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The conversion of tropical forests to rubber plantations accelerates soil acidification and changes the distribution of soil metal ions in topsoil layers

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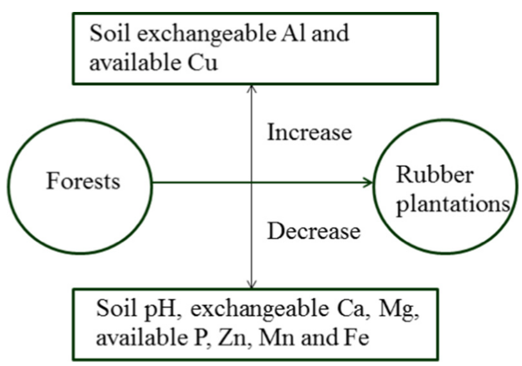
HIGHLIGHTS

- Conversion of tropical forests to rubber plantations led to soil acidification.
- Conversion of tropical forests to rubber plantations caused leaching of base cations.
- Conversion of tropical forests to rubber plantations increased soil available Al.
- Conversion of tropical forests to rubber plantations decreased available Zn and Mn.

GRAPHICAL ABSTRACT

Soil pH, exchangeable Ca, Mg, Al, available P, Cu, Zn, Mn and Fe in topsoil layers of tropical forests and rubber plantations.



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ABSTRACT

Unprecedented economic growth in Southeast Asia has encouraged the expansion of rubber plantations. This study aimed to clarify the effects of the conversion of tropical forests to rubber plantations on soil acidification processes, exchangeable cations, exchangeable aluminum (Al), available copper (Cu), zinc (Zn), manganese (Mn) and iron (Fe). The results showed that these conversions significantly decreased soil pH, exchangeable Ca, Mg, available Zn, Mn and Fe, and increased exchangeable Al and available Cu in the topsoil layers. In both the rainy and dry seasons, the conversion of tropical forests to mature rubber plantations increased the average soil exchangeable Al by 930.1 and 54.4%, and soil available Cu by 82.7 and 65.8%, and decreased soil pH by 13.4 and 9.9%, soil exchangeable Ca by 70.9 and 79.9%, soil exchangeable Mg by 76.5 and 77.8%, soil available Zn by 73.8 and 51.6%, soil available Mn by 33.1 and 47.5% and soil available Fe by 15.9 and 22.2% in the 0–10 and 10–30 cm soil layers, respectively. The change of soil exchangeable Al was greatly affected by soil acidification processes and soil organic carbon, exchangeable Ca, Mg and available Cu was greatly affected by soil acidification

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Soil pH
Xishuangbanna

processes, as were available Zn, Mn, and Fe by soil organic carbon. The large losses of soil exchangeable Ca, Mg, and available Zn in the rubber plantations limited plant growth. The release of large amounts of exchangeable Al in the rubber plantations not only decreased soil available P but also threatened the safety of the surrounding environment.

1. Introduction

In 2018, worldwide demand for natural rubber reached 13.78 million tons (http://www.rubberstudy.com/). Southeast Asia is the epicenter of the world's natural production (Warren-Thomas et al., 2015). In Southeast Asia, >5 million ha of non-traditional rubber growing land has been converted into rubber plantations to satisfy the rapidly growing demand for natural rubber from 1961 to 2014 (FAO, 2017). The projected rubber demand is likely to require another 4–8.5 million ha of land globally by 2024, which will threaten significant areas of Asian forest (Warren-Thomas et al., 2015). Xishuangbanna is the most biodiverse area of China (Mann, 2009), located in the Indo-Burma biodiversity hotspot (Myers et al., 2000). Currently, the tropical rainforests of Xishuangbanna in southwestern China have been deforested and replaced with >0.47 million ha of rubber plantations, or >24% of the total land area (Mei, 2015). To improve rubber production, large amounts of nitrogen fertilizer have been applied to these rubber plantations each year (Zhou et al., 2016), along with sulfur powder to control rubber powdery mildew. Nitrogen and sulfur or their depositions (e.g., SO_2 and NOx) are major drivers of soil acidification in cropland, grassland and forest ecosystems (Rodríguez-Lado and Macías, 2006; Liu et al., 2013; Guo et al., 2018; Chen et al., 2019a). Therefore, the application of nitrogen fertilizer and sulfur powder in rubber plantations may have caused soil acidification.

Soil base cations are important for maintaining soil buffering and storage capacities, which represent the major plant-available reservoir (Kopittke et al., 2017; Rheinheimer et al., 2018). Soil acidification, induced by long-term nitrogen application, significantly reduced soil exchangeable Ca, Mg, and K in tea plantation fields in China (Yang et al., 2018). Nitrogen deposition could affect forest soil properties, and cause leaching of base cations (particularly exchangeable Ca and Mg) (Lu et al., 2009). The leaching of base cations threatens the sustainability of agricultural systems and forest ecosystems.

Aluminum (Al) is the third most abundant and ubiquitously distributed metallic element and mainly occurs as harmless oxides and aluminosilicates. When soil becomes acidic, the extractable-exchangeable Al is released, which rapidly inhibits root elongation, and subsequently affects nutrient uptake (Singh et al., 2017; Hubová et al., 2018). Al toxicity is a major limiting factor for plant growth in acidic soils (Chen and Liao, 2016), and many plant species are sensitive to high contents of extractable-exchangeable Al (Ávarez et al., 2005; Alleoni et al., 2010). Aluminum toxicity reduces microbial activity and biomass by repressing soil enzyme activities (Kunito et al., 2016). It has been determined that, when soil pH falls below 5.5 in acidic soils, a large amount of soluble ionic Al will be released (Kabata-Pendias and Pendias, 2001; Alleoni et al., 2010). Nitrogen fertilization and the deposition of sulfur and nitrogen are major drivers of soil acidification (Lajtha and Jones, 2013; Yang et al., 2018). Aluminum can participate in strong complexation reactions with organic matter (SOM) in the soil, and the mixing of some biocharsh as strongly reduced the leaching effects of soluble ionic Al (Wang et al., 2016; Gu et al., 2017).

Copper (Cu) is a redox-active metal, and moderate amounts of Cu can promote plant growth. However, when the soil Cu content reaches or exceeds a certain concentration, it will affect photosynthesis, respiration and water metabolism, which slows plant growth (Peng et al., 2013; Adrees et al., 2015; Ivanov et al., 2016). Soil available Cu increased significantly with increasing acidification, and a significant negative correlation has been observed between soil available Cu and pH in acidic soils (Wang et al., 2008; Song et al., 2014; Fernández-Calviño and Bååth, 2016). Zinc (Zn), Manganese (Mn) and Iron (Fe) are essential elements for plant growth. The concentrations of available Zn, Mn, and Fe in the soil depend on soil pH, and a negative correlation between soil pH and availability of Zn, Mn and Fe to plants has been well documented (Chen et al., 2002; Zeng et al., 2011; Zhao et al., 2011). Soil organic matter content is another important factor affecting the availability of Zn, Mn and Fe in soils (Zeng et al., 2011; Rutkowska et al., 2014; Halim et al., 2015; Chen et al., 2019b).

