

## RESEARCH ARTICLE

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## Key Points:

- CO<sub>2</sub> enrichment led to accelerated base cation leaching loss
- The N addition decreased the effect of CO<sub>2</sub> enrichment on the base cation loss
- The N addition induced greater metal cation leaching loss

## Supporting Information:

- Figures S1–S3
- Readme

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## Quantify the loss of major ions induced by CO<sub>2</sub> enrichment and nitrogen addition in subtropical model forest ecosystems

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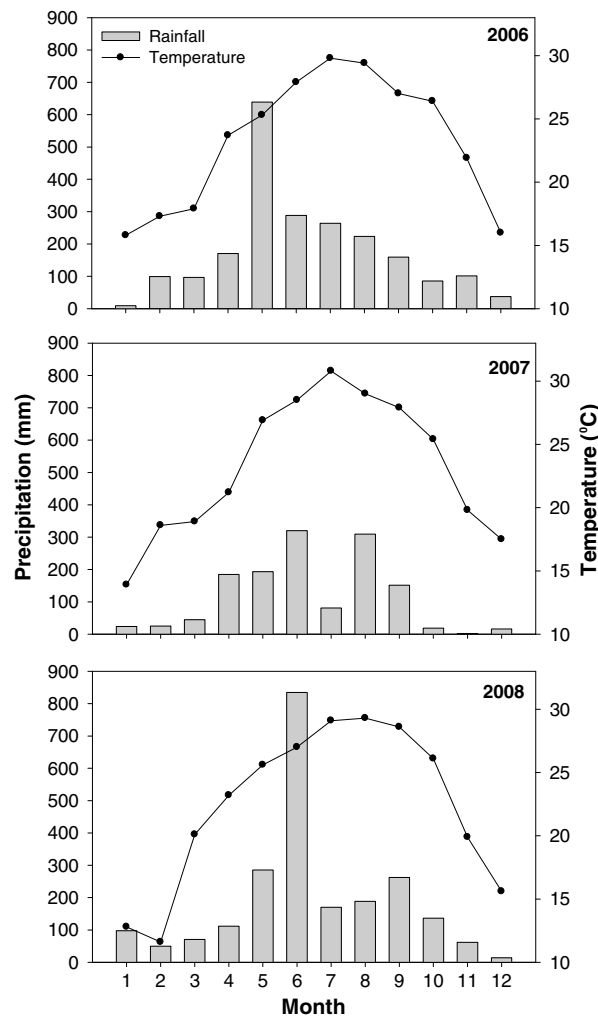
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**Abstract** Previous studies have reported that atmospheric CO<sub>2</sub> enrichment would increase the ion concentrations in the soil water. However, none of these studies could exactly quantify the amount of ion changes in the soil water induced by elevated CO<sub>2</sub> and all of these experiments were carried out only in the temperate areas. Using an open-top chamber design, we studied the effects of CO<sub>2</sub> enrichment alone and together with nitrogen (N) addition on soil water chemistry in the subtropics. Three years of exposure to an atmospheric CO<sub>2</sub> concentration of 700 ppm resulted in accelerated base cation loss via leaching water below the 70 cm soil profile. The total of base cation (K<sup>+</sup> + Na<sup>+</sup> + Ca<sup>2+</sup> + Mg<sup>2+</sup>) loss in the elevated CO<sub>2</sub> treatment was higher than that of the control by 220%, 115%, and 106% in 2006, 2007, and 2008, respectively. The N treatment decreased the effect of high CO<sub>2</sub> treatment on the base cation loss in the leachates. Compared to the control, N addition induced greater metal cation (Al<sup>3+</sup> and Mn<sup>2+</sup>) leaching loss in 2008 and net Al<sup>3+</sup> and Mn<sup>2+</sup> loss in the high N treatment increased by 100% and 67%, respectively. However, the CO<sub>2</sub> treatment decreased the effect of high N treatment on the metal cation loss. Changes of ion export followed by the exposure to the elevated CO<sub>2</sub>, and N treatments were related to both ion concentrations and leached water amount. We hypothesize that forests in subtropical China might suffer from nutrient limitation and some poisonous metal activation in plant biomass under future global change.

### 1. Introduction

Under elevated atmospheric CO<sub>2</sub>, increased soil CO<sub>2</sub> flux has been demonstrated by a growing number of both open-top chamber experiments with elevated CO<sub>2</sub> and Free-Air CO<sub>2</sub> Enrichment studies [Gill *et al.*, 2002; Suwa *et al.*, 2004; Bernhardt *et al.*, 2006]. The increased soil water content induced by elevated atmospheric CO<sub>2</sub> has also been found [Bunce, 2004; Deng *et al.*, 2010]. Soil CO<sub>2</sub> reacts with water to produce carbonic acid, which then can generate protons. Protons from carbonic acid are consumed in both cation exchange and mineral dissolution reactions, resulting in the release of base cations to soil water. Previous studies also showed that enhanced soil moisture under high CO<sub>2</sub> might induce important secondary effects on soil ecological processes [Niklaus *et al.*, 1998]. Soil microbial processes are stimulated by soil humidity, which subsequently improves litter decomposition and nutrient mineralization [Niklaus *et al.*, 1998]. Hence, soil water chemistry, especially the concentration of nutrient ions, would normally be changed under elevated atmospheric CO<sub>2</sub>. To date, many studies have examined the changes in soil water chemistry due to the increased soil CO<sub>2</sub> [Karberg *et al.*, 2005; Schleppi *et al.*, 2012]; however, few studies could exactly quantify the changes of major ions in the soil water-induced by elevated CO<sub>2</sub>.

