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Original Article

Manganese status in upland and lowland rubber-growing soils in Songkhla province, southern Thailand

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ABSTRACT

Rubber trees, the most economic crop in southern Thailand, are generally cultivated in acid upland soils and currently have been extended into lowland areas which induce higher solubility of manganese (Mn) which may result in Mn toxicity to rubber. This study investigated soil Mn and leaf Mn levels in rubber trees grown in upland and lowland soils. Ninety soil samples from upland and lowland rubber plantations in Songkhla province were collected and analyzed for water soluble Mn, NH_4OAc Mn, diethylenetriaminepentaacetic acid test (DTPA) Mn, reducible Mn and total Mn forms. Leaf Mn analysis was also undertaken on samples of each plantation. The results revealed that the Mn concentrations of all soil Mn forms and leaf Mn in the lowland soils were higher than those of the upland samples. Comparing the optimum level reported by the Rubber Research Institute, both DTPA Mn and leaf Mn in the upland and lowland samples were high. Correlation analysis showed high and significant positive correlations of DTPA Mn and water Mn ($r = 0.715$), NH_4OAc Mn ($r = 0.975$), reducible Mn ($r = 0.953$) and total Mn ($r = 0.809$) in the lowland samples. Medium to high positive correlations among Mn forms were also found in the upland samples. The correlation of soil properties (pH, electrical conductivity, organic matter, available K, exchangeable Ca, Mg and Na and cation exchange capacity) and soil Mn were clearly defined. These results indicated that soil properties affect the release of Mn. However, a correlation between soil Mn and leaf Mn was not observed.

Introduction

Rubber trees are widely cultivated in acid upland soils and currently have been expanded into lowland areas and abandoned paddy fields (Chiarawipa and Yeedum, 2010) which are not suitable and possibly contain high Mn because of reduction of Mn oxide to soluble Mn^{2+} (McBride, 1994). Manganese is a micronutrient whose concentration is greatly increased under acidic and poor drainage conditions (Havlin et al., 2005). Therefore, a high amount of Mn will present in highly weathered acid soils, such as Ultisols and Oxisols (Tan, 2005). In Thailand, Ultisols occupy 44.81% (51.3 million ha) and Oxisols represent 0.26% (0.13 million ha) of the country (Kheoruenromne and Kesawapitak, 1989). In southern Thailand, acid soils occupy over 3.5 million ha or 68% of the total cultivated areas on which rubber trees are the main crop in this region (Kheoruenromne and Kesawapitak, 1989).

In 2010, the total rubber cultivation areas in Thailand was approximately 2.931 million ha and mainly (65.11%) in the south (Rubber Research Institute of Thailand (2012)). Chiarawipa and Yeedum (2010) noted that the growth and yield of rubber significantly decreased in abandoned paddy fields in Phattalung province. Likewise, an experiment of six varieties of wheat grown in acidic soil (Khabaz-Saberi et al., 2006) found that waterlogging increased the Mn solubility in soils and Mn uptake by the plants (Havlin et al., 2005), as the reducing oxide fraction (Mn^{3+}, Mn^{4+} and easily reducible MnO_2) affected the increasing level of mobile Mn under those conditions (Khabaz-Saberi et al., 2006; Iu et al., 1981; Stepniewska et al., 2010). The equilibrium of Mn among these forms is influenced greatly by soil pH and redox potential (Barber, 1984; Karavanova et al., 2006). In other words, soil waterlogging will reduce O_2 and lower the redox potential, which increase the concentration of soluble Mn, especially in acidic soils and Mn toxicity possibly occurs (Havlin et al., 2005).

Soil Mn exists as Mn^{2+}, Mn^{3+} and Mn^{4+} which are absorbed by plant roots primarily as Mn^{2+}, since Mn^{3+} and Mn^{4+} are insoluble and unstable forms (Barber, 1984). Soil Mn is classified into various

