



Research paper

Effects of long-term nitrogen application on soil acidification and solution chemistry of a tea plantation in China



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ABSTRACT

In tea (*Camellia sinensis*) plantation areas, soil acidification mainly results from excessive nitrogen fertilization. However, the proposed theoretical explanations for soil acidification due to nitrogen fertilization are still lacking empirical validation because most studies have used short-term incubation periods or pot experiments. Here, both soil and soil solution samples were taken from a tea plantation field (Ultisol in USDA taxonomy system, or Alisol in WRB taxonomy system) treated using different nitrogen application rates: 0 (N0), 119 (N119), 285 (N285), and 569 (N569) kg N ha⁻¹ yr⁻¹ for 8 years (2006–2013). Soil pH and the concentrations of the relevant cations and anions were also determined. With no nitrogen fertilization (N0), the surface soil pH decreased from 4.16 to 3.32 after 8 years in the tea plantation. Compared with no nitrogen fertilization (N0), high nitrogen fertilization (N569) significantly decreased the soil pH from 3.32 to 3.15 and 3.67 to 3.35 in the soil at depths of 0–40 cm and 40–90 cm, respectively. However, the low (N119) and moderate (N285) nitrogen treatments showed non-significant effects upon soil pH. Our results confirm the previous findings that a high nitrogen application rate can accelerate soil acidification in a tea plantation, and that the subsoil is particularly susceptible to acidification after heavy nitrogen fertilization. Soil acidification also significantly decreased the nutrient base cations Ca²⁺, Mg²⁺, and K⁺ in the soil. Our results suggest that heavy synthetic nitrogen fertilization should be partly replaced with compound or organic fertilizers to mitigate soil acidification and nutrient cation deficiency in tea plantation fields.

1. Introduction

The tea plant (*Camellia sinensis*) is an important cash crop cultivated in many tropical and subtropical countries. Unlike many other crops, tea is a perennial leaf-harvested crop that grows best in acidic soil with an optimum pH between 4.0 and 5.5 (Ruan et al., 2007; Fung et al., 2008). Nevertheless, soil acidification can lead to the accumulation of aluminum (Al) and deficiencies in phosphorus (P), potassium (K), and magnesium (Mg) nutrients in tea field soil (Tachibana et al., 1995; Wang et al., 1997; Ruan et al., 2012). Concerning the quality of tea, soil acidification can increase the content of heavy metals (e.g., lead, Pb) and fluorine (F) in the harvested leaves, which may entail a risk to human health (Ruan et al., 2003; Jin et al., 2005; Zhang and Fang, 2007).

Generally, N fertilization or deposition is considered the major driver of soil acidification in croplands (Debreczeni and Kismanyoky,

2005; Schroder et al., 2011; Cai et al., 2015), grasslands (Martins et al., 2014; Chen et al., 2015), and forest ecosystems (Hogberg et al., 2006; Zhu et al., 2016). Specifically, it is thought that the accelerated soil acidification from N fertilization is directly caused by the production of protons via the nitrification process after ammonium nitrogen fertilization occurs (Barak et al., 1997; Zhou et al., 2014). The generated hydrogen ions (H⁺) are buffered by a suite of factors, including carbonate, silicate, exchangeable base cations, and the Al and/or iron (Fe) content, which depend on the soil pH (Bowman et al., 2008). Since base cations enter the soil solution as accompanying ions with the leaching NO₃⁻, the buffering capacity of soil is consequently decreased under increasingly acidic conditions (Lucas et al., 2011).

How much N fertilization contributes to soil acidification remains unclear since the latter could happen naturally in tea plantation settings. Ding and Huang (1991) proposed that this might arise when the accumulated Al in the tea plant residue returns to the soil via litter fall

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and regular pruning. Recent studies have revealed that the root uptake of NH_4^+ and Al^{3+} , and the subsequent release of protons, could also cause soil acidification in tea plantations (Ruan et al., 2004; Wan et al., 2012).

However, several processes may also weaken the rate of soil acidification in tea plantation soil. The contribution of nitrification to soil acidification could be diminished by reductions in the availability of substrate, as tea plants preferentially assimilate NH_4^+ (Ruan et al., 2007). Additionally, the soil acidification rate may be reduced by less nitrate leaching, since the nitrification rate is typically inhibited by a low soil pH (Kemmitt et al., 2005). Moreover, soil acidification can be mitigated by the presence of soil buffering minerals, such as iron oxides (Li et al., 2012) and kaolinite in the soil (Lesturgez et al., 2006). So, rather than the total production of protons *per se*, soil acidification strongly depends on the soil buffering capacity and the depletion of the soil base cation pool (Bowman et al., 2008). But in the absence of long-term observations, what we know of soil acidification and its theoretical explanation has come mostly from short-term incubation studies or pot experiments. The long-term effects of N applications on soil acidification in tea plantation systems are not certain; nor have these effects upon soil chemistry and soil solution been clearly elucidated yet.

In this study, we conducted an 8-year-long field experiment that considered a range of N additions in Zhejiang, an important green tea production area in China, for which we tested the soil pH and the ion concentrations in the soil solution. Our objectives were 1) to reveal the contribution of N fertilization to soil acidification in a tea plantation; 2) to illustrate the extent of cation and anion changes in the soil solution under a high N application in a tea plantation; and 3) to distinguish and evaluate the main factors controlling soil pH in the tea plantation.

2. Materials and methods

2.1. Site description

The field experiment was located at Hangzhou, in Zhejiang province in China (120°05'E, 30°10'N), within the country's main region for green tea cultivation. The experimental site has a monsoon climate, with 1533 mm yr^{-1} in precipitation and a mean annual temperature of 17.0 °C. The soil at the site is classified as Ultisol (Soil Survey Staff, 2014) or Alisol (IUSS Working Group WRB, 2015), developed from parent material of a Quaternary eolian red deposit, with a texture that is loamy clay. The surface (0–20 cm) soil properties that existed at the site prior to the experiment are shown in Table S1.

Before the experiment, tea plants of the variety 'Longjing 43' grew for 6 years in the studied field. They had been planted in single lines 1.5-m apart, with an in-line distance of 0.33 m; this represents a planting density of approximately 60 000 plants ha^{-1} . To sustain the growth and the yield of these tea plants, 450 kg ha^{-1} of urea and 4500 kg ha^{-1} of organic fertilizer (rapeseed cake) were applied yearly before the experiment.