Soil acidification in rubber plantations may lead to leaching of soil exchangeable Ca, Mg, K and Na in the topsoil layers. The conversion of tropical forests to rubber plantations has significantly reduced organic carbon (SOC) in the topsoil layers (de Blécourt et al., 2014). Soil acidification, along with reduced SOC in rubber plantations, may have accelerated the release of exchangeable Al. Phosphate anions have been immobilized by Al through sorption and/or precipitation, which has reduced available P (Sherman et al., 2006). Soil acidification and reduced SOC in rubber plantations may also affect the distribution of soil available Cu, Zn, Mn, and Fe in the topsoil layers.

This study tested the following hypotheses: (1) the conversion of tropical forests to rubber plantations has decreased soil pH, enhanced leaching of exchangeable cations and increased exchangeable Al; (2) the increase in soil exchangeable Al in rubber plantations has decreased soil available P; (3) changes in soil available Cu, Zn, Mn, and Fe have greatly affected soil pH and SOC in rubber plantations.

2. Materials and methods

2.1. Description of the study site

This study was conducted in the Xishuangbanna region (21°33'N, 101°28'E; 880 to 900 m asl) of Yunnan Province, which is located in southwestern China. The region is characterized by a typical tropical monsoon climate, with an annual mean temperature of 21.8 °C. The area receives mean annual precipitation of approximately 1500 mm, 80% of which occurs during the May to October rainy season (Li et al., 2012). Xishuangbanna contains the largest tropical rainforest area in China. As part of the Indo-Burma world biodiversity hotspot, it has rich biodiversity (Myers et al., 2000). The soils in this area are rhodic ferralsol, according to the world soil classification system (FAO/UNESCO, 1988).

Between 1991 and 2000, tropical forests with slopes ranging from 25 to 30° were deforested. Rubber trees were planted on these sites in May 1994 and 2003 at a density of 450 rubber trees ha^{-1} (2.5 m spacing with in rows and 8 m spacing between rows). In accordance with the local practices for rubber trees less than three years of age, fertilizers were applied between the rubber trees at depths of 20 cm using spades at rates of 27.0 kg ha^{-1} N, 5.9 kg ha^{-1} P and 11.2 kg ha^{-1} K, which were split into two applications per year (May and October). After three years, the fertilizer application rates changed to 54.0 kg ha^{-1} N, 11.8 kg ha^{-1} P and 22.4 kg ha^{-1} K. Rubber plantation farmers generally spray sulfur powder at 30–60 kg ha^{-1} y^{-1} to control powdery mildew on the rubber trees. Weeds in the plantations were cut using a sickle twice per year (April/May and November/December) and left on the ground. From 9 to 10 years onward, rubber trees are tapped from April to November, with rubber latex harvested every second day.

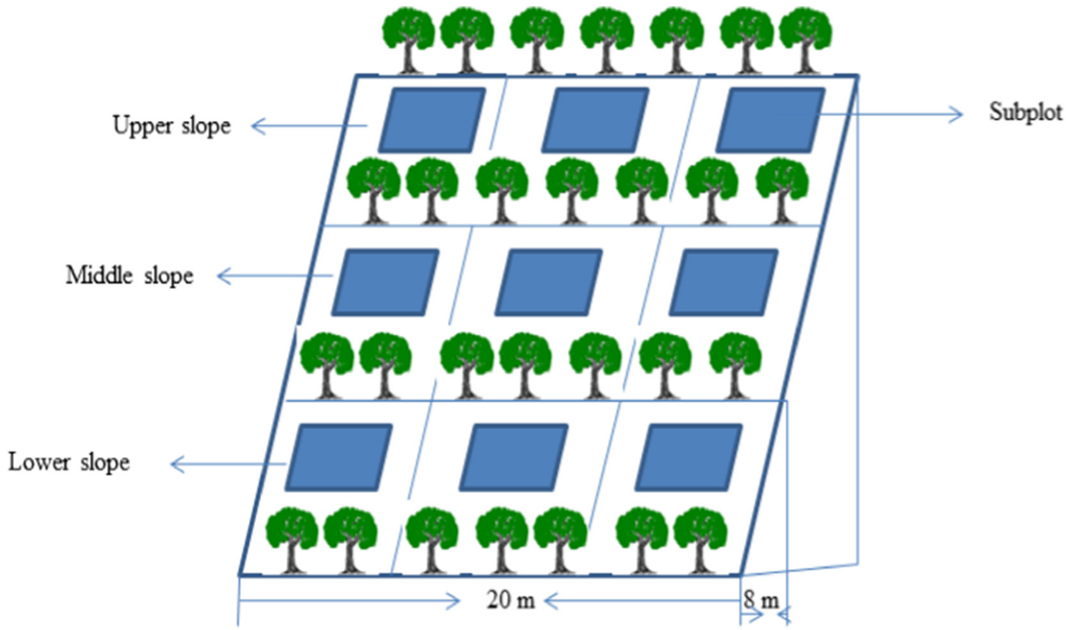

Fig. 1. Sketch of sampling design for each replicate site (three per cover type) in tropical forests and different-aged rubber plantations.

2.2. Experimental design, sampling, and measurements

The tropical forests (F) and two different-aged rubber plantations (R1, 13-years-old, and R2, 22-years-old, in 2016) were selected for this study. The tropical forest was located approximately 500 m from the rubber plantations. Three replicate sites were chosen within the tropical forests and the two rubber plantations. Each replicate site consisted of 20 × 25 m^2 survey plots (four rows of rubber trees, and three 8-m wide hedgerows for the different-aged rubber plantations) containing nine sampling subplots (8 × 6 m^2), with three located at