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forms—exchangeable, water soluble, specifically adsorbed Mn, complexed by soil organic matter and insoluble precipitate (Gambrell, 1996) and easily reducible as MnO_2 (Tisdale et al., 1990; Guest et al., 2002). Total soil Mn is generally in the range 20–3000 mg/kg (Barber, 1984; Tisdale et al., 1990; Havlin et al., 2005; Troeh and Thompson, 2005). Commonly, the Mn concentration for optimum growth should be 2–3 mg/kg, 0.2–5 mg/kg and 25–65 mg/kg for the water soluble, exchangeable and easily reducible forms, respectively (Havlin et al., 2005; Tisdale et al., 1990). However, the optimum Mn concentration for rubber should be 2–4 mg/kg (based on the diethylenetriaminepentaacetic acid test; DTPA) in the soil and 45–150 mg/kg in leaves (Kungpisadan, 2009). The current study aimed to determine and compare leaf Mn of rubber trees and soil Mn forms in upland and lowland areas and to analyze the correlation among soil Mn forms, leaf Mn and soil properties.

Materials and methods

Soil sampling and analysis

Ninety soils were sampled during July 2011 using a cross-shaped layout (9 cores/plantation) at a depth of 0–30 cm from upland and lowland rubber plantation areas, consisting of 47 farms with immature rubber (aged 4 yr) and 43 farms with mature rubber (aged 8 yr) in Rattaphum, Na Thawi, and Khlong Hoi Kong districts, Songkhla province, southern Thailand. The soils consisted of 45 upland soils (Typic Kandiudults; Kohong and Lithic Udorthents/Typic Hapludults; Ranong associated with the Phato series) and 45 lowland soils (Typic Paleaquults; Bang Nara, Typic Plinthaquults; Visai and Typic Plinthaquults; Nam Krachai associated with the Sathon series). The upland soils showed no mottling throughout the soil profiles whereas lowland soils had mottling in the soil profiles. The soil samples were air dried and passed through a 2 mm screen sieve. The soil samples were determined for Mn forms—water soluble Mn (soil:water; 1:10), exchangeable Mn (soil:1 M NH_4OAc; 1:10) and DTPA Mn (soil:DTPA; 1:2), reducible Mn (soil:1 M NH_4OAc-hydroquinone; 1:10) and total Mn in soil (H_2O_2, H_2SO_4, HNO_3, $HClO_4$ and HF) according to Gambrell (1996). Manganese in each extractant was analyzed using atomic absorption spectrophotometry (AAS). Some basic soil properties—pH, total N, available P and K, exchangeable Ca, Mg and Na, cation exchange capacity (CEC), organic matter (OM) and electrical conductivity (EC)—were also analyzed (Onthong and Poonpakdee, 2012).

Leaf sampling and analysis

Mature (aged 100–150 d) first or second compound leaves of the growing whorl of rubber branches were sampled (Kungpisadan, 2009) from 9 trees/plantation using a cross-shaped design. The leaves were dried at 70 °C and ground through a 20 mesh screen of a hammer mill. Then, the leaf Mn concentration was analyzed by digesting with mixed acid (HNO_3:$HClO_4$; 3:1) and determined using AAS (Onthong and Poonpakdee, 2012).

Statistics and data analysis

The mean and interval estimation of soil and leaf Mn values were calculated and Mn values in the upland and lowland areas were compared using an independent Student's t test (significant at $p \leq 0.05$ and highly significant at $p \leq 0.01$). The correlation between Mn in the soil and Mn in leaves, as well as soil Mn and soil properties were computed.

Results

The basic soil characteristics of upland and lowland rubber-growing soils are given in Table 1. Most of the soils were acidic and the CEC, available P, OM, total N, exchangeable Ca, Mg and Na contents were higher in the lowland soils compared with the upland ones.

The concentrations of Mn forms in the upland and lowland rubber-growing soils are summarized in Table 2. The results showed that the concentrations of all Mn forms, in both immature and mature rubber plantations in the lowland were higher than those of the upland (Tables 2 and 3).

The results also showed that the highest value was for the total Mn followed by reducible Mn, DTPA Mn, NH_4OAc Mn and water soluble Mn, respectively. The leaf Mn in both mature and immature rubber plants showed significant differences which were also greater in the lowland (405.35 mg/kg and 380.95 mg/kg, respectively) than the upland (371.08 mg/kg and 303.16 mg/kg, respectively) as shown in Table 4.

