Short Original Communications

Effects of Acidic Solutions on Element Dynamics in the Monsoon Evergreen Broad-leaved Forest at Dinghushan, China

Part 2: Dynamics of Fe, Cu, Mn and Al

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DOI: http://dx.doi.org/10.1065/espr2006.08.337

Abstract

Background. Soil metal dynamics are affected by acid deposition. Little knowledge is available about the process in the lateritic soils under the monsoon forest in south China.

Methods. Samplings of *Acmera acuminatissima*, *Cryptocarya concinna* and *Schima superba* were grown from October, 2000 to July, 2002 in pots with a natural acid lateritic forest soil from Dinghushan. Pots were watered weekly with an acid solution (pH 3.05, 3.52, 4.00 or 4.40) or with tap water. Fe, Mn, Cu and Al were measured in soils, leachates and sapling leaves.

Results. Soil extractable Fe and leachate Al and Mn concentrations increased with a decreasing treatment pH. Soil reactive Al exhibited the opposite trend and decreased over time. The Ca/Al and Mg/(Al+Mn) ratios did not decrease in the leaves of *Schima superba*, but decreased with a decreasing treatment pH for *Cryptocaria concinna*. Both ratios only decreased in the pH 3.05 treatment for *Acmena acuminatissima*.

Conclusions. Cu will not be toxic for plants since soil extractable Cu was not high and Fe will not be toxic either given that its root uptake was inhibited by Mn. Acid rains will lead to increased Mn and Al mobility in soil. *Cryptocaria concinna* will be the most sensible species to these changes (nutrient deficiency and direct Mn toxicity), while *Schima superba* should retain a good growth.

Keywords: Acid deposition; *Acmera acuminatissima*; China; *Cryptocarya concinna*; metal dynamic; monsoon forests; *Schima superba*; soil acidification; soil leachate

Introduction

Acid deposition causes alterations of soil forming processes and biogeochemical cycles (Gerald et al. 2001). When a soil is acidified, the depletion of exchangeable base cations, the soil weathering and the changes in pH lead to an increased solubility of Al (Reuss & Johnson 1986), and Al mobilization becomes one of the main mechanisms for buffering proton input in acidified forest soils (Blake et al. 1999). Reactive Al is toxic for many plants species (Vitorello et al. 2005), as it inhibits the root cell division and elongation (Samac & Tesfaye 2003), and reduces Ca, Mg and K absorption (Marschner 1995, Mclaughlin & Wimmer 1999). Soil extractable Cu also increases at a low soil pH (Alva et al. 2000) and can damage root cell plasma membranes when it is available in toxic concentrations. Although Mn is a plant nutrient at low concentrations, extractable Mn can increase with soil acidity up to toxic levels for plants (Blake et al. 1999). It can compete with the root uptake of Mg and Fe (Marschner 1995), and damage leaf cell plasma membranes (Horst 1988).

Understanding the changes that will occur in the metal dynamics following soil acidification is important since it will affect the forest health. Moreover, forests act as hydrological filters and soil acidification may impair this function, leading to an excess leaching of ecotoxic metals. Being submitted to acid deposition and growing on acid lateritic soils that hold large amount of aluminum oxides, southern China forests appear to be very susceptible to the effects of soil acidification. We studied the changes in Fe, Mn, Cu and Al dynamics that occurred following soil acidification at Dinghushan Reserve, a typical forest of southern China. Our goal was to show (1) whether the acid deposition had an impact on the soil metal chemistry, (2) what the changes were in this special environment and (3) how it affected some of the local tree species.

1 Materials and Methods

Experimental design and data analyses have been described thoroughly in the first part of this study (Liu et al 2006). Soil Fe, Mn and Cu were extracted with a 1 M KCl solution (1:10 soil to extractant ratio, 30 min shaking). Fe, Mn and Cu concentrations in extracts and soil leachates were measured by atomic absorption spectrometry (GBC932AA, GBC Scientific Equipment, Australia), as well as foliar Fe, Mn and Cu after leaves were incinerated. The soil reactive Al was extracted by the oxalate/oxalic acid method (Lofts et al. 2001) and measured by ICP-AES (Optima 2000). The foliar Al was extracted by grinding the dried leaves in a ball mill and digesting them using a HNO_3-$HClO_4$ mix. The leaf extract and leachate Al concentrations were determined by the pyrocatechol violet method (Kerven et al. 1989).

