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Divergent Responses of Soil Buffering Capacity to Long-Term N Deposition in Three Typical Tropical Forests with Different Land-Use History

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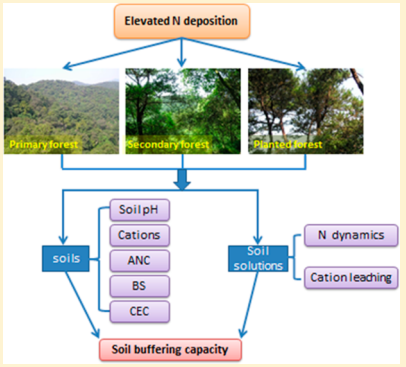
Supporting Information

ABSTRACT: Elevated anthropogenic nitrogen (N) deposition has become an important driver of soil acidification at both regional and global scales. It remains unclear, however, how long-term N deposition affects soil buffering capacity in tropical forest ecosystems and in ecosystems of contrasting land-use history. Here, we expand on a long-term N deposition experiment in three tropical forests that vary in land-use history (primary, secondary, and planted forests) in Southern China, with N addition as NH_4NO_3 of 0, 50, 100, and 150 kg N ha^{-1} yr^{-1}, respectively. Results showed that all three forests were acid-sensitive ecosystems with poor soil buffering capacity, while the primary forest had higher base saturation and cation exchange capacity than others. However, long-term N addition significantly accelerated soil acidification and decreased soil buffering capacity in the primary forest, but not in the degraded secondary and planted forests. We suggest that ecosystem N status, influenced by different land-use history, is primarily responsible for these divergent responses. N-rich primary forests may be more sensitive to external N inputs than others with low N status, and should be given more attention under global changes in the future, because lack of nutrient cations is irreversible.



INTRODUCTION

Soil buffering capacity is the ability of soils to resist changes in pH.[1] Changes in soil buffering capacity arise from soil characteristics, such as base saturation (BS), cation exchange capacity (CEC), and acid neutralizing capacity (ANC), and are tightly linked with soil acidification.[2−5] The primary reaction for buffering in acid soils (defined as soils with pH <5.5 in their surface layers) is the exchange between H^+ and base cations of Ca^{2+}, Mg^{2+}, K^+, and Na^+. Greater CEC implies that soils could provide more cation exchange sites to buffer input of acid. Once base cations have been exhausted, aluminum (Al) is mobilized from soils; thus, the dynamics of soil pH can be buffered by Al compounds as a replacement for base cations at low pH (e.g., <4.2).[5−7] Buffering capacity is important in stabilizing soil pH and related soil processes, microbial dynamics, root function, decomposition of organic matter, and soil cation availability, all of which can affect plant growth and biodiversity.[7−12]

Anthropogenic activities, such as accelerated land-use changes[13] and increased N emissions leading to elevated N deposition,[14] have heavily disturbed ecosystem structure and function by potentially altering soil buffering capacity. For example, because of the rapid expansion in deforestation, many primary forests have been transformed into secondary forests and plantations. Currently, primary forests account for about 36% of total forested area, and are decreasing at the rate of 0.4% annually since 2000.[15] The vast majority of losses is in the tropics, where secondary forests are extensive, accounting for about half of total forested area.[15] Because of the intensity of these human disturbances, secondary forests and plantations are often seriously degraded, showing loss of soil structure and organic matter and nutrient depletion, compared to primary forests.[16,17]

Anthropogenic increase in atmospheric N deposition, as an important source of environmental acidification,[18−20] can decline soil buffering capacity, and is becoming one main driver of soil acidification in natural and seminatural ecosystems around the world.[3−5,21,22] In general, chronically enhanced N deposition increases the availability and thus mobility and

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leaching of inorganic N (especially for nitrate), leading to exhausted soil base cations and elevated Al/Fe mobilization and resulting toxicity to biota, all of which increase net acid loads in soils.[3,9,23,24] Furthermore, excess N deposition can lead to a state of N saturation, where N input exceeds the biological demand of ecosystem and its ability to bind nitrogen, and thus further induce soil acidification and decrease soil buffering capacity.[25−27]