Highly significant, medium to high positive correlations between Mn forms were observed, especially between total Mn and water soluble Mn (r = 0.572), NH_4OAc Mn (r = 0.846), DTPA Mn (r = 0.809) and reducible Mn (r = 0.880) in the lowland soils which were greater than in the upland soils (Table 5). The correlations between soil Mn and soil properties are presented in Table 6. In the upland, the correlation between water Mn and EC (r = 0.728) and available K (r = 0.578) showed a highly significant, positive correlation, while there was a significant correlation between total Mn and exchangeable Na (r = 0.369). However, NH_4OAc Mn (r = −0.323) and DTPA Mn (r = −0.326) had a significant, negative correlation with OM. In the lowland, pH gave close, positive correlations with NH_4OAc Mn (r = 0.515, highly significant), DTPA Mn (r = 0.491, significant), reducible Mn (r = 0.533, highly significant) and total Mn (r = 0.448, significant). Similar correlations between exchangeable Ca, Mg and CEC and each Mn fraction were clearly observed.

Discussion

Basic properties of soils

The soil acidic condition in rubber plantation areas (Table 1) is generally caused by high weathering and leaching which generally

Table 1
Some chemical soil properties in upland and lowland rubber-growing soils, with range values derived from interval estimation at $p \leq 0.05$.

Chemical property[a]	Top soil (0–30 cm)			
	Immature		Mature	
	Upland	Lowland	Upland	Lowland
pH (soil:water = 1:5)	5.24–5.46	5.41–5.65	5.27–5.44	4.96–5.57
EC (1:5) (dS m^{-1})	0.01–0.02	0.02–0.03	0.01–0.02	0.02–0.04
OM (g/kg)	9.86–12.41	9.94–11.34	10.17–11.99	8.93–13.10
Total N (g/kg)	0.50–0.74	0.67–0.81	0.59–0.70	0.54–0.66
Avail P (mg/kg)	4.43–8.73	3.57–9.12	4.70–7.87	5.92–7.72
Avail K (mg/kg)	4.36–16.55	3.86–12.43	5.29–10.14	13.63–20.53
Exch Ca ($cmol_c$/kg)	0.13–0.29	0.23–0.39	0.14–0.20	0.09–0.22
Exch Mg ($cmol_c$/kg)	0.03–0.05	0.05–0.12	0.03–0.04	0.03–0.06
Exch Na ($cmol_c$/kg)	0.02–0.03	0.04–0.08	0.03–0.04	0.04–0.06
CEC ($cmol_c$/kg)	1.94–2.38	1.60–3.24	1.36–1.72	0.97–1.74
Sand (%)	34–50	32–47	51–63	49–62
Silt (%)	26–36	28–39	19–25	20–26
Clay (%)	22–30	23–31	16–24	17–26

[a] EC = electrical conductivity; OM = organic matter; Avail = available; Exch = exchangeable; CEC = cation exchange capacity.

Table 2
Concentrations (mean ± SD) of Mn forms in upland and lowland rubber-growing soils at 0–30 cm, with range values derived from interval estimation at $p \leq 0.05$.

Mn form[a]	Value[b]	Immature rubber (mg/kg)		Mature rubber (mg/kg)	
		Upland	Lowland	Upland	Lowland
Water Mn	Min–Max	ND[c]–3.02	ND–3.23	ND–0.61	ND–2.06
	Range	NC	NC	NC	NC
	Mean ± SD	0.34 ± 0.76	0.42 ± 0.87	0.15 ± 0.16	0.51 ± 0.75
DTPA Mn	Min–Max	1.36–24.04	1.11–88.73	1.42–15.73	1.27–31.65
	Range	1.62–6.48	3.84–9.36	3.28–4.74	6.97–14.58
	Mean ± SD	9.31 ± 7.46	20.93 ± 24.38	7.25 ± 4.32	12.45 ± 9.67
NH_4OAc Mn	Min–Max	0.89–25.94	0.68–112.82	1.18–12.85	0.98–24.89
	Range	1.11–3.34	3.15–7.58	2.51–4.12	5.04–12.56
	Mean ± SD	7.95 ± 7.72	20.36 ± 29.86	5.89 ± 3.72	10.21 ± 8.24
Reduc Mn	Min–Max	1.57–37.60	0.72–152.68	1.36–27.10	1.15–37.19
	Range	1.74–4.41	3.31–8.59	3.69–4.57	6.76–14.86
	Mean ± SD	10.75 ± 10.84	26.51 ± 40.23	8.69 ± 6.75	12.76 ± 10.75
Total Mn	Min–Max	9.30–54.38	14.89–162.05	7.15–58.31	13.98–51.89
	Range	15.81–28.64	18.27–38.95	13.01–16.55	37.89–44.31
	Mean ± SD	31.45 ± 16.62	54.03 ± 39.68	24.01 ± 14.42	39.17 ± 10.55

[a] DTPA = diethylenetriaminepentaacetic acid test; Reduc = reducible.
[b] Min = minimum; Max = maximum.
[c] ND = not detectable; NC = not determined.