2 Results

Ca, Mg and pH results were described in Liu et al. (2006). The acid treatments affected the soil extractable Fe that was significantly higher in the pH 3.05 treatment ($p<0.001$,

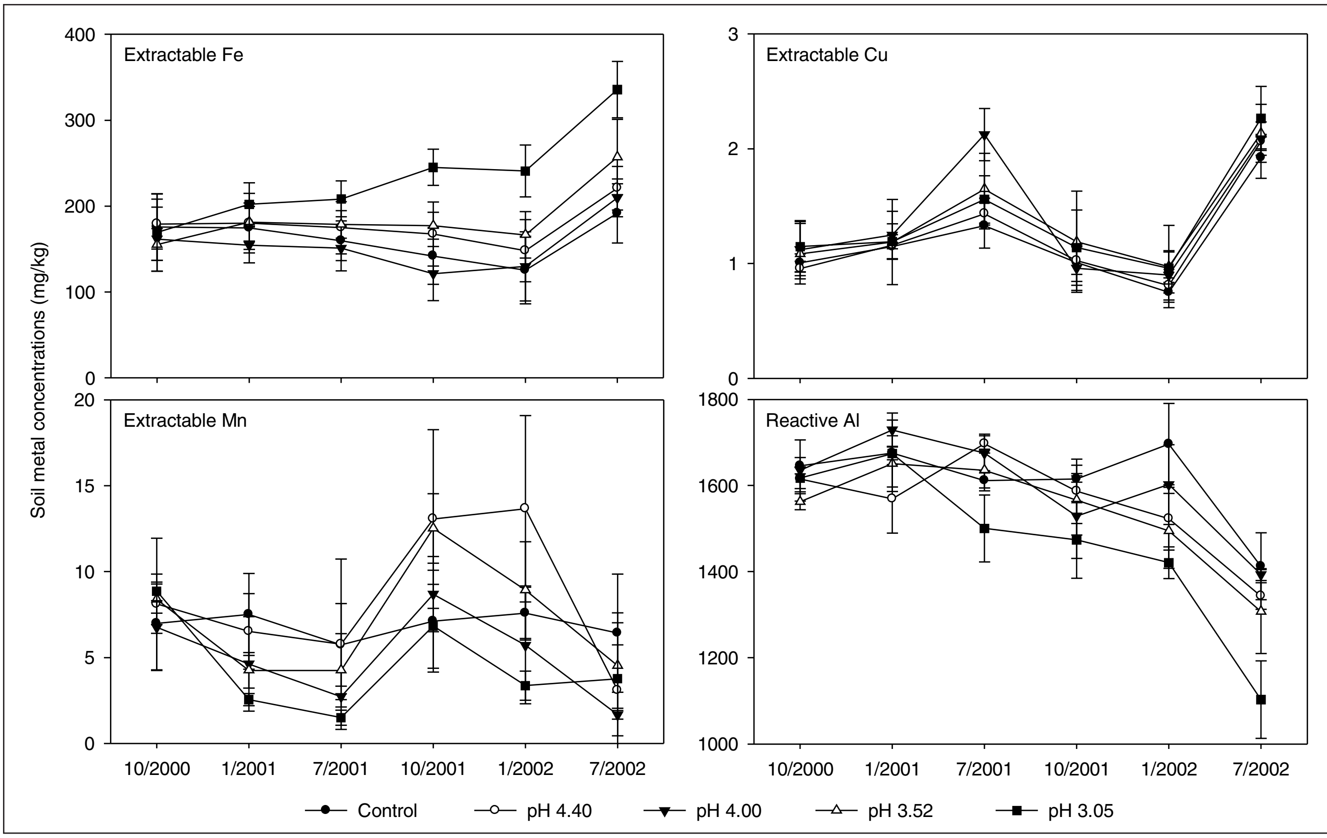

Fig. 1: Effect of acidic solution treatments on soil metal concentration changes during the experimental period (n=12 ±SD)

Table 1: Effect of acidic solution treatments on leachate metal concentrations (mg/L) and element mole ratios (n=72). Data within columns that do not have common indices are significantly different (p<0.05)

Treatment	Fe	Mn	Cu	Al	Ca/Al	Mg/(Al+Mn)
Control	0.291^{a}	0.097^{a}	0.034^{a}	0.39^{a}	11.81^{a}	1.39^{a}
pH 4.40	0.350^{a}	0.137^{a}	0.040^{a}	0.98^{ab}	5.07^{b}	0.61^{b}
pH 4.00	0.263^{a}	0.121^{a}	0.032^{a}	1.78^{ab}	2.59^{c}	0.41^{c}
pH 3.52	0.301^{a}	0.142^{ab}	0.043^{a}	3.03^{b}	2.59^{c}	0.29^{c}
pH 3.05	0.378^{a}	0.183^{b}	0.038^{a}	11.8^{c}	0.56^{d}	0.10^{d}

Fig. 1). Soil Fe concentrations increased in all treatments at the end of the experiment ($p<0.01$). The treatments did not affect Fe in leachates (**Table 1**). Leaf Fe concentrations were low in all species (**Fig. 2**) and, for *Cryptocaria c.*, they changed between treatments ($p<0.01$) in a negative correlation to the soil extractable Mn concentrations ($R^2=0.902$).