2.2. Experimental design

The field experiment began in 2005 and consisted of four treatments of N application rates: 0 kg N $\text{ha}^{-1} \text{yr}^{-1}$ (control, N0), 119 kg N $\text{ha}^{-1} \text{yr}^{-1}$ ('low N', N119), 285 kg N $\text{ha}^{-1} \text{yr}^{-1}$ ('moderate N', N285), and 569 kg N $\text{ha}^{-1} \text{yr}^{-1}$ ('high N', N569). The N fertilizer was urea, and it was split into four seasonal applications; i.e., 30% in early February, before spring tea; 20% in late May, after spring tea but before summer tea; 20% in early July, before autumn tea; and 30% late October, after autumn tea. Phosphorus, as super phosphate, and potassium, as potash of sulfate, were both applied in October as the base fertilizer of all the treatments (Table S2). All the fertilizers were applied in the band furrows (at a depth of 15 cm) between two rows of tea plants, and then covered with soil after their application.

Each treatment consisted of four replicate plots, with all 16 plots

were randomly distributed. Each plot was 24 m^2 in size and consisted of two 8-m-long lines of tea plants. The entire experimental area was on flat terrain, and the plots were separated from each other by one blank line of tea plants or a 1-m-wide segment.

2.3. Soil sampling and analysis

In February 2013, soil samples were collected from the topsoil layer (i.e., 0–40 cm depth), where most roots are found, and from the subsoil layer (i.e., 40–90 cm depth) with a 5-cm-diameter stainless steel corer. Each composite soil sample consisted of six or seven randomly selected points within each plot; these subsamples were completely mixed, and any roots, plant residues, and stones were removed by hand. The fresh soil was passed through a 2-mm-mesh sieve and divided into two parts: one was stored at 4 °C in a refrigerator, while the other was air-dried for the later determination of soil pH, exchangeable cations, and the water-soluble ions.

Soil pH was measured in pastes of 1:1 (w/v) in deionized water with an ORION 3 STAR pH meter (Thermo Ltd., USA). Available NH_4^+ and NO_3^- were extracted by 2 M of KCl and quantified by a Flow Injection Analyzer (SAN++ , SKALAR Ltd., Netherlands).

The soil exchangeable cations were extracted with 0.1 M of BaCl_2 at a ratio of 1:50 (w/v) for 30 min, and passed through 0.45- μm -sized cellulose-acetate paper filters for further measurement (Lu et al., 2014). From the ensuing extracts, the contents of base cations (Ca^{2+} , Mg^{2+} , K^+ , Fe^{3+} , Mn^{2+} , and Na^+) were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; Thermo Jarrell Ash Ltd., USA), while those of exchangeable Al^{3+} and H^+ were determined by NaOH-neutralization titration. The available P, available K, and available sulfur (S) in the soil were extracted by shaking 2.5 g of soil with 25 ml of a Mehlich-3 solution for 5 min (Mehlich, 1984); their contents were determined by ICP-AES.

Free Al/Fe oxides and amorphous Fe/Al oxides were extracted by using the Sodium citrate-bicarbonate-dithionite (DCB) method and the acid ammonium oxalate method, respectively (Mehra and Jackson, 1960).

The water-soluble ions (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , NO_3^- , SO_4^{2-} , F^- , and Cl^-) in the soil samples were extracted with deionized water at a ratio of 1:5 (w/v) for 30 min, and after filtration the samples were analyzed for their cations and anions. NO_3^- and NH_4^+ were quantified in a SAN++ Flow Injection Analyzer (SKALAR Ltd., Netherlands). The cations (K^+ , Na^+ , Ca^{2+} , and Mg^{2+}) were measured by using ICP-AES and the anions (SO_4^{2-} , F^- , and Cl^-) measured by using Ion Chromatography (Dionex DX-2000, USA).

2.4. Soil solution sampling and analysis

In each plot, two ceramic porous lysimeters (Model 1900, Soilmoisture Equipment Corp., Santa Barbara, CA, USA) were installed at soil depths of –15 cm (i.e., within the main rooting zone) and –90 cm (i.e., beyond the rooting zone) in October 2012 to collect their respective soil solutions. These solutions were sucked into bottles using a vacuum pump after each rain event from March to October 2013. The volumes of collected soil solution were recorded by the weighting method.

All the soil solution samples were passed through 0.45- μm filters and stored in a refrigerator at 4 °C. Their ion concentrations (K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , NH_4^+ , NO_3^- , SO_4^{2-} , F^- , and Cl^-) were determined as described above. The mean ion concentrations for each soil solution depth per treatment level at a specific sampling date were calculated from the respective volume-weighted average of the replicates.

2.5. Data analysis

Soil cation exchange capacity (CEC) was calculated as the sum of

the exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , and H^+), as determined by the BaCl_2 extract:

$$\text{CEC}(\text{cmol}_+\text{kg}^{-1}) = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] + [\text{Al}^{3+}] + [\text{H}^+]$$

where $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{K}^+]$, $[\text{Na}^+]$, $[\text{Al}^{3+}]$, and $[\text{H}^+]$ are the respective ion concentrations (expressed as $\text{cmol}_+\text{kg}^{-1}$) in the BaCl_2 -extracted solution. The fraction of base cations ($[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{K}^+]$, and $[\text{Na}^+]$) in CEC was calculated as the base saturation (BS).

Ion exchange occurs on the surface of minerals and solutions, and the acid neutralizing capacity (ANC) is a way to quantify the sensitivity of leached water to acidification. In this study, ANC was used to quantify the extent of soil acidification and calculated as the sum of the water-soluble base cations minus the total water-soluble strong acid anions, on an equivalent basis:

$$\text{ANC}(\text{cmol}_+) = ([\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{K}^+] + [\text{Na}^+] + [\text{NH}_4^+]) - ([\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + [\text{F}^-])$$

where $[\text{Ca}^{2+}]$, $[\text{Mg}^{2+}]$, $[\text{K}^+]$, $[\text{Na}^+]$, $[\text{NH}_4^+]$, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{Cl}^-]$, and $[\text{F}^-]$ were the concentrations of the corresponding water-soluble ions ($\text{cmol}_+\text{kg}^{-1}$) in the water-extracted solution.

One-way analysis of variance (ANOVA) tested the effect of the N application rate (four levels) on soil pH, with the treatment-level means subjected to a multi-comparison tests by the Tukey honest significant difference (HSD) method. The effects of both the N rate and sampling depth (two levels) on the soil chemistry variables were analyzed by multivariate analysis of variance (MANOVA).

To test the importance of the soil chemistry variables for changes in soil pH, a partial least square (PLS) regression was applied to overcome the limitation of collinearity among the independent parameters in simple linear regression that relies on ordinary least squares (OLS). This collinearity was estimated by the value of the variance inflation factor (VIF).