However, our understanding of how N deposition affects soil buffering capacity is based largely on work in temperate regions of Northern Hemisphere,[3,5,7,28,29] where ecosystems are typically N-limited.[9,25,30,31] Data necessary to rigorously evaluate the patterns of soil buffering capacity are lacking for the biota of tropical regions,[7,10,32] where N cycling is often open with high soil N availability, rapid rates of N cycling, and lack of N limitation to net primary productivity, which is substantially different from temperate ecosystems.[7,33−35] Importantly, soils in humid tropical regions are often highly weathered, with low base cation pools and dominance of kaolinite and gibbsite mineralogies[36] and, hence, poorly buffered against acid deposition.[32] In contrast to temperate ecosystems, Al buffering is often suggested in the tropics, because of the depleted base cation pool.[5−7,11,20,36] As a result, conclusions based on studies conducted in temperate regions are of little relevance for the tropics under elevated N deposition.[37,38] To our knowledge, there also have been no investigations comparing responses of soil buffering capacity to long-term N deposition between forest ecosystems with different land-use history from either temperate or tropical regions.

The objective of this study is to explore how long-term N deposition affects soil buffering capacity in three typical tropical forests of contrasting land-use histories: a primary forest (mature forest), a secondary forest, and a plantation. In 2002, we established long-term N deposition research sites in these forests at Dinghushan Biosphere Reserve of Southern China, where atmospheric N deposition rates are commonly above 19 kg N ha^{-1} yr^{-1}.[11,39,40] We hypothesize that (1) long-term N deposition declines soil buffering capacity in all forests, because of the intrinsic poor buffering capacity, and (2) the primary forest is less sensitive to N addition than the secondary forest and plantation, because primary forests generally have more closed biogeochemical cycles regarding major nutrients, and are more resilient to external disturbances than more recently disturbed forests.[41,42] Our long-term field experimental treatment offers a unique opportunity to examine soil buffering capacity among different forest types under changing environmental conditions in the same climate region and with the same soil pedogenesis.

MATERIALS AND METHODS

Study Sites. This study was conducted at UNESCO/MAB Dinghushan biosphere reserve (DHSBR) of tropical China, a region experiencing chronic high atmospheric N deposition (21−38 kg N ha^{-1} yr^{-1} as inorganic N in bulk precipitation) at least since the 1990s. We established research sites in three forest types, comprising different land-use history: a primary forest (monsoon evergreen broadleaf forest, mature forest), a secondary forest (mixed pine/broadleaf forest), and a planted forest (pine forest, plantation). The primary forest has been protected from direct human disturbance for more than 400 years. Both the planted and secondary forests have been subjected to the pressure of human activity during the past several hundred years, having been clear-cut and planted with the native pine, *Pinus massoniana*, in the 1930s. The plantation has been under constant human pressure (primarily harvesting of understory vegetation and litter) since initial planting and continuing until the late 1990s. The secondary forest originated from a planted pine forest that was naturally invaded and colonized by broadleaf species; it is considered a transitional forest from pine to monsoon evergreen broadleaf forest. The mineral soil properties varied greatly among these forests, with higher total soil C, N and P, and soil available N, and better soil structure in the primary forest than the secondary and planted forests, respectively (Table 1). Detailed information is provided in Supporting Information (SI) Text 1.

Table 1. Mineral Soil Properties (0−10 cm) in the Primary, Secondary, and Planted Forests at DHSBR in Southern China[a]

parameter	primary forest	secondary forest	planted forest
total C (%)[b]	3.21 (0.27)	1.73 (0.12)	2.27 (0.31)
total N (%)[b]	0.25 (0.02)	0.12 (0.01)	0.13 (0.01)
C/N[b]	12.84 (2.27)	14.39 (1.03)	17.01 (1.35)
total P (%)[d]	0.022 (0.001)	0.017 (0.00)	0.019 (0.001)
extractable NO_3^- (mg N/kg)[d]	5.77 (0.23)	0.91 (0.11)	2.49 (0.11)
extractable NH_4^+ (mg N/kg)[d]	1.07 (0.11)	4.1 (0.21)	2.8 (0.24)
bulk density (g/cm^3)[b]	0.98 (0.06)	1.22 (0.01)	1.16 (0.05)
moisture content (%)[c]	43.91 (1.70)	28.39 (1.04)	27.83 (1.22)

[a]SE in parentheses. [b]Cited from ref 8. [c]Cited from ref 17. [d]Cited from ref 10.

Experimental Treatments. Nitrogen amendment experiments were initiated in July 2003, and have been continuous through the whole study period, with three replicate 10 m × 20 m plots per treatment established in a random design. There were four N addition treatments in the primary forest: 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}), and three treatments (Control, Low-N, and Medium-N) in each of the secondary forest and planted forest. The reason for having additional High-N treatment in the primary forest is that this forest has a significantly higher initial soil N status than other two forests (Table 1). Monthly applications of NH_4NO_3 solution were sprayed onto the plots as 12 equal applications over the entire year. Control treatments consisted of equal volumes (20 L) of deionized water.