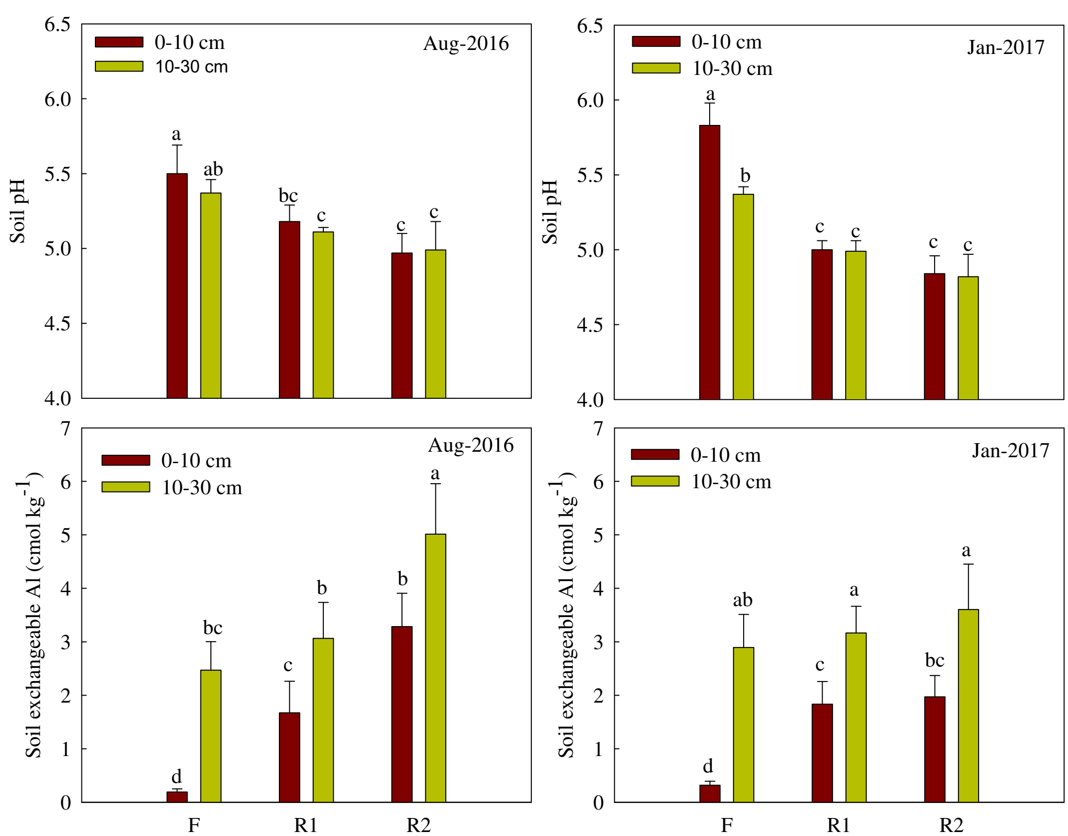

Fig. 2. Soil pH and exchangeable Al in the 0–10 and 10–30 cm soil layers of tropical forests and rubber plantations. Different letters indicate significant differences at $P \leq 0$ 0.05. Bars are standard deviations of the mean ($n = 3$). F: Tropical forests; R1: Rubber plantations established in 2003; R2: Rubber plantations established in 1994.

each slope position (upper, middle, and lower slope) (Fig. 1). The angle inclination in each slope position is about 25°.

For each of the nine subplots, soil samples were collected using a soil auger, avoiding the fertilization holes, at two depths (0–10 cm and 10–30 cm) after carefully removing the litter-fall and/or grass layer. The soil core samples were collected in August 2016 (rainy reason) and January 2017 (dry season). The nine soil cores at each replication site were combined into a composite sample, which was air-dried, ground, and sieved (at<2 mm) to measure pH, NH_4^+, NO_3^-, AP, exchangeable Ca, Mg, K, Na, exchangeable Al and available Cu, Zn, Mn and Fe. The samples were then sieved again (at<0.25 mm) to determine SOC and TP content.

The soil pH values were determined in CO_2-free de-ionized water using a pH electrode, with a soil-liquid ratio of 1:2.5 (*w*/*v*). Dried samples, each weighing 5 g, were added to 50 mL of 2 M KCl, shaken for one hour, and analyzed with an Auto Analyzer 3 (SEAL Analytical GmbH, Germany) to determine NH_4^+ and NO_3^- contents (Zhong et al., 2015). Soil AP was extracted using 0.03 mol L^{-1} of NH_4F and 0.025 mol L^{-1} of HC1 and then analyzed colorimetrically (Anderson and Ingram, 1989). Soil exchangeable Ca, Mg, K and Na were extracted with 1 mol L^{-1} NH_4OAc, and the concentrations of the cations in the extracts measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) (Yuan et al., 2007). Exchangeable Al was extracted using1 mol^{-1} of KC1 and determined by titration with NaOH (Hou et al., 2012). Available Cu, Zn, Mn, and Fe were determined by ICP-AES (iCAP 6300, Thermo Fisher Scientific U.S.A). Cu and Zn were extracted with 0.1 mol L^{-1} HCl, Mn, and Fe were extracted with 0.005 mol L^{-1} DTPA +0.01 mol L^{-1} $CaCl_2$ + 0.1 mol L^{-1} TEA. The SOC

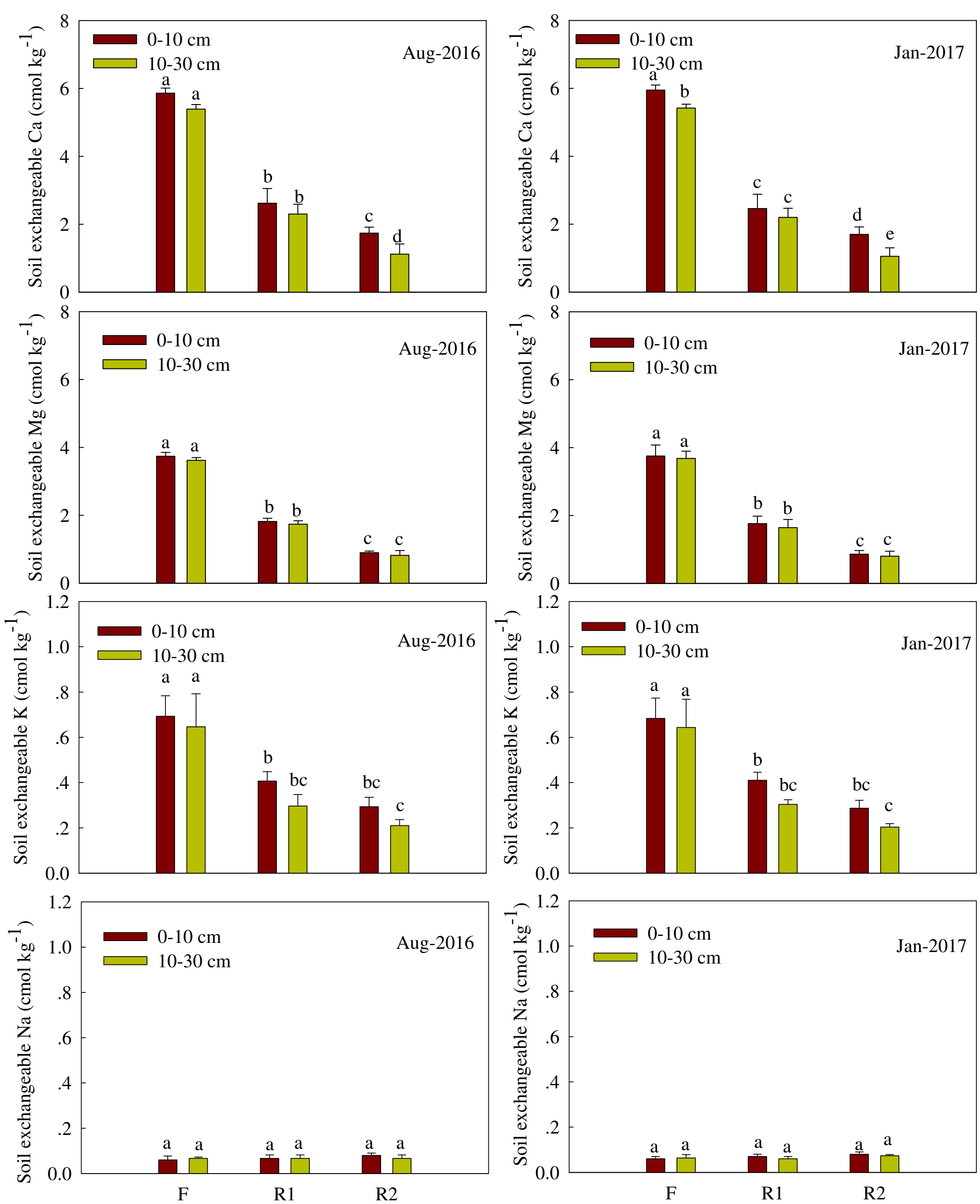

Fig. 3. Soil exchangeable Ca, Mg, K and Na in the 0–10 and 10–30 cm soil layers of tropical forests and rubber plantations. Different letters indicate significant differences at $P \le 0.05$. Bars are standard deviations of the mean ($n = 3$). F: Tropical forests; R1: Rubber plantations established in 2003; R2: Rubber plantations established in 1994.

of the bulk soil was determined with a Vario MAX CN-Analyzer (Elementar Analysensysteme GmbH, Germany). Soil TP was determined colorimetrically following digestion with perchloric acid.