All of the above statistical analyses—t-test, ANOVA, MANOVA, linear regression and PLS—were carried out in the R platform with the ‘stats’ package (v3.3.3).

3. Results

3.1. Soil pH, ANC, and inorganic N

Linear regression of surface soil (0–40 cm) pH on sampling year showed a significant negative correlation, for both treatments with and without N fertilization, but the heavy N application (N569) had slightly steeper negative slope than did N0 (Fig. 1). After 8 years, compared with initial soil pH of 4.16 in 2005, the soil pH in the tea plantation had decreased significantly to 2.94–3.64 in the 0–40 cm depth ($p < 0.001$). The pH in the subsoil was significantly higher than that in the topsoil ($p < 0.001$). N rate significantly affected soil pH, but compared with N0, only the high N treatment (N569) showed a significant pH decrease ($p = 0.001$, Table 1).

The ANC was ~50% lower in the subsoil than in the topsoil ($p < 0.001$). In the latter, N569 caused 36% less ANC relative to N0 ($p < 0.01$). But the effect of N rate on ANC was non-significant in the subsoil ($p = 0.154$, Table 1).

Exchangeable NH_4^+ in the topsoil increased significantly only in high N treatment; in the subsoil it was unaffected by the N fertilization (Table 1). The contents of exchangeable NO_3^- responded positively and significantly to the increasing N applications. Under the control treatment (N0), NH_4^+ was the dominant inorganic N: the $\text{NH}_4^+/\text{NO}_3^-$ ratios were 2.7 and 3.3 in the topsoil and subsoil, respectively. Under the high N treatment, however, the $\text{NH}_4^+/\text{NO}_3^-$ ratio decreased to 1.0–1.2 in the topsoil and even further in the subsoil, to 0.56.

3.2. Exchangeable cations, CEC, and base cations (BCs) in the soil

The MANOVA results in Table 1 shows that the composition of soil cations was significantly affected by the N application rate ($p = 0.013$), but more so by sampling depth ($p = 0.002$).

Exchangeable Al^{3+} increased with the N application level in both topsoil and subsoil layers (Table 1). Compared with N0, the N569 treatment increased the exchangeable Al^{3+} content by 18% and 13% in the topsoil and subsoil, respectively. The exchangeable H^+ also showed a tendency to increase with the N application rate, but this response was not statistically significant ($p = 0.725$).

Exchangeable K^+ , Ca^{2+} , and Mg^{2+} responded differently to the N applications. In the topsoil, while they all decreased with more N, relative to N0, N569 decreased the exchangeable Ca^{2+} , K^+ , and Mg^{2+} contents by 40%, 32%, and 29%, respectively. By contrast, exchangeable Na^+ seemed unaffected by the N application rate; however, its content was significantly influenced by the sampling depth (Table 1).

Soil exchangeable Fe^{3+} contents among the treatments were similar in the topsoil, but tended to increase with the N application rate in the subsoil. The exchangeable Mn^{2+} differed between the two depths, in that the Mn^{2+} concentration in the 0–40 cm depth layer was double that in 40–90 cm (Table 1).

CEC in the subsoil was significantly lower than in the topsoil ($p = 0.012$), but it was not affected by N rate at either depth ($p = 0.328$). In topsoil, the total exchangeable base cations (BCs)—i.e. the sum of exchangeable K^+ , Ca^{2+} , Mg^{2+} , and Na^+ —of N569 was 34% lower than that of N0 (Table 1). While the BCs under the N569 treatment were significantly lower than under the N0 treatment, this difference became non-significant in subsoil (Table 1). Similar to BC, relative to N0, the BS was also significantly lower in the topsoil of N569 but was unaffected in the subsoil (Table 1).

3.3. Soil solution: pH and cations

Fig. 2 shows the changes in and relationships of pH and cations in the soil solutions with an increasing N application rate. The soil solution pH ranged from 2.9–4.8 at the –15 cm depth, and from 3.6–4.4 at the –90 cm depth. These pH values at the –15 cm depth was significantly negatively correlated with the N rate ($r^2 = 0.491$, $p < 0.001$) whereas it was not at the –90 cm depth ($r^2 < 0.01$, $p > 0.05$) (Fig. 2a).

The concentrations of Al^{3+} and Ca^{2+} in the soil solution at both depths were significantly increased by the N application rate (Fig. 2b,c). However, the responses of K^+ and Mg^{2+} in the soil solution differed depending on the sampling depth. They were increased significantly by the N application rate at the –15 cm depth, but non-significantly so at the –90 cm depth (Fig. 2d,e). The concentrations of Na^+ in the soil solution did not change significantly with N rate at either depth (Fig. 2f).

Relative to the control, the sum of cations (‘Cations’, i.e. Al^{3+} , Ca^{2+} , Mg^{2+} , K^+ , and Na^+) and base cations (BCs, i.e. Ca^{2+} , Mg^{2+} , K^+ , and Na^+) on a molar charge basis in the soil solution with high N treatment were increased by 4.2- and 2.2-fold at the –15 cm depth, and by 2.3- and 2.1-fold at the –90 cm depth, respectively.

In the soil solution at the –15 cm depth, the proportion of Ca^{2+} in the cations (i.e., $\text{Ca}^{2+}/\text{Cations}$) decreased from 59% under the N0 to 33% under the N569 treatment, whereas that of Al^{3+} ($\text{Al}^{3+}/\text{Cations}$) increased correspondingly from 18% to 44% (Fig. 2g,h). Accordingly, the molar charge ratio of $\text{Al}^{3+}/\text{Ca}^{2+}$ in the soil solution at the –15 cm depth was greater at increased levels of the N application rate ($r^2 = 0.552$, $p < 0.001$) (Fig. 2i). At the –90 cm depth, Al^{3+} and Ca^{2+} respectively accounted for 31%–53% and 29%–39% of the Cations, indicating that they co-dominated the soil solution contents (Fig. 2g, h). This suggested that the dominant cation had switched from being Ca^{2+} to Al^{3+} after the high N application was made.