Field Soil and Water Sampling and Laboratory Analysis. Mineral soil samples were collected for pH and cation measurements in August 2009, with a 5-cm diameter corer at 10-cm depth intervals to a 40-cm depth, typically the depth to bedrock. Exchangeable cations (H^+, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}) and water-soluble ions (K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}, NH_4^+, NO_3^-, SO_4^{2-}, F^-, Cl^-) were extracted with 0.1 mol/L $BaCl_2$ (50:1, solution/soil) and deionized water (5:1, water/soil), respectively. We collected soil solution from all plots at depths of 20 and 40 cm from May 2009 to July 2010. We sampled soil solution after each rain event. Concentrations of NH_4^+-N, NO_3^--N, K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, and Fe^{3+} were determined for each sample date. Detailed information is provided in SI Text 2 and 3.

Data Analyses. Soil ANC was calculated as the difference between sum of water-soluble base cations and sum of water-

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soluble acid anions on an equivalent basis. Repeated measures analysis of variance (ANOVA) was performed to examine temporal variation in effects of N treatments on leaching dynamics of soil solution chemistry during the study period. One-way ANOVA with Fisher least-significant difference multiple range test was employed to identify N treatment effects on soil exchangeable cations, BS, CEC, soil pH, and soil ANC. A paired t test was used to test differences of these parameters between different soil depths and between different forests for the same soil layer. Detailed information is provided in SI Text 4.

RESULTS

Soil ANC, pH, BS, and CEC. Acid neutralizing capacity (ANC) was negative across all plots and at both soil layers (Figure 1), and soil pH was typically less than 4.3, while soil BS was less than 8%. In control plots, for the same soil layer, the primary forest had higher ANC, BS, and CEC, and lower soil pH than the other two forests, respectively. However, there were no significant differences for ANC among three forests ($P > 0.05$), and there were only significant differences for pH between the primary forest and secondary forest ($P = 0.007$).

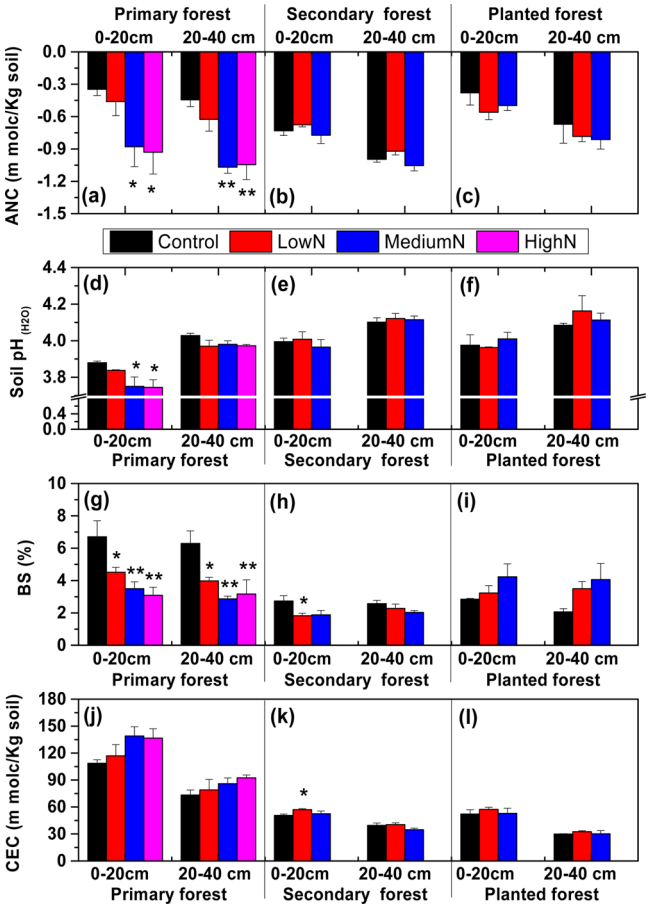

Figure 1. Responses of acid neutralizing capacity (ANC), soil pH, soil base saturation (BS), and cation exchange capacity (CEC) to long-term N addition at 0−20 cm and 20−40 cm soils in the primary (a, d, g, j), secondary (b, e, h, k), and planted (c, f, i, l) forests of Southern China. Asterisks (*) and (**) indicate that there are significant differences at $P < 0.05$ and $P < 0.01$ levels between N treatments and the Controls, respectively. The different plots within each panel have variable ranges on the y-axes.