The soil extractable Cu concentrations were not affected by the acid treatments and increased at the last sampling time ($p<0.01$). The acid treatments did not affect Cu in leachates (see Table 1). Leaf Cu was higher in July than in January (*Schima s.*: $p<0.05$, other: $p<0.01$, see Fig. 2). For *Acmena a.*, it was higher than for other species ($p<0.001$) and decreased in the pH 3.05 treatment ($p<0.01$).

The treatments did not affect soil extractable Mn (see Fig. 1). Over time, Mn decreased until July, 2001 then increased and decreased again from January, 2002 ($p<0.05$). Mn concentration in leachates was higher in the pH 3.05 treatment than in other treatments ($p<0.001$, see Table 1). *Schima s.* and *Cryptocaria c.* showed significant leaf Mn variations between treatments ($p<0.001$, Fig. 2), but they were not correlated to the acidity of the treatment. They correlated with the soil extractable Mn in January. Leaf Mn concentrations in *Acmena a.* were lower than in other species ($p<0.001$) and were not affected by the treatments.

The treatments affected the soil reactive Al that was lower in the pH 3.05 treatment than in other treatments at the last sampling time ($p<0.01$, see Fig. 1). During the experiment, soil reactive Al concentrations decreased slowly from July, 2001 for all treatments except for the control ($p<0.01$). They showed a steeper decrease in July, 2002 in all treatments. Al concentrations in the leachates increased when the pH of the treatment decreased ($p<0.001$, see Table 1). *Cryptocaria c.* showed increased foliar Al concentrations when the pH of the treatment decreased ($p<0.01$, see Fig. 2) while, for *Schima s.*, the Al concentration increased from the control to the pH 4.00 treatment and then decreased ($p<0.001$). The foliar Al concentrations were significantly different between the species as follows: *Schima s.* >> *Cryptocaria c.* > *Acmena a.* ($p<0.001$).

The Ca/Al mole ratio in leachates decreased in correlation with the pH of the treatment ($p<0.001$, see Table 1). *Acmena a.* had the highest leaf Ca/Al mole ratio (see Fig. 2), followed by *Cryptocaria c.* and *Schima s.* ($p<0.001$). In the leaves of *Schima s.*, Ca/Al was not affected by the treatments during the wet season and it increased in the pH 3.52 and 3.05