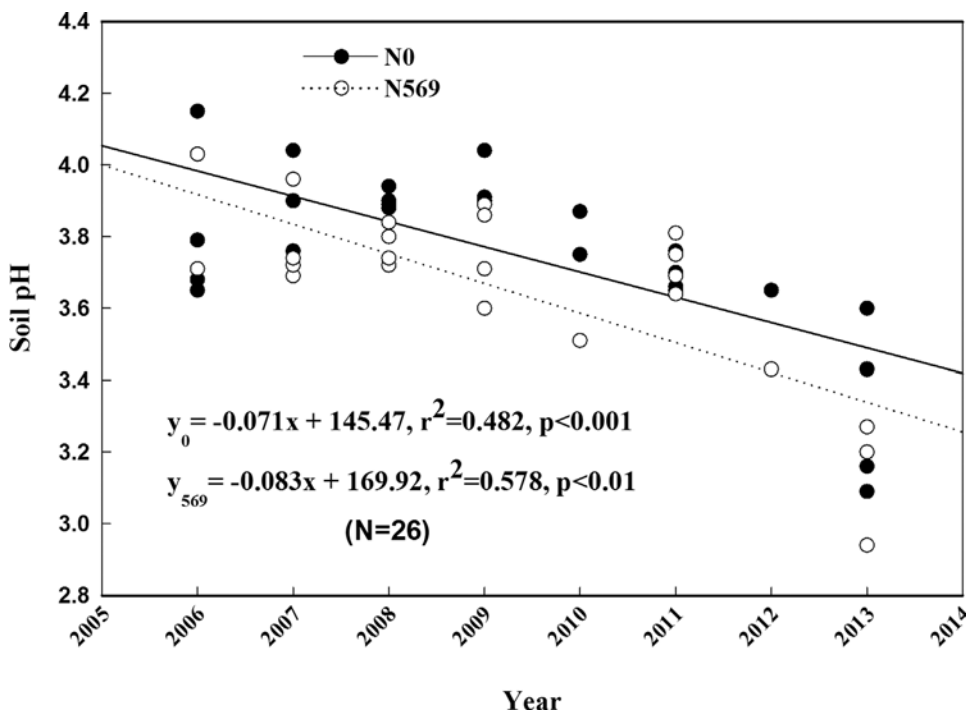


Fig. 1. The pH of surface soil (0–40 cm) treated with an N fertilization of 569 kg N ha⁻¹ yr⁻¹ (N569) and without N (N0) during an 8-year period for a tea plantation in China.

3.4. Anions in the soil solution

In contrast to inorganic N in the soil samples, NO₃⁻ was the dominant form of inorganic N in the soil solutions irrespective of the N treatment level, but it gradually increased with N application rate at both the -15 cm and -90 cm depths (r² = 0.579, p < 0.001 and r² = 0.73, p < 0.001, respectively) (Fig. 3a).

The concentration of SO₄²⁻ at the -15 cm depth was significantly reduced by N569, the high N application rate (r² = 0.246, p = 0.013), whereas no such change was observed at the -90 cm depth (r² < 0.01, p = 0.365) (Fig. 3b). Similar to NO₃⁻, The F⁻ concentration in the soil solution increased significantly with an increasing N application rate at both depths (Fig. 3c).

The molar charge sum of anions ('Anions') in the soil solution significantly increased at the both -15 cm and -90 cm depths with an increasing N application rate (r² = 0.402, p < 0.001 and r² = 0.487, p < 0.001, respectively). The dominant anion in the soil solution was

SO₄²⁻, except at the -15 cm depth in the high N treatment level, for which the dominant anion was NO₃⁻ (Fig. 3d,e). At both depths, however, the proportion of NO₃⁻ in the Anions increased with an increasing N application rate. The ratio of Cations/Anions (the molar charge sum of cations/the molar charge sum of anions) in the soil solution ranged from 1.0–3.3 at the -15 cm depth, and from 0.8–2.3 at the -90 cm depth, thus indicating that the predominance of Cations over Anions (Fig. 3f).

3.5. PLS regression

Many of the soil chemistry variables with were significantly correlated with each other (Table S3). The VIF with 11 explanatory variables (e.g., soil exchangeable Al³⁺, K⁺, Mg²⁺, Fe³⁺, and Ca²⁺) in the soil was 86.85, which is much higher than 10, the threshold value for judging collinearity among variables (VIF > 10 implies severe collinearity). Thus, doing here a multivariate linear regression with OLS

Table 1
Responses of soil pH and ion composition to N rates (N) and sampling depths (D).