Base saturation and CEC were significantly higher in the primary forest than in the other two forests, but there were generally no significant differences between the secondary and planted forests. Soil ANC, pH, BS, and CEC were generally higher at upper 0−20 cm soils than those at lower 20−40 cm soils.

Nitrogen additions significantly decreased soil ANC at both soil layers in the primary forest, especially in the Medium-N and High-N plots (Figure 1a). Similar responses were found for soil pH at 0−20 cm depth, but not at 20−40 cm (Figure 1d). However, there were no significant responses of soil ANC and pH in the other forests at any soil layer (Figure 1b, c, e, f). BS decreased significantly with elevated N addition at both soil layers in the primary forest ($P < 0.01$; Figure 1g), but only at upper 20 cm layer in the secondary forest ($P = 0.035$; Figure 1h). In the planted forest, however, BS showed increasing trends with N addition, though there were no significant differences between treatments (Figure 1i). CEC increased greatly under N treatments in the primary forest, especially at upper 20 cm layer ($P = 0.086$; Figure 1j), but there were no significant differences between treatments in the other forests (Figure 1k,l).

Soil Exchangeable Cations and Relative Cation Composition. In control plots of three forests, concentrations of soil exchangeable cations generally decreased with elevated soil depth (Figure 2). Concentrations of soil exchangeable H^+ and Al^{3+} were significantly higher than other cations, and both of them accounted for more than 90% of total exchangeable cation pools along soil profiles (Figure 3), with the dominant component being Al^{3+}. Base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) accounted for less than 8% of total exchangeable cations, and Fe^{3+} typically accounted for less than 1% of the total along soil profiles (Figure 3). Concentrations of soil exchangeable cations (except H^+) were significantly higher in the primary forest than the others in both soil layers (Figure 2). At upper 20 cm soils, concentrations of exchangeable H^+ were significantly higher in the planted forest than the secondary forest, but there were no significant differences for exchangeable Al and total base cations. At lower 20−40 cm soils, the secondary forest had higher contents of exchangeable Al and total base cations than the planted forest.

In the primary forest, N addition significantly increased exchangeable H^+ and Fe^{3+} (Figure 2a, c), but decreased exchangeable Ca^{2+} and Mg^{2+} at both soil layers, especially in the Medium-N and High-N plots (Figure 2e, g); there were no responses to N addition for exchangeable Al^{3+}, K^+, and Na^+ (Figure 2b, d, f). In the secondary forest, N addition had no significant effects on these cations except Ca^{2+}, which decreased greatly under N treatments (Figure 2). In the planted forest, however, exchangeable Ca^{2+} and Mg^{2+} increased significantly under N treatments, especially in the Medium-N plots, but there were no responses for other cations.

For relative composition of soil exchangeable cations, the primary forest was more sensitive to N addition than the others. In the primary forest, N addition significantly increased the proportion of exchangeable H^+, which dominated changes of soil cation pools, but decreased that of base cations at both soil layers ($P < 0.001$; Figure 3a, b). Meanwhile, the proportion of exchangeable Al^{3+} showed greatly decreasing trends at upper 20 cm soil layer ($P < 0.001$). In the secondary forest, N addition significantly decreased the proportion of base cations only at upper 20 cm layer, and there were no significant changes for the other composition at both soil layers (Figure 3c, d). In the

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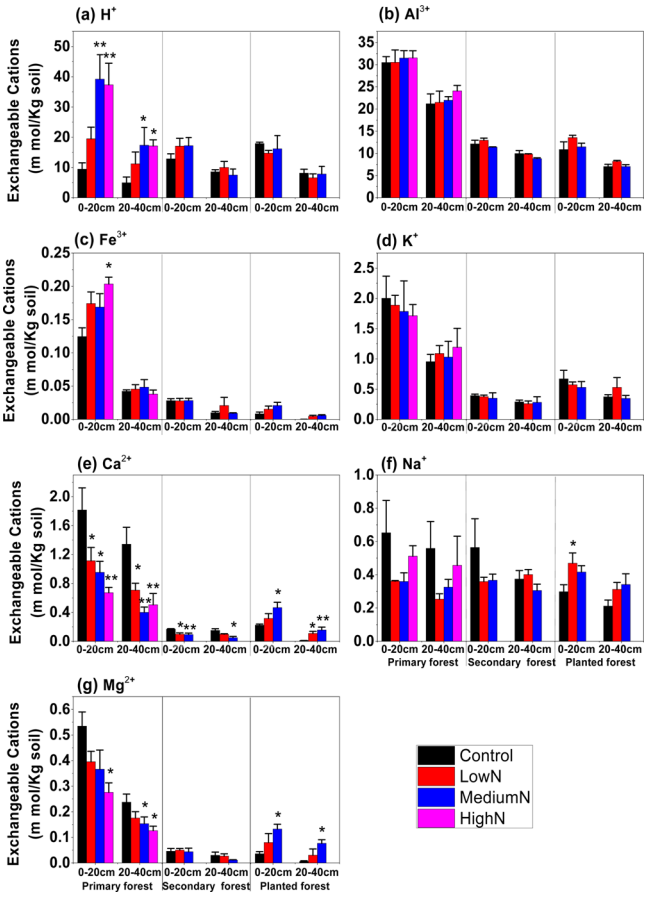