2.3. Statistical analysis

Statistical analysis was carried out using the SAS statistical analysis software version 8.0. Differences between tropical forests and different-aged rubber plantations were evaluated with Duncan's multiple range test at $P \le 0.05$. Proc CORR in SAS was used to examine correlation relationships between variables. A path analysis model was used to determine the effects of pH, SOC, soil layers, and seasons on soil exchangeable Ca, Mg, Al, available Cu, Zn, Mn, and Fe.

3. Results

3.1. Soil pH, exchangeable cations, exchangeable Al, and available Cu, Zn, Mn, and Fe

In the dry (August 2016) and rainy (January 2017) seasons, soil pH in the 0–10 and 10–30 cm soil layers was significantly higher in F than R1 and R2, with no significant differences between R1 and R2 (Fig. 2).

In the dry and rainy seasons, soil exchangeable Ca and Mg in the 0–10 and 10–30 cm soil layers decreased significantly, in the order F > R1 > R2 (Fig. 3). In the dry and rainy seasons, soil exchangeable K in the 0–10 and 10–30 cm soil layers was significantly higher in F than R1 and R2, with no significant differences between R1 and R2. Soil layers had no significant effect on the distribution of soil exchangeable Mg and

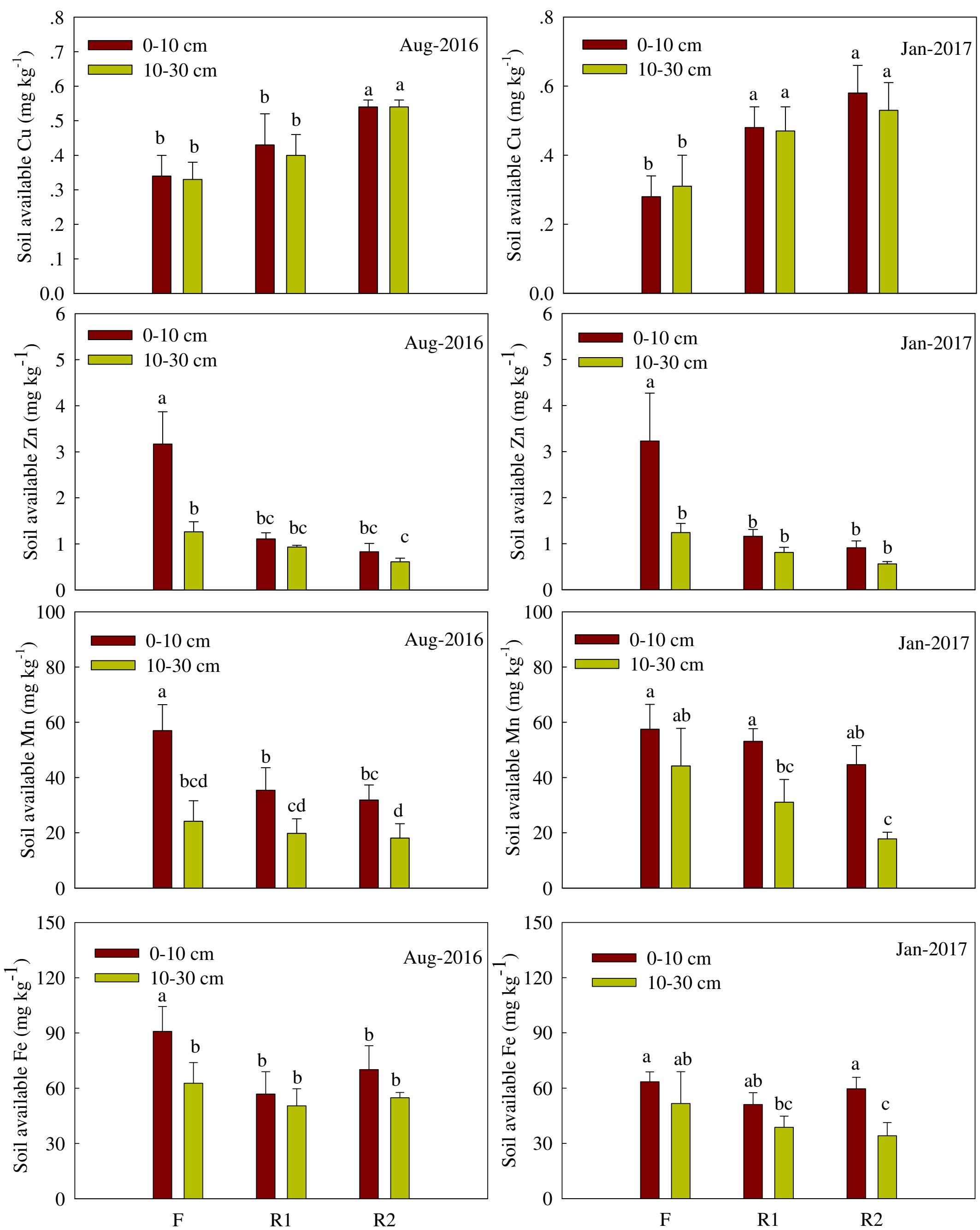

Fig. 4. Soil available Cu, Zn, Mn and Fe in the 0–10 and 10–30 cm soil layers of tropical forests and rubber plantations. Different letters indicate significant differences at $P \le 0.05$. Bars are standard deviations of the mean ($n = 3$). F: Tropical forests; R1: Rubber plantations established in 2003; R2: Rubber plantations established in 1994.