Response variable	0–40 cm				40–90 cm				p value		
	N0	N119	N285	N569	N0	N119	N285	N569	N	D	N x D
Soil pH	3.32(0.12) ^{ab}	3.47(0.04) ^a	3.46(0.10) ^a	3.15(0.07) ^b	3.67(0.68) ^A	3.73(0.03) ^A	3.60(0.08) ^A	3.35(0.07) ^B	0.001	< 0.001	0.634
Exch NH ₄ ⁺ (mg kg ⁻¹)	11.25(2.22) ^a	11.53(1.14) ^a	12.81(0.99) ^{ab}	17.06(2.00) ^b	8.86(0.86) ^{ns}	10.06(0.96)	12.37(1.75)	11.58(1.00)	0.051	0.030	0.488
Exch NO ₃ ⁻ (mg kg ⁻¹)	4.15(1.06) ^a	9.33(1.41) ^b	12.79(1.62) ^{bc}	15.84(2.17) ^c	2.69(0.88) ^A	8.40(1.55) ^B	14.41(1.30) ^C	20.81(2.89) ^D	< 0.001	0.472	0.317
NH ₄ ⁺ /NO ₃ ⁻	3.03(0.62) ^a	1.29(0.15) ^b	1.04(0.14) ^b	1.09(0.04) ^b	5.29(2.11) ^A	1.25(0.13) ^B	0.85(0.08) ^B	0.58(0.06) ^B	0.003	0.547	0.392
Exch Fe ³⁺ (cmol kg ⁻¹)	1.08(0.11) ^{ns}	0.80(0.28)	1.02(0.45)	0.92(0.15)	0.87(0.24) ^{ns}	0.87(0.12)	1.04(0.34)	1.13(0.37)	0.867	0.909	0.884
Exch Mn ²⁺ (cmol kg ⁻¹)	3.31(0.61) ^a	2.48(0.32) ^{ab}	3.51(0.35) ^a	1.51(0.27) ^b	1.20(0.15) ^{ns}	1.60(0.33)	1.70(0.17)	1.12(0.18)	0.011	< 0.001	0.077
Exch Al ³⁺ (cmol kg ⁻¹)	4.98(0.08) ^a	5.07(0.34) ^{ab}	5.32(0.25) ^{ab}	5.88(0.25) ^b	5.11(0.16) ^A	5.11(0.17) ^A	5.53(0.19) ^{AB}	5.76(0.13) ^B	0.004	0.684	0.888
Exch H ⁺ (cmol kg ⁻¹)	1.54(0.10) ^{ns}	1.53(0.02)	1.61(0.20)	1.66(0.11)	1.64(0.03) ^{ns}	1.53(0.06)	1.52(0.04)	1.60(0.08)	0.725	0.871	0.793
Exch Ca ²⁺ (cmol kg ⁻¹)	1.24(0.21) ^a	0.98(0.10) ^{ab}	0.93(0.02) ^{ab}	0.75(0.03) ^b	0.64(0.06) ^{ns}	0.58(0.02)	0.67(0.06)	0.69(0.11)	0.223	< 0.001	0.093
Exch Mg ²⁺ (cmol kg ⁻¹)	0.34(0.03) ^a	0.28(0.02) ^{ab}	0.27(0.01) ^{ab}	0.24(0.01) ^b	0.21(0.03) ^{ns}	0.20(0.01)	0.20(0.01)	0.19(0.01)	0.055	< 0.001	0.264
Exch K ⁺ (cmol kg ⁻¹)	1.24(0.21) ^a	1.38(0.10) ^a	1.12(0.02) ^{ab}	0.85(0.03) ^b	0.75(0.05) ^A	0.98(0.08) ^B	0.77(0.03) ^A	0.69(0.02) ^A	0.003	< 0.001	0.378
Exch Na ⁺ (cmol kg ⁻¹)	0.11(0.01) ^{ns}	0.13(0.02)	0.11(0.01)	0.11(0.01)	0.11(0.02) ^{ns}	0.11(0.01)	0.11(0.01)	0.12(0.02)	0.055	< 0.001	0.264
CEC (cmol kg ⁻¹)	9.46(0.30) ^{ns}	9.37(0.28)	9.37(0.17)	9.48(0.35)	8.46(0.28) ^{ns}	8.51(0.23)	8.79(0.14)	9.06(0.14)	0.328	0.012	0.933
ANC (cmol kg ⁻¹)	0.74(0.04) ^a	0.50(0.07) ^{bc}	0.62(0.08) ^{ab}	0.48(0.02) ^c	0.26(0.03) ^{ns}	0.30(0.05)	0.24(0.02)	0.31(0.06)	0.154	< 0.001	0.016
BC (cmol kg ⁻¹)	2.94(0.31) ^a	2.78(0.17) ^a	2.44(0.09) ^{ab}	1.95(0.13) ^b	1.71(0.14) ^A	1.87(0.07) ^B	1.74(0.06) ^{AB}	1.70(0.12) ^A	0.005	< 0.001	0.649
BS	0.31(0.25) ^a	0.30 (0.20) ^a	0.26(0.12) ^{ab}	0.21(0.01) ^b	0.20(0.01) ^{ns}	0.22(0.01)	0.20 (0.01)	0.19(0.01)	0.002	< 0.001	0.057

Values are means and standard errors. Different letters or "NS" indicate significant (p < 0.05) or insignificant differences at the specified depth (p < 0.05).

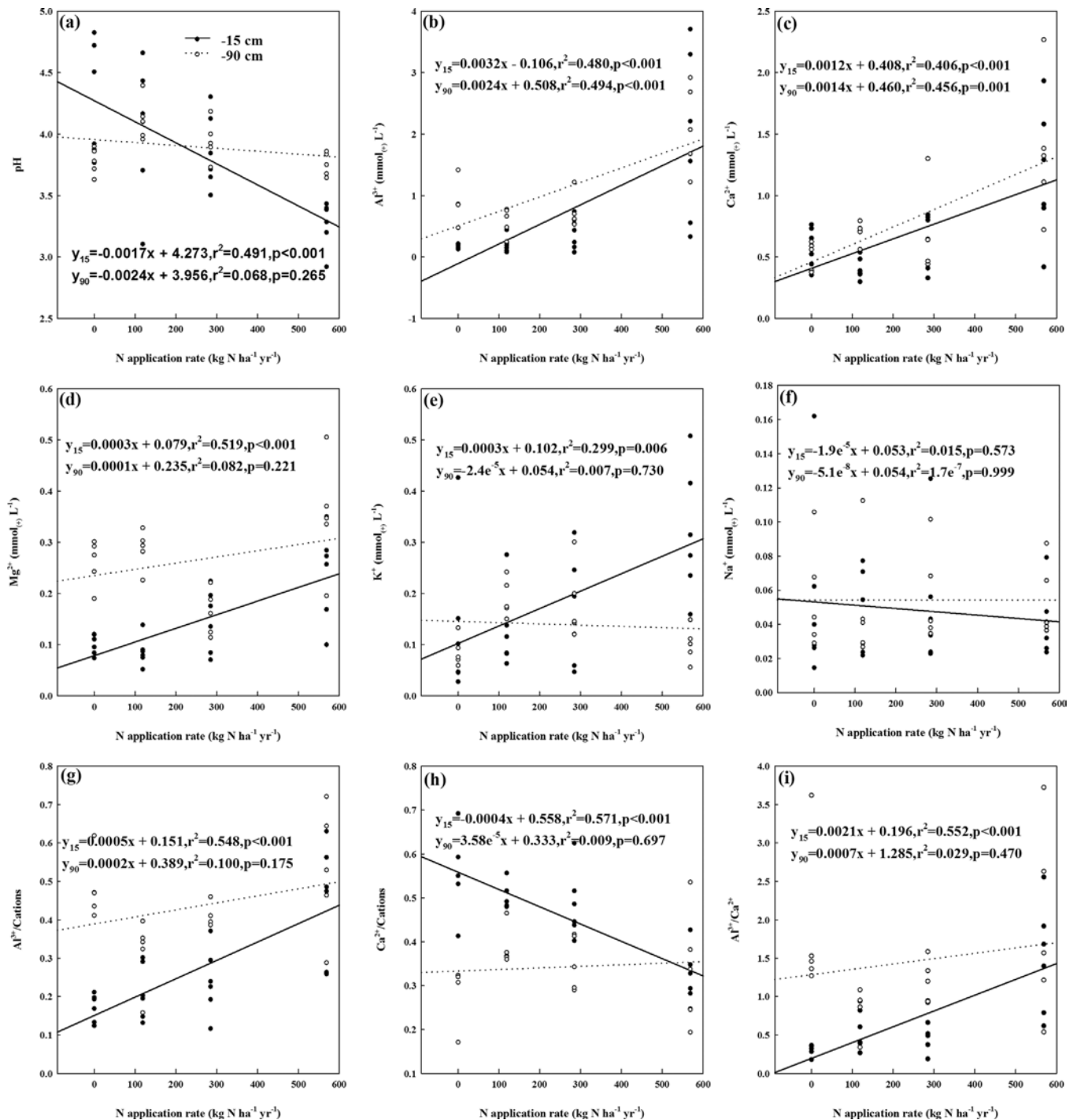


Fig. 2. Linear regressions of pH (a), cation contents (b-f), and cation indicators (g-i) as a function of N fertilization levels in the sucked solution collected from two soil depths (-15 and -90 cm).

would lead to inappropriate statistical inference. PLS regression overcomes the limitation of collinearity by projecting the explanatory variables onto orthotropic axes (components), and then calculating the correlation between the dependent variables and the projected components.