Figure 2. Responses of soil exchangeable cations to long-term N addition at 0−20 cm and 20−40 cm soils in the primary, secondary, and planted forests of Southern China. Asterisks (*) and (**) indicate that there are significant differences at $P < 0.05$ and $P < 0.01$ levels between N treatments and the Controls, respectively. The different plots within each panel have variable ranges on the *y*-axes.

planted forest, relative composition of soil exchangeable cations commonly showed no significant responses to N addition, except that the proportion of base cations increased at 20−40 cm soil layer ($P = 0.073$; Figure 3e, f).

Relationships between Soil pH and Other Soil Properties. In the primary forest, soil pH values were significantly related to N treatment levels ($P = 0.006$), exchangeable H^+ and Mg^{2+} ($P = 0.02$), CEC ($P = 0.08$), BS ($P = 0.02$), and ANC ($P = 0.07$) at 0−20 cm soils, respectively; at 20−40 cm soils, only exchangeable H^+ was significantly related to soil pH ($P = 0.06$; SI Table S1). However, in the secondary and planted forests, there were no significant relationships between soil pH values and any other soil properties and N treatments.

Leaching Dynamics of Ions in Soil Solutions. In control plots, concentrations of NO_3^-, Ca^{2+}, and Mg^{2+} generally showed increasing trends from 20 to 40 cm soil depth in the primary forest during the study period (SI Figure S1). However, concentrations of Al^{3+} ranged depending on soil depth, with higher values at 20 cm depth. At the same depth, concentrations of NO_3^- were commonly higher in the primary forest than the other two forests (SI Figures S1, S2, S3). In the planted forest, concentrations of Ca^{2+} showed increasing trends with elevated soil depth, and Al^{3+} showed the similar trends to the primary forest (SI Figure S3).

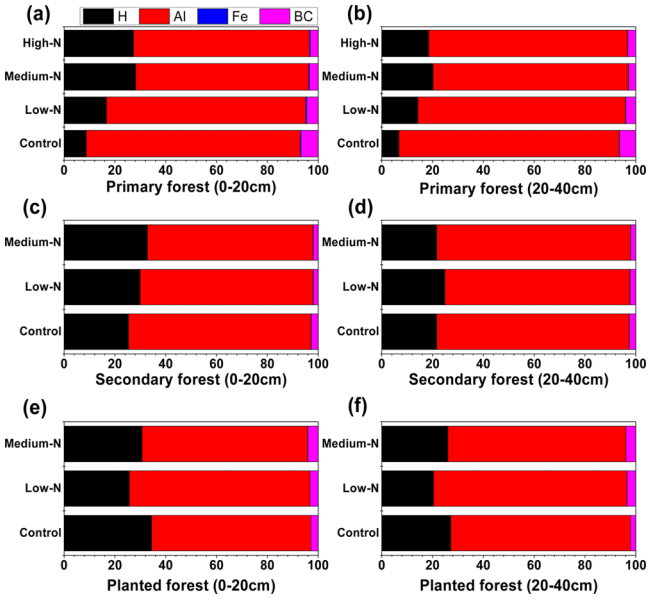

Figure 3. Effects of long-term N addition on relative proportion of soil exchangeable cations (%, at an equivalent basis) at 0−20 cm and 20−40 cm soils in the primary (a,b), secondary (c,d), and planted (e,f) forests of Southern China. BC represents total base cations of K^+, Na^+, Ca^{2+}, and Mg^{2+}.