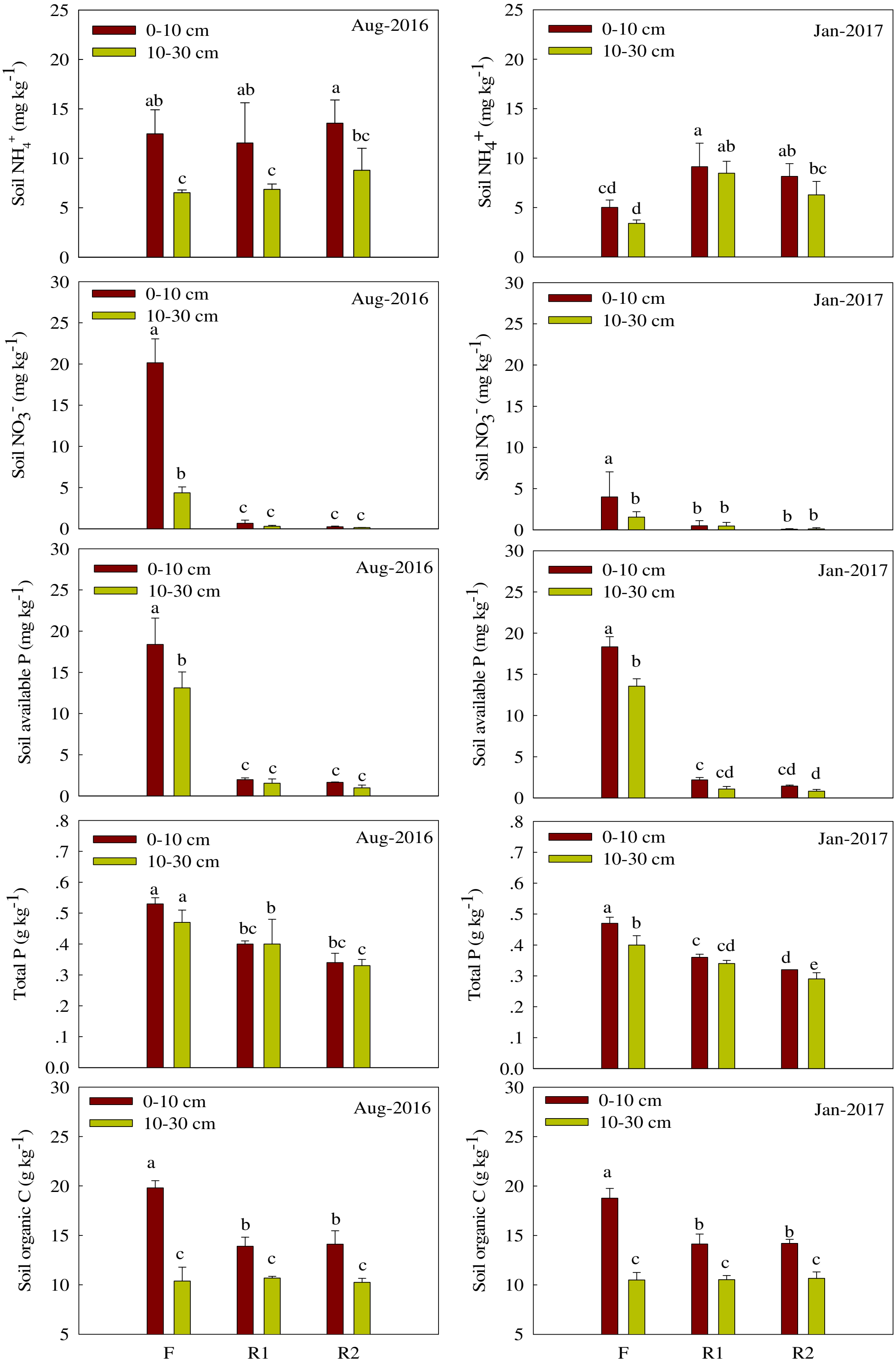

Fig. 5. Soil NH_4^+, NO_3^-, available P, total P and organic C in the 0–10 and 10–30 cm soil layers of tropical forests and rubber plantations. Different letters indicate significant differences at $P \le 0.05$. Bars are standard deviations of the mean ($n = 3$). F: Tropical forests; R1: Rubber plantations established in 2003; R2: Rubber plantations established in 1994.

K in any land-use type. Soil exchangeable cations mainly comprised exchangeable Ca and Mg, accounting for 90–95% of total soil exchangeable cations (Fig. 3). Soil exchangeable Na in topsoil layers was very low, at<0.1 cmol kg^{-1} in all land-use types.

In the dry and rainy seasons, soil exchangeable Al in the 0–10 cm soil layer was significantly lower in F than R1 and R2 (Fig. 2). In the dry season, soil exchangeable Al in the 10–30 cm soil layer was significantly lower in F and R1 than R2. Furthermore, in the rainy season, no significant differences were observed between the tropical forest and the two rubber plantations. In the dry and rainy seasons, soil exchangeable Al was significantly higher in the 0–10 cm soil layers, relative to the 10–30 cm soil layers in each plantation type.

In the dry and rainy seasons, soil available Cu in the 0–10 and 10–30 cm soil layers was significantly lower in F than R2 (Fig. 4). No significant differences were observed between F and R1 in the dry season or between R1 and R2 in the rainy season. In the dry and rainy seasons, soil available Zn in the 0–10 cm soil layer was significantly higher in F than R1 and R2 (Fig. 4). In the dry season, soil available Zn in the 10–30 cm soil layer was significantly higher in F than R2. In the dry season, soil available Mn and Fe in the 0–10 cm soil layer were significantly higher in F than R1 and R2 (Fig. 4); in the 10–30 cm soil layer, no significant differences in soil available Mn and Fe were observed between the tropical forest and the two rubber plantations. In the rainy season, no significant differences in soil available Mn and Fe in the 0–10 cm soil layer were observed between the tropical forest and the different-aged rubber plantations; soil available Mn and Fe in the 10–30 cm soil layers were significantly higher in F than R2.

3.2. Soil NH_4^+, NO_3^-, available P, total P, and SOC

In the rainy season, soil NH_4^+ in the 0–10 and 10–30 cm soil layers was significantly higher in R2 than F (Fig. 5). In the dry and rainy seasons, soil NO_3^- in the 0–10 cm soil layer was significantly higher in F than R1 and R2, with no significant differences between R1 and R2 (Fig. 5). In the dry season, soil NO_3^- in the 10–30 cm soil layer was significantly higher in F thanR1 and R2.

In the dry and rainy seasons, soil AP and TP in the 0–10 and 10–30 cm soil layers was significantly higher in F than R1 and R2 (Fig. 5). In the rubber plantations after forest conversion, SOC declined mainly due to losses in the topsoil (Fig. 5).

3.3. Relationships between soil Ca^{2+}, Mg^{2+}, exchangeable Al, available Cu, Zn, Mn and Fe, and soil chemical properties

Soil exchangeable Ca and Mg decreased sharply with the decline in soil pH from 5.5 to 5.0 (Fig. 6). For each of the land-use types, there was a positive correlation between pH and AP ($R = 0.92$, $P < 0.001$) (Fig. 6), available Zn ($R = 0.83$, $P < 0.001$), Mn ($R = 0.55$, $P = 0.0646$) and Fe ($R = 0.48$, $P = 0.1153$) (Fig. 7), and between SOC with the available Zn ($R = 0.86$, $P < 0.001$), Mn ($R = 0.81$, $P < 0.01$) and Fe ($R = 0.74$, $P = 0.0062$) (Fig. 7), and a significant negative correlation between exchangeable Al and pH ($R = -0.66$, $P < 0.05$), AP ($R = -0.66$, $P < 0.05$) and SOC ($R = -0.86$, $P < 0.001$), and pH and available Cu ($R = -0.94$, $P < 0.0001$) (Figs. 6, 7 and 8).