Table 3
Comparison each soil manganese form in upland and lowland rubber-growing soils.

Rubber	Topography	DTPA[a] Mn	NH_4OAc Mn	Reduc[a] Mn	Total Mn
Immature (mg/kg)	Upland	9.31	7.95	10.75	31.45
	Lowland	20.93	20.36	26.51	54.03
	t test[‡]	NS	*	*	*
Mature (mg/kg)	Upland	7.25	5.89	8.69	24.01
	Lowland	12.45	10.21	12.76	39.17
	t test[‡]	*	*	NS	**

[‡] *, **Significantly different ($p \leq 0.05$) and highly significantly different ($p \leq 0.01$), respectively; NS = not significantly different ($p > 0.05$).
[a] DTPA = diethylenetriaminepentaacetic acid test; Reduc = reduction.

Table 4
Leaf Mn concentrations of rubber trees grown in upland and lowland plantations, with range values derived from interval estimation at $p \leq 0.05$.

Rubber	Leaf Mn (mg/kg)		
	Value	Upland	Lowland
Immature rubber	Min–Max[a]	201.60–1257.92	120.48–1297.88
	Range	311.23–430.93	357.01–453.69
	Mean[†]	371.08	405.35
Mature rubber	Min–Max[a]	136.45–1155.81	221.28–2062.57
	Range	270.53–335.80	323.11–438.80
	Mean[†]	303.16	380.95

[†]Significantly different ($p \leq 0.05$).
[a] Min = minimum; Max = maximum.

Table 5
Correlation coefficient between manganese forms in the soil and leaf Mn.

Mn Form[a]	Water	NH_4OAc	DTPA	Reducible	Total	Leaves
Upland						
Water	1.000					
NH_4OAc	0.276	1.000				
DTPA	0.329*[‡]	0.974**	1.000			
Reducible	0.271	0.969**	0.955**	1.000		
Total	0.157	0.583**	0.625**	0.660**	1.000	
Leaves	0.176	−0.103	−0.072	−0.129	−0.162	1.000
Lowland						
Water	1.000					
NH_4OAc	0.746**	1.000				
DTPA	0.715**	0.975**	1.000			
Reducible	0.729**	0.991**	0.953**	1.000		
Total	0.572**	0.846**	0.809**	0.880**	1.000	
Leaves	0.161	0.334	0.346	0.328	0.266	1.000

[‡] *, **Significantly different ($p \leq 0.05$) and highly significantly different ($p \leq 0.01$), respectively; NS = not significantly different ($p > 0.05$).
[a] DTPA = diethylenetriaminepentaacetic acid test.

occurs in tropical soils (Brady and Weil, 2008). The optimum soil pH for general crops is around 5.5–7.0 (Havlin et al., 2005) whereas for rubber trees, it is around 4.0–5.5 (Suchartgul et al., 2012). The results showed that the pH levels of the upland and lowland rubber-growing soils were in the optimum pH range for rubber which is lower than that for general cropping. While the reason for this difference is still unclear, increasing the pH of rubber-growing, acidic soils was not appropriate because of plant nutrients competition and imbalances, especially in the ratios of Ca to Mg and Ca to Cu (Damrongrak et al., 2014). Under this acidic condition ($pH < 5.5$), Mn toxicity commonly occurs because of reducing Mn oxides (Millaleo et al., 2010; Adams, 1984). The greater accumulation of organic matter in the lowland soils makes the total nitrogen level higher, but it was lower compared to the optimum level for rubber (1.0–2.5%) according to Kungpisadan (2011). The greater dominance of clay particles in lowland soils causes higher nutrient concentrations when compared to the upland ones (Table 1). However, the available P and K, and exchangeable Ca and Mg both in the upland and lowland soils were lower than the optimum level for rubber trees (Kungpisadan, 2011; Suchartgul et al., 2012). Thus, inorganic and organic fertilizers are needed for rubber trees as recommended by Kungpisadan (2011).