In PLS score plot, the first two components respectively captured 42.8% and 13.2% of the variation in the explanatory variables for the topsoil. The PLS model successfully modeled pH variance, since the R₂Y was 74.7% (Fig. 4a). For the subsoil, the first two components accounted for 44.5% of the variation in soil ion composition, but 90.6% of pH variation (Fig. 4b).

The loading plots of the variables are shown in Fig. 4c,d. The soil exchangeable base cations (i.e., Ca²⁺, Mg²⁺, K⁺, and Mn²⁺), H⁺, and exchangeable NH₄⁺ showed strong correlation effects with soil pH, since their positions were far from the origin. The PLS regression coefficients make it possible to explain how strongly Y is correlated to the systematic part of each of the X variables. Since all the variables were scaled in the PLS regression, the coefficients could be interpreted to indicate the sensitivity of the variables. In the topsoil, H⁺, K⁺, NH₄⁺, Fe³⁺, and Mn²⁺ showed strong sensitivity to pH, while in the subsoil, Al³⁺, Ca²⁺, Mg²⁺, and NO₃⁻ also became important (Fig. 4e,f).

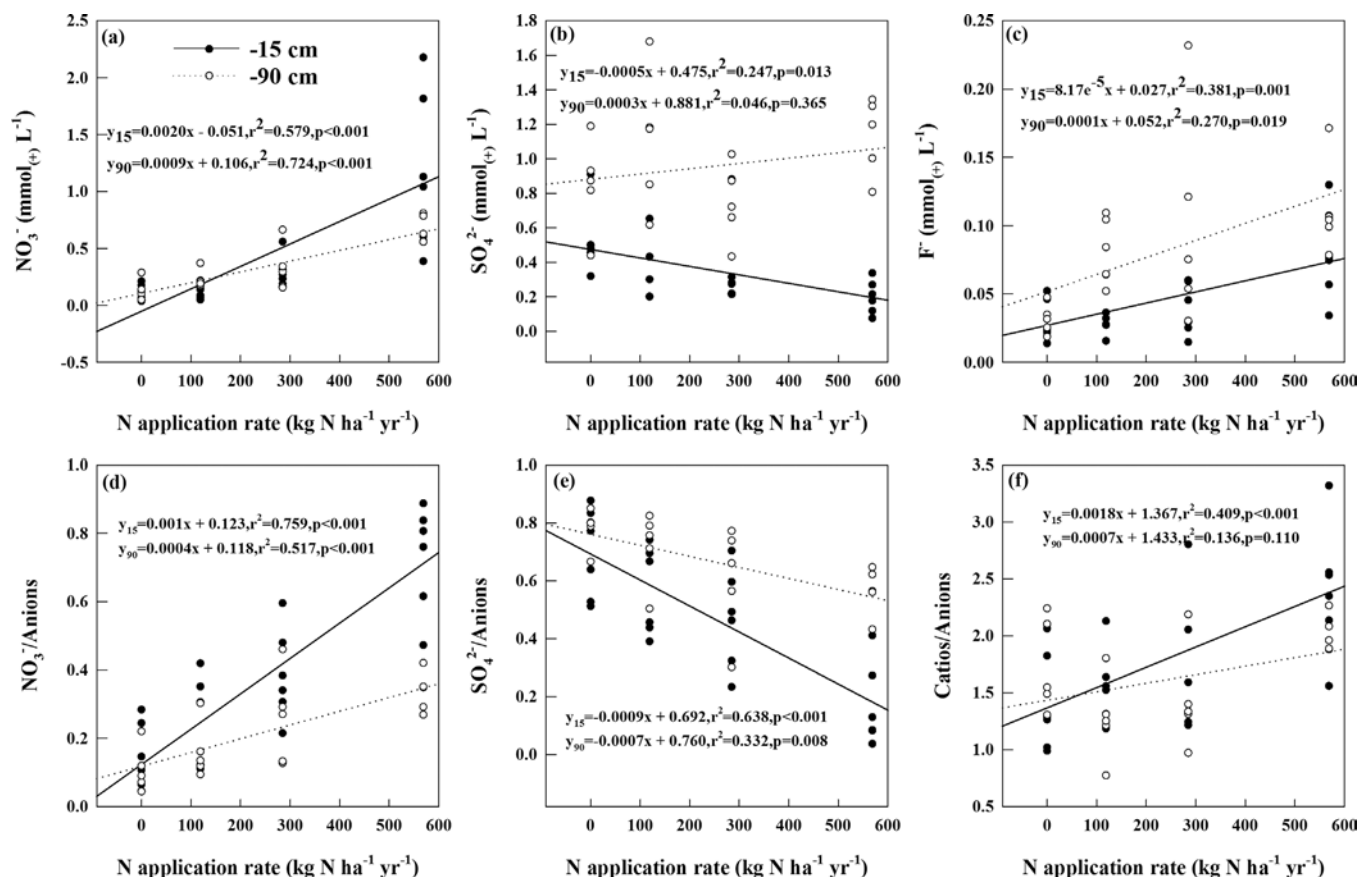


Fig. 3. Linear regressions of the anion contents (a–c) and anion indicators (d–f) as a function of N fertilization levels in the sucked solution collected from two soil depths (–15 and –90 cm) for a tea plantation in China.

Variable importance for the projection (VIP) quantifies how important the variables are for explaining X and for correlating to Y. In the topsoil, the K⁺, NH₄⁺, H⁺ and NO₃⁻ were more important than the other variables, whereas NO₃⁻, Al³⁺, K⁺ and Mn²⁺ were the most important variables in subsoil, since their VIP-values > 1 (Fig. 4g,f).