4. Discussion

Soil acidification is the process in which non-acid cations are leached, and H^+ increases. Soil acidification is a natural process of proton-generating reactions. However, agricultural and industrial activities can potentially accelerate this process (Raut et al., 2012; Li et al., 2014; Hou et al., 2015). Soil acidification has become a major global concern, and not only leads to soil nutrient losses but also decreases the biodiversity of forest ecosystems (Calster et al., 2007; Šebesta et al., 2011; Hruška et al., 2012). Changes in pH levels indicate modifications to soil reactions. The conversion of tropical natural forests to rubber plantations has significantly decreased the pH in topsoil layers, particularly with increasing age of the rubber plantation. Goulding and Annis

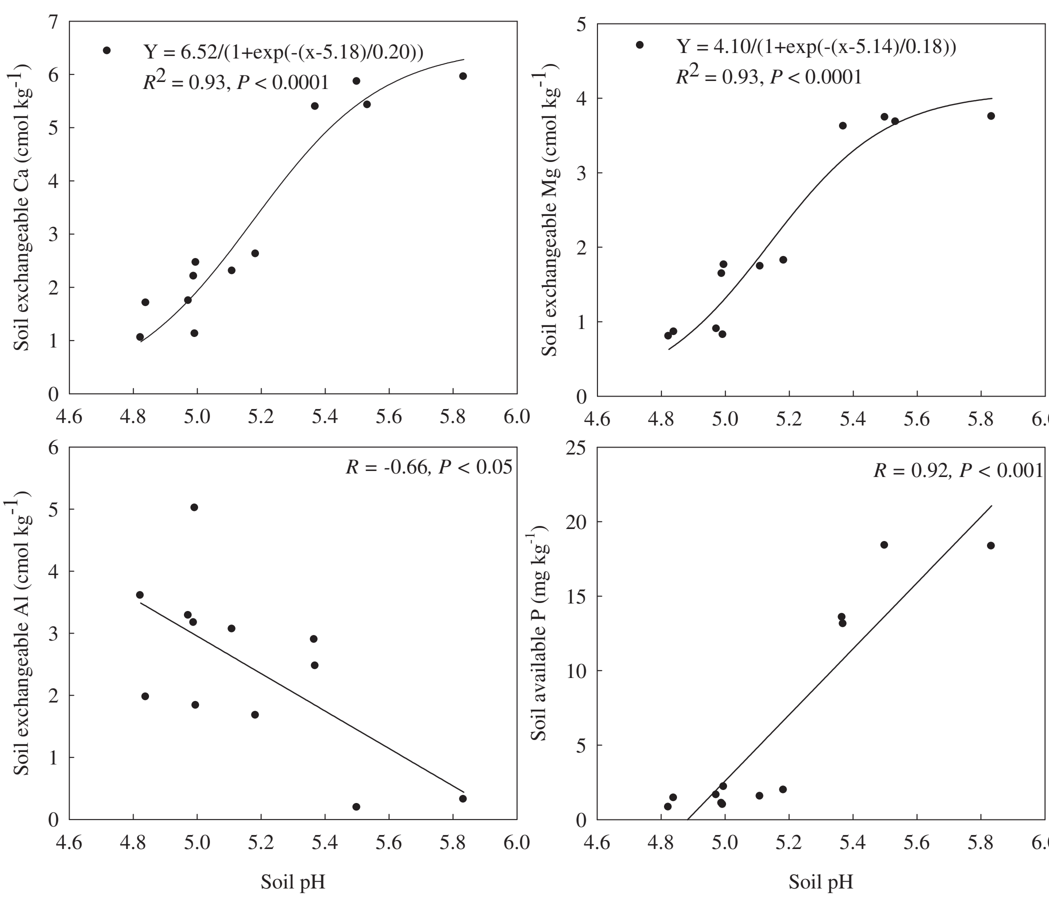

Fig. 6. Relationships between pH and exchangeable Ca, Mg exchangeable Al and available P in the 0–30 cm soil layers of tropical forests and rubber plantations.

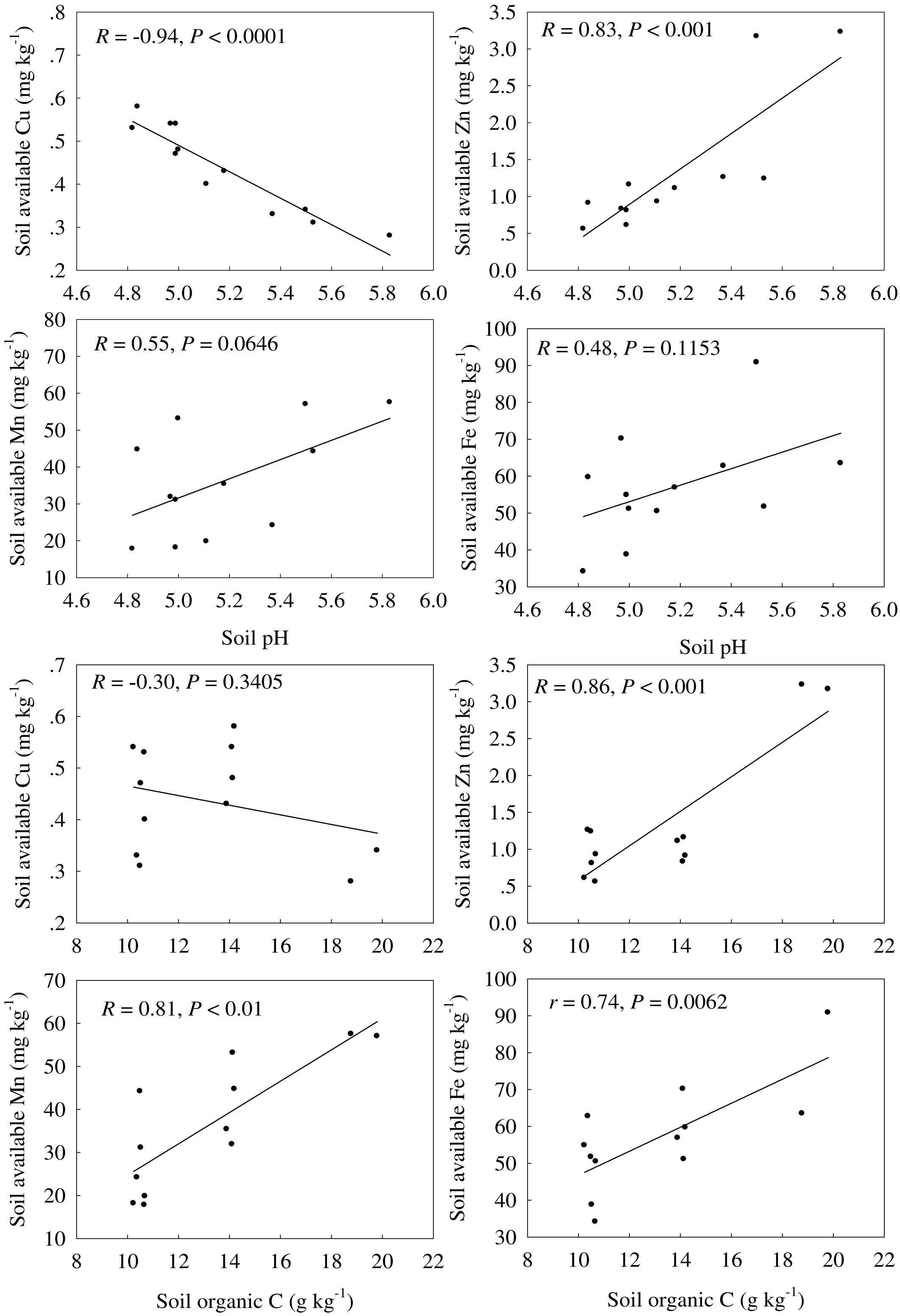

Fig. 7. Relationships between pH, organic C and available Cu, Zn, Mn and Fe in the 0–30 cm soil layers of tropical forests and rubber plantations.