In three forests, long-term N addition generally increased concentrations of NO_3^- at both 20 and 40 cm soil solutions during the study period (SI Figures S1a,b, S2a,b, and S3a,b). Responses of solution cations to N addition were divergent among forests. In the primary forest (SI Figure S1), for Ca^{2+}, there were decreasing trends at 20 cm soil solutions, but increasing trends at 40 cm with elevated N addition. However, Mg^{2+} increased greatly at both 20 and 40 cm soil solutions. Repeated measures ANOVA showed that N additions significantly increased Al^{3+} at 20 cm soil solutions, while there were no significant N treatment effects at 40 cm. In the secondary and planted forests (SI Figures S2, 3), concentrations of Ca^{2+} generally showed increasing trends under N addition, and there were no significant responses for Mg^{2+} and Al^{3+} during the study period. Detailed information is provided in SI Text S.

DISCUSSION

Characteristics of Soil Buffering Capacity in Tropical Forests. Soil acidification is widespread in the humid Tropics, resulting from major pedogenetic processes that occur in climates where precipitation exceeds evapotranspiration.[43] In this study, we found that all three forests had very low soil pH (commonly <4.3) and BS (<10%), indicating that these forests are highly acidified ecosystems, belonging to tropical type of acidification.[32,43] Hicks et al. suggested that BS of 20% could be used as a threshold for predicting damage due to acidification.[4] Low BS in the tropics is likely tightly linked to high rates of weathering and leaching,[44,45] arising from the humid tropical climate with high rainfall and temperatures that favor rapid dissolution and leaching of weatherable minerals.

In tropical forests, high weathering processes often change mineral dominance from primary and 2:1 silicate minerals to 1:1 secondary minerals such as kaolinitic clays and even sesquioxides.[46] Relative to 2:1 clay minerals, 1:1 kaolinite makes a minor contribution to soil CEC and leads to lower soil

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pH buffering capacity.[47] The continued weathering process will lead to Al^{3+} release from 1:1 minerals and subsequent dominance in soil. Furthermore, hydrolysis of Al^{3+} can result in release of H^+ to soil solution, constantly lowering its pH.[48] Our results confirm this suggestion, showing that exchangeable acid cations (H^+ and Al^{3+}) predominated soil cation pools, and both their concentrations were significantly higher than any base cation at the base of equivalent. These cation composition patterns also reflect that the soils are at the stage of Al buffering,[6] which is distinctly different from that of most temperate ecosystems, where exchangeable base cations generally dominate soil cation pools.[3,7,49,50] High concentrations of Al oxides and low BS have also been found in many other tropical ecosystems, where they are regarded as common characteristics.[30,45,51,52] In addition, we further found that the studied forests had negative soil ANC, indicating that these forest soils are quite acid-sensitive, because negative ANC means that a given system cannot neutralize and hold excess acid input.[53] These findings suggest that our studied forests have poor soil buffering capacity.

The primary forest had the lowest soil pH and highest CEC and BS, compared to those of the secondary and planted forests. These differences are likely attributable to different land-use history, which can greatly alter soil structure and related properties.[16,54−57] As mentioned, the primary forest has been protected from direct human impacts for more than 400 years and is at late stage of succession. However, the original sites of the planted and secondary forests have been degraded by human activities during the past several hundred years, and even have been clean cut before the pine forest was planted in the 1930s. Hence, these sites were badly eroded and degraded, and many dramatic changes in soil properties occurred after deforestation.[16,54,55,58] One of the most significant impacts is the loss of soil structure, as evidenced by increasing in bulk density and decreasing in soil porosity.[59] Importantly, a variety of chemical changes also occur after land conversion, such as leaching losses in soil organic matter and decreases in nutrient availability through time.[16,17]

Furthermore, the planted forest has been under constant human pressures such as harvesting of understory and litter since planted (about 2−3 times a year).[54,55] This harvesting practice not only removes essential nutrients, but also removes organic matter and, thus, substrate for microbial activity, resulting in higher leaching losses of nitrogen and base cations. As a result, the site productivity and N level were low (Table1).[17,54,55] Similarly, the secondary forest, originating from a planted pine forest that was naturally invaded and colonized by broadleaf species, has not fully recovered its soil nutrient availability during the past several decades, and its soil organic matter and nutrients were still low, compared to the primary forest nearby (Table1, Figure 2).[8,17]

Soil properties can greatly affect soil buffering capacity.[47,60−62] Soil organic matter serves both as a nutrient source via decomposition and a cation exchange source, and thus plays an important role in mediating nutrient availability.[63] Studying in the tropical and subtropical regions of China, Xu et al. found that soil pH buffering capacity was positively related to the contents of soil organic matter and soil CEC, and suggested that protonation/deprotonation was the main mechanism for organic matter contribution to soil pH buffering capacity.[47] The greater CEC indicates that soil can provide more cation exchange sites to take up H^+ and to buffer input of acid to soils. Commonly, low CEC soils are more likely to develop base cation (such as Ca^{2+} and Mg^{2+}) deficiencies, whereas high CEC soils are less susceptible to leaching losses of these cations. Thus, it is reasonable to suggest that the primary forest can buffer external acid inputs better than the secondary and planted forests, considering that the primary forest has a better soil structure and higher soil organic matter, CEC, and BS (Table 1, Figure 1).