4. Discussion

4.1. Acidification characteristics of the tea plantation soil

Soil acidification could happen naturally during tea cultivation, even without any imposed N additions (Abe et al., 2006; Oh et al., 2006; Wang et al., 2010). From 2005 to 2013, the surface soil pH in the plots without N fertilization annually decreased by 0.071 (Fig. 1). This result contrasts with that of Li et al. (2016a, 2016b), who reported the pH increasing in the surface soil (0–40 cm) in a long-established tea plantation in Southern China. This discrepancy may be partly attributed to the higher plant density in our present study. One of the representative interpretations for soil acidification in tea plantation is root-excreting acidic compounds, such as organic acids, carbonic acid, and polyphenols (Yang, 2005). Different from other researches using chronosequence tea plantation, which may have different N levels or initial status (Li et al., 2016a,b), the present study established the long-term fertilization experiment to avoid this possible flaw. Nevertheless, more long-term validation is still required, since the presented results were only drawn from 8 years' observation.

The soil in the present experiment was highly acidified, with a pH of 3.15–3.47, which agrees well with pH values reported for Chinese and Japanese tea plantations (Oh et al., 2006; Ruan et al., 2004). The low pH in the subsoil at a depth of 40–90 cm (pH range: 3.35–3.73), suggests acidification occurred far below the ground, in deep soil. An

earlier study also found that soil acidification induced by a tea plantation extended downward to a depth of 70 cm (Alekseeva et al., 2011).

Soil acidification status can be coarsely classified into 'very strong', according to the scheme based on soil pH values and the fraction of exchangeable acid cations (H⁺, Al³⁺, Mn²⁺, Fe³⁺) proposed by Blaser et al. (2008). This strong soil acidification under tea plantation implied the requirement of the addition of alkaline material, such as slag (Minasny et al., 2016), biochar (Dai et al., 2014) and plant residues (Tang and Yu, 1999) to mitigate the soil acidification in tea plantation.

For both depths in our study, the soil featured a low CEC and low BS, but a high proportion of exchangeable Al³⁺, a finding frequently reported for tropical and subtropical forest ecosystems (Lu et al., 2014). The exchange sites among the soil structure complex were mostly occupied by the exchange acidity (exchangeable Al³⁺ and H⁺). The fractions of exchange acidity in the CEC had a range of 75%–85%. Furthermore, given that exchangeable Al³⁺ accounted for 76%–78% of the total exchange acidity, it clearly played a predominant role in driving soil acidity at the studied tea plantation.

4.2. Accelerating soil acidification through N application

We found that a high N application (N569) caused significant pH reductions, by 5% and 8% at the depths of 0–40 cm and 40–90 cm, respectively. This finding confirmed the downward acidification in the soil profile (Li et al., 2016a,b), and further indicates that the subsoil is likely more vulnerable to the overuse of N fertilizers in tea plantation systems.

Protons and Al³⁺ are the two important ions for soil acidity. While we found that Al³⁺ was increased by the N applications, H⁺ did not, a result differing from that observed in Chinese tropical forest soils, where N deposition contributed to an increased exchangeable H⁺, CEC,

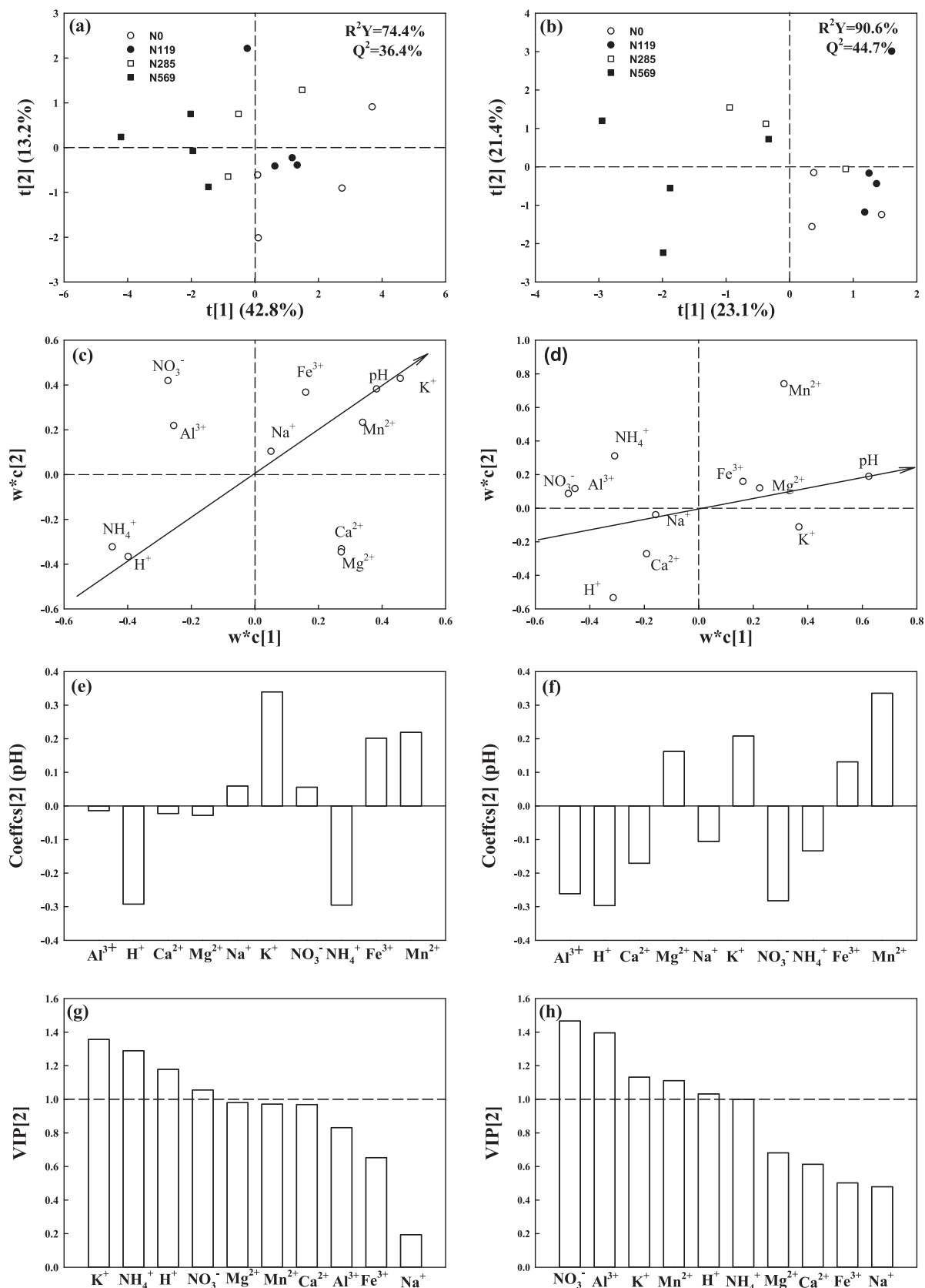


Fig. 4. Scores (a, b), loadings (c, d), coefficients (e, f), and VIP (g, h) plots for the PLS regression of pH with the soil ion composition variables for soil depths of 0–40 cm (left panels) and 40–90 cm (right panels) for a tea plantation in China.