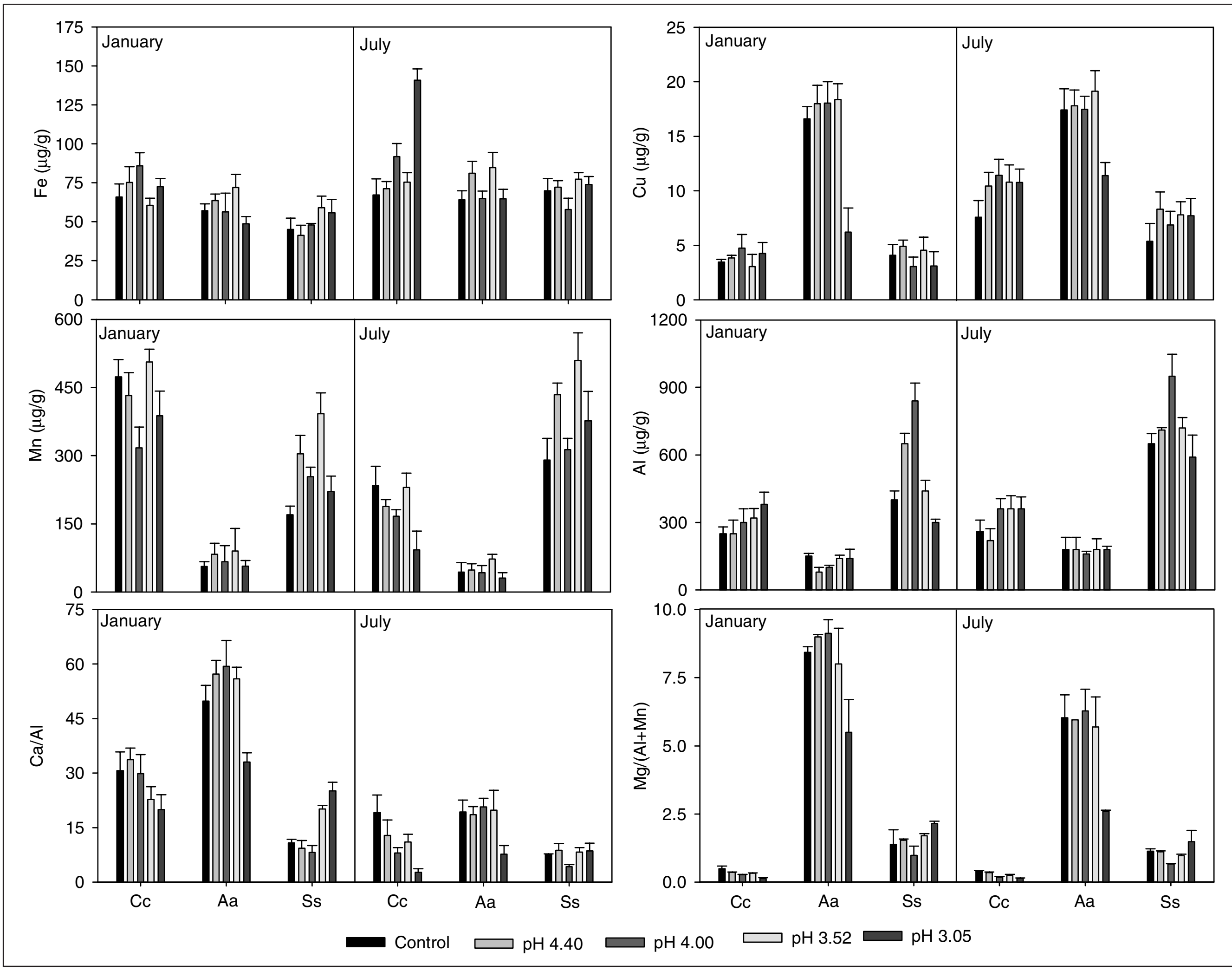

Fig. 2: Effect of acidic solution treatments on mean foliar metal concentrations and element mole ratios of *Cryptocarya concinna* (Cc), *Acmena accuminatissima* (Aa) and *Schima superba* (Ss) saplings (n=4, ± SD)

treatments during the dry season ($p<0.05$). For *Cryptocaria c.*, Ca/Al decreased in correlation with the pH of the treatment ($p<0.001$) and it decreased only in the pH 3.05 treatment ($p<0.001$) for *Acmena a.*. For all the species, the ratio was lower during the wet season ($p<0.01$).

The Mg/(Al+Mn) mole ratio in the leachates decreased readily when the acidity of the treatment increased ($p<0.001$, see Table 1). *Acmena a.* and *Schima s.* showed for this ratio the same results as for Ca/Al (see Fig. 2). *Cryptocaria c.* had the smallest leaf Mg/(Al+Mn) ratio ($p<0.01$) and it decreased slowly when the acidity of the treatment increased ($p<0.05$).

3 Discussion

Extractable Fe only increased in the pH 3.05 treatment, probably because the soil pH only changed substantially in this treatment. A similar result was found by Pennanen et al. (1998). Although the soil extractable Fe was high, the foliar Fe concentrations for all species were in the range of values reported to cause iron deficiency (Marschner 1995). This contradictory result is probably due to an inhibition of root Fe uptake by other metals in the soil, especially Mn. In an artificial soil with sufficient Fe, Alam et al. (2000) showed that a high soil Mn concentration can cause plant Fe deficiency by inhibiting the root absorption and translocation of Fe to leaves. The negative correlation between *Cryptocaria c.* foliar Fe and soil extractable Mn supports this idea.

The acid treatments did not affect the concentration of soil extractable Cu, although other studies reported that extractable Cu increases in soils which are acidified (Alva et al. 2000). This is probably due to the relatively low concentration of Cu in Dinghushan soil. As a consequence, this metal will not be toxic for plant species. Conversely, it may become deficient for plant growth. *Acmena a.* saplings showed decreased foliar Cu concentrations when they were treated with the pH 3.05 acid solution, and leaf Cu for *Schima s.* and *Cryptocaria c.* was in the range of deficiency in January (Marschner 1995).