Responses of Soil Buffering Capacity to Long-Term N Addition. Our results showed that responses of soil acidification and soil buffering capacity to long-term N addition were different among the three forests, which further verified our previous findings after two years of N addition.[10] In general, the primary forest was very sensitive to elevated N addition, which accelerated soil acidification and declined soil buffering capacity. In contrast, the secondary and planted forests were not sensitive to long-term N addition, which is inconsistent with our hypothesis. In the primary forest, long-term N addition significantly increased net soil acid load as proton (lower pH), depleted soil base cations (especially for Ca^{2+} and Mg^{2+}), and thus further declined soil BS. We found that the decreased soil pH values were tightly related to changes in exchangeable H^+, BS, and ANC (SI Table S1). These findings have been verified well in large areas of Europe and North American, where there has been high atmospheric N deposition during the last decades.[3,5,20,23,64] There are several reasons for these divergent response patterns in tropical climate.

First, the primary forest is N-rich and N saturated,[8,11,40,65] and elevated N inputs can accelerate inorganic N leaching loss mainly as NO_3^- (SI Figure S1), leaching of which is accompanied by base cations.[9,66,67] Ca^{2+} and Mg^{2+} leaching and mobilization with tight relationships with NO_3^-, as the solution drains from soils, support this suggestion (SI Figure S1c−f, Table S2). High NO_3^- efflux from soils under elevated N addition was suggested as an important driving force of soil acidification.[5,10,68] Second, the primary forest has a poor soil buffering capacity with negative soil ANC, so that soils could not neutralize and hold excess acid input. Hence, a positive feedback between soil ANC and elevated N addition exists to further decrease soil ANC (Figure 1), and increase leaching of base cations. Third, elevated net soil proton load, which dominates changes of soil cation pool under N treatments (Figure 3), enhances leaching losses of base cations, considering that acid cations (e.g., H^+ and Al^{3+}) have a stronger bond strength with cation exchange sites than base cations.[24,69] However, long-term N addition did not alter soil exchangeable Al^{3+} (Figure 2b), sharply contrasting results from our previous short-term findings[10] and other studies,[3,70−73] wherein soil acidification commonly has led to Al mobilization and subsequent toxicity in soil ecosystems. As mentioned above, soils in the primary forest were at the stage of Al buffering, and high proton load can mobilize more Al^{3+} from soil complex into water solution.[18,74] Meanwhile, base cations played a minor role in soil exchangeable cation pools, and N addition continued to decline base cations from soil complex (Figure 3). To balance leaching of mobile NO_3^-, however, more free Al^{3+} was leached out (SI Table S2), so that long-term N addition had no effects on soil exchangeable Al^{3+}.

In the secondary and planted forests, however, long-term N addition had no negative effects on soil acidity, ANC, and CEC as expected. In the secondary forest, N treatments also had no effects on BS in soils, though BS showed declining trends in the upper 0−20 cm soils, which was attributed to the decrease of

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base cations (especially for Ca^{2+}). Interestingly, elevated N addition increased base cations (especially for Ca^{2+} and Mg^{2+}) and thus BS in the planted forest. Meanwhile, unlike the primary forest, soil solution chemistry showed that N addition did not change Al^{3+} concentration in other two forests (SI Figures S1g, S2d, and S3g), which indicated that potential Al toxicity would not happen in downward aquatic ecosystems with elevated N deposition. These findings contrast with other studies under the background of long-term N deposition, raising the following question: why is the primary forest more sensitive to elevated N addition than the degraded secondary and planted forests?