Table 2

Pearson correlation coefficients of the soil solution properties at both –15 cm and –90 cm depths. BCs, Sum concentrations of base cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+); Cations, sum concentrations of cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , Al^{3+}); Anions, sum concentrations of anions (NO_3^- , SO_4^{2-} , F^- , Cl^-); An- NO_3^- , sum concentrations of anions without NO_3^- .

	Depth –15 cm (n = 24)			Depth –90 cm (n = 20)		
	N rate	pH	NO_3^-	N rate	pH	NO_3^-
pH	–0.67**	/	–0.63**	–0.26	/	–0.39
Al^{3+}	0.68***	–0.62**	0.98***	0.70***	–0.64**	0.73***
Ca^{2+}	0.64**	–0.58**	0.89***	0.68**	–0.26	0.81***
Mg^{2+}	0.70***	–0.68**	0.88***	0.29	–0.19	0.45*
K^+	0.68***	–0.74***	0.85***	–0.08	0.40	0.09
NH_4^+	0.69***	–0.47*	0.24	0.56**	0.01	0.24
Cations	0.71***	–0.65**	0.97***	0.80***	–0.55*	0.90***
BCs	0.67**	–0.64**	0.90***	0.60**	–0.21	0.77***
NO_3^-	0.74***	–0.63**	/	0.85***	–0.39	/
SO_4^{2-}	–0.48*	0.08	–0.45*	0.21	0.16	0.05
F^-	0.62**	–0.67**	0.91***	0.52*	–0.18	0.73***
Anions	0.62**	–0.68**	0.93***	0.70***	–0.13	0.70***
An- NO_3^-	–0.43	–0.03	–0.34	0.30	0.12	0.19

and soil acidification but did not change the exchangeable Al^{3+} (Lu et al., 2014). Such a discrepancy likely reflects different responses to different soil properties in ecosystems to N addition, either as deposition or fertilization (Tian and Niu, 2015). Nonetheless, while H^+ did not change markedly in response to the N application rates, the PLS results showed that H^+ , rather than Al^{3+} , was more sensitive to soil pH and very important variable for predicting soil pH (Fig. 4). This was inferred from the lower deviation of Al^{3+} than H^+ , since PLS attribute a higher weighting coefficient to the variable that has higher variation.

In the high N application (N569), Al^{3+} displaced Ca^{2+} as the dominant cation in the surface soil solution (Fig. 3). Therefore, it is quite probable that Al^{3+} plays a critically important role beyond the base cations (Ca^{2+} , Mg^{2+} , and K^+) in buffering against soil acidification as induced by high N application in tea plantations (De Vries and Breeuwsma, 1987; Tian and Niu, 2015). This finding agrees well with the general view that buffering by Al^{3+} becomes the most important component under conditions of low soil pH (< 4.2), or once the base cations have been exhausted (Ulrich, 1986; Blaser et al., 2008). Deeper underground in the subsoil solution, Al^{3+} was the dominant cation at a charge basis, a result similar to a previous finding in a Netherland forest affected by acid deposition (Mulder and Stein, 1994).

A possible explanation for the higher Al^{3+} under the high N treatment is the dissolution of hydroxyl-Al interlayers caused by H^+ during mineral weathering (Alekseeva et al., 2011). This would occur if more H^+ were produced via nitrification under the high N application so that more Al^{3+} were released from the hydroxyl-Al interlayers. This interpretation is supported by the positive correlations we found between the concentrations of Al^{3+} and NO_3^- , and with the N application rates (Table 2). The tea plant is well known as a typical Al accumulator, able to uptake large amounts of Al from soil; hence, the return of plant Al from the leaves to the soil via pruning and subsequent decomposition may also be a factor that contributes to the higher Al^{3+} after high N treatment (Ding and Huang, 1991). But the relative contribution from the dissolution of the hydroxyl-Al interlayers by more proton production and from the return of Al via litter remains unclear. There relative contributions may be important for explaining the different dynamics driving the direction of pH changes due to organic fertilization (Ruan et al., 2004; Wang et al., 2009; Li et al., 2016a,b).

Under a high N input to soils, released protons (H^+) may replace the soil exchange sites of base cations, thus displacing the base cations into the soil solution (Schulze, 1989; Edwards et al., 2002; Tomlinson, 2003). This effect was supported by our results for the base cations (e.g., Ca^{2+} , Mg^{2+} and K^+) in the soil solution, whose concentrations all increased with the N application rate (Fig. 2), in addition to their

significantly reduced contents in the soil (Table 1). The replaced base cations are liable to loss through soil NO_3^- leaching. A significantly higher NO_3^- accumulation in the soil solution occurred under the high N treatment (Fig. 3a). The significantly positive correlations found between the NO_3^- and the base cations in the soil solutions at both depths (Table 2) suggests that the leaching of NO_3^- was accompanied by cations in an equivalent quantity (Lucas et al., 2011; Fatemi et al., 2012; Cusack et al., 2016). Stronger leaching of base cations under high N fertilization also caused the reduction of BS, which implies a decrease in the soil acidity buffering capacity. Finally, the reduction of base cations in the soil, e.g. Ca^{2+} , Mg^{2+} and K^+ , points to potential nutrient deficiencies occurring after soil acidification as consequence of heavy N inputs.

5. Conclusions

The presented study confirmed that naturally occurring soil acidification occurs in a tea plantation at an estimated annual rate of 0.071. A high N application accelerated the soil acidification process, and reduced the ANC and BS, whereas apparently neither low N nor moderate N applications influenced the soil acidity. The applied N rate also significantly altered the cation and anion composition in both the topsoil and subsoil. Base cations were remarkably decreased under the high N treatment in the topsoil, but no so in the subsoil. Conversely, the high N input favored the accumulation of exchangeable Al^{3+} , rather than exchangeable H^+ , in both the topsoil and subsoil. Based on these results, an appropriate synthetic N application rate or alkaline materials should be recommended in tea plantations to mitigate the risk of soil acidification and deficiencies in the vital nutrients K^+ , Ca^{2+} , and Mg^{2+} .

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.agee.2017.10.004>.

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