(1998) reported that every 50 kg ha^{-1} of added ammonium-N generated about 4 kmol H^+ ha^{-1} y^{-1} in their field conditions. Sulfur powder in rubber plantations can be oxidized by soil microorganisms to form H^+ and SO_4^{2-}. In this region, rubber plantation farmers generally spray sulfur powder at 30–60 kg ha^{-1} y^{-1} to control powdery mildew on the rubber trees, which generates 2–4 kmol H^+ ha^{-1} y^{-1}. Leaching of base cations from the soil and plant uptake of Ca and Mg also lead to soil acidification. Nutrient losses of Ca and Mg from the latex were 0.12 and 0.34 kg ha^{-1} y^{-1}, and 0.80 and 2.61 kg $tree^{-1}$ y^{-1} from 8- and 22-year-old rubber trees, respectively (Cao et al., 2010a). The average biomass increment (including trunks, branches, leaves, and roots) was 12.6 and 7.2 t ha^{-1} y^{-1} in R1 and R2 (Wang, 2015). The Ca and Mg contents of trunks, branches, leaves, and roots of rubber trees were about 2.8 and 0.8, 16.8 and 1.8, 12.2 and 3.0, 12.5 and 2.0 g kg^{-1},

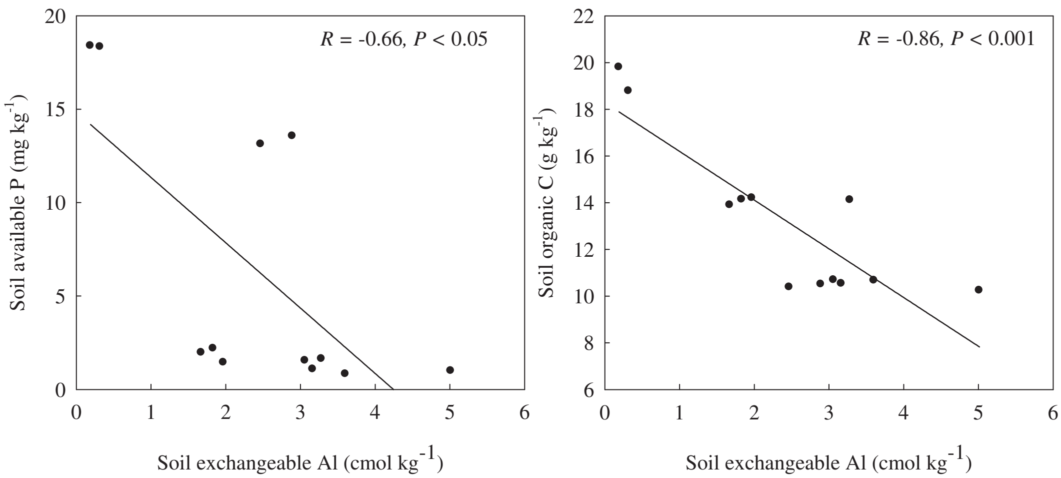

Fig. 8. Relationships between soil exchangeable Al and available P and organic C in the 0–30 cm soil layers of tropical forests and rubber plantations.

respectively (Cao et al., 2010b). Therefore, uptake of Ca in R1 and R2 was 92.7, and 52.9 kg ha^{-1} y^{-1}, respectively, and Mg in R1 and R2 was 16.0 and 9.2 kg ha^{-1} y^{-1}, respectively. However, average losses of exchangeable Ca in the 0–30 cm soil layer were 351.2, and 284.1 kg ha^{-1} y^{-1} in R1 and R2, respectively, and exchangeable Mg were 126.2 and 113.7 kg ha^{-1} y^{-1} in R1and R2, respectively. Therefore, inputting large amounts of nitrogen fertilizer and sulfur powder in rubber plantations is an important driving factor for soil acidification. The path analyses identified that soil pH, soil layers and seasons explained as much as 86% of the variability in soil exchangeable Ca and 85% of the variability of soil exchangeable Mg in the 0–30 cm soil layer. The change of soil exchangeable Ca and Mg was greatly affected by soil acidification processes when tropical forests were converted into rubber plantations (Table 1).

Soil acidification enhances the leaching of exchangeable cations (Lu et al., 2009). In this study, soil exchangeable Ca and Mg sharply decreased when tropical forests were converted into rubber plantations. A decrease in exchangeable Ca and Mg is generally related to nutrient leaching (Yang et al., 2018). In this study, the conversion of tropical forests to rubber plantations decreased soil NO_3^-.

Soluble ionic Al increases when soil pH falls below 5.5 (Mulder, 1988; Kabata-Pendias and Pendias, 2001; Alleoni et al., 2010). In our study, during the dry and rainy seasons, soil pH in the tropical forests was approximately 5.5, but below 5.0 in the mature rubber plantations. The conversion of tropical natural forests to rubber plantations significantly increased exchangeable Al levels in the 0–10 cm soil layer, more so as the rubber plantations aged. A significant negative correlation was found between soil exchangeable Al and soil pH ($P < 0.05$). In the 0–10 cm soil layer, the tropical forests only had 0.32 cmol kg^{-1} exchangeable Al during the rainy seasons but reached up to 3.28 cmol kg^{-1} in the mature rubber plantations. In the 10–30 cm soil layer, the tropical forests had 2.47 cmol kg^{-1} exchangeable Al during the rainy season but reached up to 5.01 cmol kg^{-1} in the mature rubber plantations. Van Breemen et al. (1984) reported apparent Al toxicity symptoms in plants when exchangeable Al in the soil surpassed 2.0 cmol kg^{-1}. Wu et al. (2013) reported significant growth inhibition and smaller root systems in soybean plants when the exchangeable Al in the soil was >4.4 cmol kg^{-1}. The large amounts of exchangeable Al released in the rubber plantations could threaten the safety of the surrounding environment due to the effects of runoff and soil erosion. Aluminum can participate in strong complexation reactions with soil organic matter, as well as alleviate soil acidification and reduce Al phytotoxicity (Wang et al., 2016). In the current study, the conversion of tropical natural forests to rubber plantations significantly decreased SOC in the 0–10 cm soil layer, which is likely due to (1) a decline in carbon inputs from above ground litter-fall (Zhang and Zou, 2009), and (2) serious soil erosion in rubber plantations (Zhang and Zou, 2009; Liu et al., 2017). Low SOC contents potentially accelerate the release of exchangeable Al (Jiang et al., 2018). A significant negative correlation was found between soil exchangeable Al and SOC ($P < 0.001$) in this study. The conversion of tropical natural forests to rubber plantations significantly decreased the available phosphorus content, which agrees

Table 1
Path analyses examining the direct and indirect effects of soil pH, soil organic carbon (SOC), soil layers (0–10 cm and 10–30 cm) and seasons on soil exchangeable Ca, Mg, available Zn, Mn and Fe in the 0–30 cm soil layer. The total effect was estimated as the sum of direct and indirect effects. R^2 indicates the proportion of variation explained by the multiple regression models in each case.