The primary forest has significant higher N capital (total and available N) and lower C/N ratios than other two forests (Table 1).[10,17] Primary forests are commonly expected to have larger N pools and higher N availability than the young, secondary forests.[75] Our long-term measurements in the first three years has shown that the primary forest should lose more N when being exposed to high-level N inputs than the secondary and planted forests, because of the open, rapid N cycling and greater N fluxes,[65,81] confirming our present findings that the primary forest has higher NO_3^- concentration in soil solutions than the other two forests (SI Figures S1a,b, S2a, and S3a,b). By estimating the overall nitrogen balance under experimental N additions, Fang et al.[65] observed that the rates of N leaching loss (mainly as NO_3^-) were higher in the primary forest (78−101 kg N ha^{-1} yr^{-1} or 53−95% of the total inputs) than the secondary and planted forests (27−62 N ha^{-1} yr^{-1} or 34−51%). However, the average fertilization-derived N_2O emission was only 0.2−1.2 kg N ha^{-1} yr^{-1} or 0.4−2% of the experimental N additions, suggesting that N_2O is of minor importance in these forests in response to elevated N input. Further analysis showed that losses of DON and N gases (e.g., N_2O) did not change the pattern of N loss and N retention among forests.[65] Therefore, dissolved inorganic N (especially NO_3^-) dominated the pattern of N losses from ecosystems. In sum, we suggest that ecosystem N status determines the capacity to retain N, and thus the direction of responses of soil buffering capacity to elevated N addition.

Because of N saturation,[25] the primary forest cannot assimilate and effectively retain external N input; excess N will be leached out rapidly from the impacted ecosystem, inducing soil acidification and decreasing soil buffering capacity. In contrast, the secondary and planted forests are still developing[76−78] and exhibit conservative N-cycling properties with greater capacity to retain N.[79] As Nadelhoffer et al. suggest, pools for N retained in forest ecosystems are primarily plant biomass and soil organic matter.[80] In the planted forest, where human disturbance had ceased, recent estimates suggested that overstory trees, understory plants, and standing floor litter accumulated 9.1, 6.0, and 6.5 kg N ha^{-1} yr^{-1}, respectively, during the period from 1990 to 2000.[76] The total amount of 21.6 kg N ha^{-1} yr^{-1}, sequestrated in these three aboveground pools, is sufficient to explain the observed 21 kg N ha^{-1} yr^{-1} retained above the upper 20 cm soil through precipitation inputs.[81] Similarly, in the secondary forest, N accumulation in plant biomass and litter layer was probably higher than in the pine forest, due to higher litter production and higher foliar N concentration,[77] and might as well account for the 28 kg N ha^{-1} yr^{-1} retained in this forest.[81] It is also suggested that the balance between N supply and biological N demand generally controls leaching of NO_3^- and cations.[82] Therefore, high plant demand for nutrients in the planted and secondary forests could be the main reason for slowing the rate of leaching loss of both NO_3^- and base cations and subsequently soil acidification. However, nutrient pools in each component and their long-term dynamic changes in these soil−vegetation ecosystems merit well further study in the future.

Environmental Implications. Our study showed that all three types of tropical forests were acid-sensitive ecosystems with high acidification and poor soil buffering capacity, which could be regarded as a common characteristic of forest ecosystems in humid tropics. However, not all forests exhibited declines in soil buffering capacity as expected, and there were clearly divergent responses among these forests. The primary forest was the most sensitive to elevated N addition, which enhanced leaching loss of nitrate, accelerated soil acidification, and decreased soil buffering capacity. In contrast, the degraded secondary and planted forests were not sensitive to long-term N addition.

We suggest that changes in ecosystem N status, influenced by different land-use history, are responsible for these divergent responses. Nitrogen saturation has led to enhanced leaching losses on NO_3^- and base cations, triggering the collapse of soil buffering systems in the primary forest. Meanwhile, the secondary and planted forests are aggrading ecosystems, maintaining plant uptake of nutrients as a major sink and mitigating the rate of base cation leaching with elevated N addition. These findings challenge widely held understanding regarding ecosystem stability,[41,42] and indicate that tropical primary forests can be very sensitive to external N inputs, considering that these ecosystems are often N rich.[11,32,83] Therefore, from the perspective of protection and conservation of biodiversity,[84] we should pay more attention to primary forests than secondary forests and plantations, because lack of nutrient cations is irreversible. To our knowledge, this is the first comparative study on responses of soil buffering capacity to long-term N addition in ecosystems with different land-use history, which may deepen our understanding on how to better maintain and manage forest ecosystems, particularly in the face of global changes, including land-use and elevating atmospheric N deposition in the future.

■ ASSOCIATED CONTENT

Supporting Information

SI Text 1−4, Figures S1−4, and Tables S1−2. This material is available free of charge via the Internet at http://pubs.acs.org/.

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The manuscript was written through contributions of all authors.

Notes

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