The acid treatments had no effect on soil extractable Mn, probably due to its low concentration in the soil. The evolution of soil extractable Mn over time may be a consequence of changes in soil redox conditions or temporary weathering. Mn concentration in leachates increased with the soil acidity and Mn toxicity may be a great concern for plant health in Dinghushan soil. This element reached foliar concentrations far above the reported toxicity threshold (Marschner 1995) in leaves of *Schima s.* and *Cryptocaria c.*, while *Cryptocaria c.* also showed visible symptoms of leaf Mn toxicity. Foliar Mn concentrations were very high compared to other metals, given their respective availability in the soil. This could be due to the major translocation of absorbed Mn from roots to shoots, whereas others metal are often compartmentalized in the roots (Marschner 1995).

The soil reactive Al decreased slowly over time. This may be due to a disruption between the generation of reactive Al by weathering or solubilization, and the consumption of reactive Al by complexion with other metals like Fe or by buffering H^+ input through Al leaching. The steeper decrease of soil reactive Al concentrations at the time of the last sampling, where soil Fe concentrations increased in all treatments, supports this idea. Soluble Al concentrations in leachates increased when the pH of the treatment decreased, which resulted in a faster soil reactive Al decrease in the pH 3.05 treatment. Blake et al. (1999) found similar results over a 100-year time span. *Acmena a.* exhibited low leaf Al and Mn concentrations, thereby demonstrating that it may be an excluder species. Leaf Al was well correlated to leachate Al concentrations for *Cryptocaria c.*, which indicates a limited ability to compartmentalize Al away from the shoots. Foliar Al concentrations in *Schima s.* decreased in the pH 3.52 and pH 3.05 treatments. This unexpected result may be due to a mechanism to prevent an over accumulation of Al in shoots. The decrease of *Schima s.* leaf Al concentrations in these two treatments could not be attributed to a reduced Al uptake following root damages, since the uptake of other elements did not show the same decrease.

Ca and Mg play vital roles in supporting cell functions. Al inhibits Ca and Mg uptake while Mn inhibits Mg uptake (Horst 1988). Ca/Al and Mg/(Al+Mn) ratios can help to assess the effect of Al and Mn on the plant nutrition (Mclaughlin & Wimmer 1999). In the soil solution, both ratios decreased dramatically with decreasing treatment pH. The Ca/Al ratio was below 1.0 in the pH 3.05 treatment, which indicates Al will interfere with root Ca uptake (Schroder et al. 1988). Ca and Mg nutrition may be strongly affected by metal concentrations in Dinghushan if soil is further acidified. The decrease of leaf Ca/Al and Mg/(Al+Mn) in *Cryptocaria c.*, when the acidity of treatments was increased, suggests that this species may easily suffer Al or Mn-related nutrient deficiency when exposed to acid deposition. *Acmena a.* will be less sensible and may experience nutrient deficiency only if the pH of rains decreases below 3.5. On the other hand, *Schima s.* saplings sustained constant leaf Ca/Al and Mg/(Al+Mn) ratios across the treatments and, although their Ca/Al was low, they showed a good growth and no sign of nutrient deficiency. This species may be able to sustain a normal mineral nutrition, despite increasing metal concentrations, until the rain pH decreases below 3.05. The decrease of both ratios in July is due to decreased foliar Ca and Mg concentrations at this time (Liu et al. 2006).

4 Conclusions

Soil extractable Cu concentration was not high and should not be toxic for plants. Under very acid rains, soil extractable Fe will increase, but should not be toxic under the present conditions since its uptake was limited. Although available in sufficient soil concentrations, Cu and Fe may become deficient for plant nutrition, especially under rains with a pH below 3.0. Increased mobility of Mn and Al will be a concern in case of further soil acidification. *Schima superba* should not suffer from Al or Mn-related nutrient deficiency for a rain pH over 3.0 and *Cryptocaria cconcinna* will be affected by both direct Mn toxicity and nutrient deficiency. *Acmena acuminatissima* should avoid direct Al or Mn toxicity on foliar tissues with low foliar metal concentrations, but may experience nutrient deficiency related to the nutrient uptake inhibition by metals, especially if the rain pH is below 3.5.

Acknowledgement. This work was supported by Guangdong Provincial Natural Science Foundation of China (04002320), Director Foundation of South China botanical Garden (2004-2139) and National Natural Science Foundation of China (30470306, 30570350).

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Received: February 25th, 2006
Accepted: August 31st, 2006
OnlineFirst: August 31st, 2006