	Variable	Direct effect	Indirect effect			Total effect
			→x_1	→x_2	→x_3	
Soil exchangeable Ca $R^2 = 0.86, P = 0.0010$	Soil pH (x_1)	0.938		−0.010	−0.005	0.933
	Soil layers (x_2)	0.053	−0.182		0.000	−0.129
	Seasons (x_3)	0.062	−0.073	0.000		−0.011
Soil exchangeable Mg $R^2 = 0.85, P = 0.0011$	Soil pH (x_1)	0.943		−0.028	−0.005	0.910
	Soil layers (x_2)	0.146	−0.183		0.000	−0.037
	Seasons (x_3)	0.063	−0.074	0.000		−0.011
Soil available Zn $R^2 = 0.87, P = 0.0007$	SOC (x_1)	1.476		−0.653	−0.001	0.822
	Soil layers (x_2)	0.782	−1.232		0.000	−0.450
	Seasons (x_3)	0.086	−0.012	0.000		0.074
Soil available Mn $R^2 = 0.81, P = 0.0032$	SOC (x_1)	0.692		0.125	−0.003	0.814
	Soil layers (x_2)	−0.150	−0.578		0.000	−0.728
	Seasons (x_3)	0.369	−0.005	0.000		0.364
Soil available Fe $R^2 = 0.81, P = 0.0031$	SOC (x_1)	0.797		−0.063	0.004	0.738
	Soil layers (x_2)	0.075	−0.665		0.000	−0.590
	Seasons (x_3)	−0.511	−0.006	0.000		−0.517

Table 2
Path analyses examining the direct and indirect effects of soil pH, soil organic carbon (SOC), soil layers (0–10 cm and 10–30 cm) and seasons on soil exchangeable Al and available Cu in the 0–30 cm soil layer. The total effect was estimated as the sum of direct and indirect effects. R^2 indicates the proportion of variation explained by the multiple regression models in each case.

	Variable	Direct effect	Indirect effect				Total effect
			$\rightarrow x_1$	$\rightarrow x_2$	$\rightarrow x_3$	$\rightarrow x_4$	
Soil exchangeable Al	Soil pH (x_1)	−0.405		−0.214	−0.058	0.012	−0.665
$R^2 = 0.82, P = 0.0088$	SOC (x_2)	−0.382	−0.226		−0.250	0.001	−0.857
	Soil layers (x_3)	0.299	0.079	0.319		0.000	0.697
	Seasons (x_4)	−0.156	0.032	0.003	0.000		−0.121
Soil available Cu	Soil pH (x_1)	−1.066		0.131	0.014	0.002	−0.919
$R^2 = 0.91, P = 0.0008$	SOC (x_2)	0.235	−0.595		0.058	0.000	−0.302
	Soil layers (x_2)	−0.070	0.207	−0.197		0.000	−0.060
	Seasons (x_3)	−0.022	0.083	−0.002	0.000		0.059

with previous reports that phosphateanions can be immobilized with Al through sorption and/or precipitation, leading to reduced P availability (Sherman et al., 2006). The path analyses identified that soil pH, SOC, soil layers, and seasons explained as much as 82% of the variability of soil exchangeable Al in the 0–30 cm soil layer. The change of soil exchangeable Al was greatly affected by soil pH and SOC when tropical forests were converted into rubber plantations (Table 2).

The conversion of tropical natural forests to rubber plantations significantly increased the soil available Cu content, reaching>1.8 mg kg^{-1} (0.01 mol L^{-1} HCl method) or 6.0 mg kg^{-1} (DTPA method), a level that inhibits plant growth (Liu et al., 2012). The increase in soil available Cu in mature rubber plantations does not pose a significant risk of Cu toxicity, due to its low background levels in this region (Fig. 4). Soil available Cu was also correlated with SOC, but it was not significant ($P = 0.3405$). Cu may be bound to more stable forms of soil organic matter and therefore not affected by the change in land use (Soon, 1994). The path analyses identified that soil pH, SOC, soil layers, and seasons explained as much as 91% of the variability of soil available Cu in the 0–30 cm soil layer. The change of soil available Cu was greatly affected by soil pH when tropical forests were converted into rubber plantations (Table 2).

A positive correlation existed for soil available Zn, Mn and Fe and pH ($P < 0.001$ for soil available Zn, $P = 0.0646$ for soil available Mn and $P = 0.1153$ for soil available Fe). The conversion of tropical natural forests to rubber plantations significantly decreased soil available Zn, Mn and Fe contents, which does not agree with other studies that reported increases in the concentrations of soil available Zn, Mn and Fe with decreasing soil pH (Chen et al., 2002; Zeng et al., 2011; Zhao et al., 2011). In our study, a significant positive correlation existed for soil available Zn, Mn and Fe and SOM ($P < 0.001$ for soil available Zn, $P < 0.01$ for soil available Mn and $P = 0.0062$ for soil available Fe). SOM is a major contributor to soil available heavy metals, and the addition of organic matter can increase heavy metal mobility in soils (Soon, 1994; Dlamini et al., 2014; Rutkowska et al., 2014). The conversion of tropical natural forests to rubber plantations decreased SOC, with most losses from the topsoil (Fig. 5), and resulted in large losses of soil available Zn and Mn. The relationship between soil pH and available Zn, Mn, and Fe may be an apparent phenomenon that did not reflect their true relationship. Soil available Zn, Mn and Fe were more sensitive to SOC than pH after the conversion of tropical natural forests to rubber plantations. The threshold for soil available Zn is 1.5 mg kg^{-1} (0.01 mol L^{-1} HCl method) or 1.0 mg kg^{-1} (DTPA method) for plant growth (Liu et al., 2012). In this region, the conversion of tropical natural forests to rubber plantations reduced soil available Zn. Soil available Zn was below 1.5 mg kg^{-1} (0.01 mol L^{-1} HCl method) in rubber plantations. The threshold for soil available Mn is 5.0 mg kg^{-1} for plant growth (Liu et al., 2012). The decline in soil available Mn in the mature rubber plantations had little impact due to the high background levels in this region (Fig. 4). The path analyses identified that the change of soil available Zn and Mn was greatly affected by SOC when tropical forests were converted into rubber plantations (Table 1).

5. Conclusions

The results of this study confirmed that the conversion of tropical natural forests to rubber plantations accelerates soil acidification processes, significantly decreases soil exchangeable Ca, Mg, available Zn, Mn, and Fe, and increases soil exchangeable Al and available Cu. Large losses of soil exchangeable Ca, Mg, and available Zn in the rubber plantations would limit plant growth. The release of large amounts of exchangeable Al in the rubber plantations not only decreased soil available P but also would threaten the safety of the surrounding environment. The accumulation of exchangeable Al and the rapid decrease of exchangeable Ca, Mg and available Zn in the topsoil layers of the rubber plantations is concerning, and preventative practices (e.g., application of lime and *biochar*) should be used to reduce the levels of exchangeable Al and improve the levels of exchangeable Ca, Mg and available Zn.

Declaration of competing interest

The authors declare no competing interests.

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