cm. These response patterns are distinctly different from other studies. All these findings suggest that external N additions decrease soil buffering capacity and contribute to soil acidification, and that high-N deposition may play an important role in declining soil pH during the past three decades at Dinghushan Biosphere (Fig. 1). However, considering the background of high S deposition at this site, whether sulfate is one of the main driving forces of soil acidification under elevated N addition deserve our further study in the future.

This is the first study on how long-term N addition affects soil buffering capacity in typical N-rich forest ecosystems not experiencing glaciation. Our results suggest that, even though S emissions and deposition has decreased in response to policy, excess N can contribute measurably to soil acidification. We further suggest that the observed lack of base cations (especially for Ca^{2+} and Mg^{2+}) should receive more attention rather than soil exchangeable Al^{3+} and thus its possible phytotoxicity in tropical forest ecosystems. Our findings also raise questions about current projections of ecosystem productivity and floral and faunal diversity based on large-scale vegetation censuses without considering long-term high-N input into forests. This is especially important considering that tropical forests contain about half of vegetation C stock among terrestrial biomes and have the highest biodiversity of all terrestrial ecosystems in the biosphere. Therefore, N deposition-induced soil acidification and its ecological effects on biota are worthy of further study and validation in other tropical ecosystems experiencing elevated N deposition.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Data S1. Supplementary methods.
Data S2. Supplementary references.
Table S1. Respective pool and budget of each base cation in the lowland tropical forest of Southern China.