Manganese in the upland and lowland rubber-growing soils

Actual Mn toxicity is commonly associated with water soluble or easily reducible Mn forms (Bohn et al., 2001; Hue and Mai, 2002).

Table 6
Correlation between soil Mn and soil properties in upland and lowland soils.

Chemical property[a]	Manganese form (mg/kg)				
	Water Mn	NH_4OAc Mn	DTPA[‡] Mn	Reduc[‡] Mn	Total Mn
Upland					
pH (soil: water = 1:5)	−0.251	0.039	−0.009	0.028	0.105
EC (1:5) (μS cm^{-1})	0.728**‡	0.010	0.070	0.007	−0.112
OM (g/kg)	−0.143	−0.323*	−0.326*	−0.310	−0.233
Total N (g/kg)	−0.212	−0.167	−0.165	−0.175	−0.061
Avail P (mg/kg)	0.362	0.069	0.151	0.123	0.101
Avail K (mg/kg)	0.578**	0.072	0.155	0.063	−0.058
Exch Ca ($cmol_c$/kg)	0.291	0.183	0.219	0.138	0.112
Exch Mg ($cmol_c$/kg)	−0.039	−0.099	−0.074	−0.102	−0.197
Exch Na ($cmol_c$/kg)	0.126	0.171	0.195	0.181	0.369*
CEC ($cmol_c$/kg)	−0.079	−0.203	−0.197	−0.169	−0.145
Lowland					
pH (soil: water = 1:5)	−0.104	0.515**	0.491*	0.533**	0.448*
EC (1:5) (μS cm^{-1})	0.202	−0.123	−0.069	−0.106	0.081
OM (g/kg)	−0.140	−0.193	−0.214	−0.190	−0.096
Total N (g/kg)	−0.042	−0.174	−0.173	−0.153	−0.004
Avail P (mg/kg)	−0.113	−0.224	−0.238	−0.142	0.093
Avail K (mg/kg)	0.302	0.255	0.246	0.266	0.213
Exch Ca ($cmol_c$/kg)	0.653**	0.710**	0.671**	0.679**	0.498*
Exch Mg ($cmol_c$/kg)	0.651**	0.868**	0.777**	0.883**	0.770**
Exch Na ($cmol_c$/kg)	−0.064	0.041	0.080	0.056	0.047
CEC ($cmol_c$/kg)	0.537**	0.681**	0.597**	0.683**	0.567**

‡ *, **Significantly different ($p \leq 0.05$) and highly significantly different ($p \leq 0.01$), respectively.
DTPA = diethylenetriaminepentaacetic acid test; Reduc = reducible.
[a] EC = electrical conductivity; OM = organic matter; Avail = available; Exch = exchangeable; CEC = cation exchange capacity.

The higher concentrations of water soluble Mn and reducible Mn in the lowland (Table 2) indicate that waterlogging affects the Mn solubility due to the inhibition of Mn oxidization by organisms, thereby producing Mn oxide reduction (Messing, 1965; Millaleo et al., 2010). This is consistent with experiments in barley (Yodkeaw and De Datta, 1989; Hernandez-Soriano et al., 2012) and rice (Jahan et al., 2013). The mechanism of increasing solubility by poor drainage starts with CO_2 accumulation around the roots (Havlin et al., 2005). Then, this affects reducing O_2 and the redox potential (Lucas and Knezek, 1972; Khabaz-Saberi et al., 2010).

The exchangeable Mn (DTPA Mn and NH_4OAc Mn) was also higher in the lowland than the upland because the Mn valency is quite responsive to increasing redox potential (Adams, 1984). Surprisingly, from the present study, 88% of DTPA Mn in the lowland and 66% in the upland soils were above the optimum level for rubber of 2–4 mg/kg (Kungpisadan, 2009), indicating that rubber trees tolerate high Mn levels. Wetting and drying in lowland soils leads to greater Mn mobilization and precipitation than in upland soils (Table 3) as discussed by Guest et al. (2002) and D'Amore et al. (2004). On the other hand, the higher clay content in lowland soils possibly contains higher Mn minerals and stronger bonds when compared to upland conditions (Milivojevic et al., 2011). Therefore, the water regime should be controlled to prevent a Mn excess in lowland soils.

The leaf Mn both in mature and immature rubber plants grown in the lowland soils showed higher concentrations than those in the upland soils, which was consistent with the soil Mn (Table 4). In fact, 97% of the Mn concentration in rubber leaves was above the optimum level for rubber of 40–150 mg/kg (Kungpisadan, 2009) and for plant tissue of 20–200 mg/kg (Jones, 1972; Havlin et al., 2005; Troeh and Thompson, 2005). The critical toxicity of Mn depends on the plant (Uren, 1999) and also on interactions with other micronutrients; high levels of Cu, Fe and Zn can reduce Mn uptake by plants (Havlin et al., 2005). This indicates that rubber trees tolerate Mn toxicity as has also been reported in some plants such as kikuyu (503 mg/kg), white clover (592 mg/kg) according to Rayment and Verall (1980) and *Zea mays* (550 mg/kg) according to Hai-hua et al. (2009). This higher Mn concentration may partly contribute to the lower growth and yield of rubber grown in tropical, acidic soils, especially in lowland areas. Besides the Mn concentration, drainage conditions are also an important limiting factor on the growth and yield of rubber. Therefore, rubber trees are appropriate for extensive cultivation in tropical, acidic soils—even those with a high Mn concentration—and the toxicity level of Mn on rubber trees should be further studied.

Correlations of leaf Mn, soil properties and soil Mn

Mn availability in the soil is controlled by several significant factors such as the pH, Mn oxide reducibility and soil surface conditions (Lindsay, 1979). For the lowland sites, the correlations among all soil Mn fractions were closer to the total Mn than in the upland ones (Table 5). Total Mn had the highest Mn concentration followed by reducible Mn, DTPA Mn, NH_4OAc Mn and water soluble Mn, respectively (Table 3). The Mn forms which are available for plants include water soluble Mn, exchangeable Mn and organically complexed Mn (Barber, 1984). However, reducible Mn defines the potential availability of Mn such as pyrolusite and manganite (Adams, 1984). Exchangeable Mn was extracted with DTPA and NH_4OAc. The DTPA Mn was higher when compared with the NH_4OAc Mn due to the ability of DTPA to extract soluble and stable fractions (Sutter et al., 2005). The lowest value was for the water soluble Mn, which is the most mobile form that includes free cation Mn complexed with organic and inorganic ligands (Gambrell, 1996; Millaleo et al., 2010). The higher correlation between soil Mn and soil properties found with the lowland sites demonstrates that periodic flooding, greater organic matter accumulation and finer texture affect the content, solubility and release of Mn.

Manganese is possibly released from weathering of ferromagnesian material and clay silicate such as biotite and hornblende (Brady and Weil, 2008) which was expressed through the high, positive correlation coefficients among the soil Mn forms with K, Na, Ca and Mg (Table 6). Thus, the higher positive correlations among soil Mn in each form with CEC in the lowland soils, shows that CEC influences Mn absorption and distribution by stronger bonding between soil Mn and clay. The correlations between pH and Mn in the lowland soils showed a positive correlation, in contrast to the upland (Table 6), indicating that releasing Mn not only depends on the redox potential and pH, but also on the parent material. For example, the activity of manganite is enhanced by increasing the pH in the soil solution (Lindsay, 1979). The correlation between pH and soil Mn (complexed Mn form) was highly positive which shows substantial agreement with the experiments of Sillanpaa (1982) and Milivojevic et al. (2011). The current study found no marked correlation between leaf Mn and soil Mn, implying that many factors may contribute to Mn uptake. Therefore, the effect of Mn on rubber growth and its uptake should be clearly understood. To elucidate these issues, further investigation must be performed.

Manganese concentration in the lowland soils was greater than in the upland soils, with total Mn being highest followed by reducible Mn, DTPA Mn, NH_4OAc Mn and water soluble Mn, respectively. Correlations among the soil Mn forms were found. However, a correlation between soil and leaf Mn was not clearly observed. Although most of the DTPA Mn and leaf Mn both in the upland and lowland soils were above the optimum standards, they did not markedly affect rubber growth. Therefore, the Mn toxicity level in rubber trees should be further investigated.

Conflict of interest

There is no conflict of interest.

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