Previous studies concerning the effects of elevated atmospheric CO<sub>2</sub> on soil water chemistry mostly focused on the N availability and carbon (C) leaching. It was found that the elevated atmospheric CO<sub>2</sub> concentration increased [Schleppi *et al.*, 2012], decreased [Niklaus *et al.*, 2001], and had no effect [Finzi and Schlesinger, 2003] on N availability in the soil. And the significant effect on C loss induced by the high CO<sub>2</sub> treatment was observed [Williams *et al.*, 2003; Fenner *et al.*, 2007; Liu *et al.*, 2011]. Studies focused on the impacts of elevated CO<sub>2</sub> on other element cycles were rare. An increase of 55% in atmospheric CO<sub>2</sub> concentration over 2 years resulted in a 271% increase in soil solution cation concentrations in a temperate forest was found [Andrews and Schlesinger, 2001]. However, after another 3 year study at the same research site, the increased degree of soil solution cation concentrations induced by the increased CO<sub>2</sub> was decreasing [Oh *et al.*, 2007]. Using 1 year of sampling data, our previous study showed that elevated CO<sub>2</sub> atmospheric concentration could result in



**Figure 1.** Monthly rainfall and mean temperature in Guangzhou City, China, during the experimental period from 2006 to 2008. Data were cited from Liu *et al.* [2011].

increased base cation losses by leaching in subtropical model forests [Liu *et al.*, 2008]. However, we still do not know whether this effect could last for a longer time or not.

Atmospheric N deposition is a serious problem in southern China. This leads to high N deposition in precipitation in some forests (30–73 kg N ha<sup>-1</sup> yr<sup>-1</sup>) [Mo *et al.*, 2006]. It was reported that high N deposition would accelerate soil basic cation leaching [Foster *et al.*, 1989; Gbondo-tugbawa and Driscoll, 2003; Watmough and Dillon, 2003] and mobilize heavy metal elements [Pichtel *et al.*, 1997; Marschner *et al.*, 1998], thus changing soil water chemistry. What would happen to the soil water chemistry in this subtropical area with both increasing atmospheric CO<sub>2</sub> concentration and high N deposition?

Using an open-top chamber design, we studied the effect of elevated CO<sub>2</sub> alone and together with N addition on the major ion loss via soil water over 3 years in the subtropics. Our open-top chambers have a 0.7 m deep belowground part which was delimited by brick walls that prevented any lateral or vertical water and/or element fluxes with the outside surrounding soil. This special open-top chamber design could allow us to measure the exact leaching amount of elements via soil water. Unlike the previous studies, we focused not only on the nutrient elements but also on the metal elements. The objectives of this study were (1) to quantify the changes of major ions in the soil water induced by elevated CO<sub>2</sub> over 3 years, and (2)

to investigate whether N addition would change the effects of elevated atmospheric CO<sub>2</sub> on soil water chemistry. As most studies concerning the effects of elevated CO<sub>2</sub> on soil water chemistry were only conducted in temperate forests, we believe that our research findings reported here would contribute to a better understanding and prediction of future biogeochemical cycles of elements under global change.

## 2. Material and Methods

### 2.1. Study Site and Experimental Design

The study site (23°10'46"N, 113°21'9"E) is located at South China Botanical Garden in Guangzhou City, South China. This site is characterized by a typical subtropical monsoon climate, with an average annual temperature of 21.5°C. Within a year, the highest and lowest monthly mean temperatures occur in July and January, respectively. The annual precipitation ranges from 1600 mm to 1900 mm, of which more than 80% falls in the period of April–September, clearly creating a wet season and a dry season. The mean relative humidity is 77%. Rainfall and air temperature during the experimental period are shown in Figure 1.

A model forest ecosystem was established in a circular chamber with a diameter of 3 m. The chamber system consisted of two parts. A 0.7 m deep belowground part was delimited by brick wall that prevented any lateral or vertical water exchange with the outside surrounding soil. All water flow from the chamber was collected through the three holes at the bottom around the wall. A 3 m high aboveground part (adjusted to 4.5 m later)

**Table 1.** Total Element Contents of Selected Chemical Parameters in the Initial Soil<sup>a</sup>

Depth (cm)	pH	K	Na	Ca	Mg	P	Organic C	N	Al	Cu	Mn	Zn	Pb
		(g/kg)							(mg/Kg)				
0–20	4.15 (0.15)	6.30 (0.73)	0.64 (0.19)	1.03 (0.22)	1.03 (0.13)	0.30 (0.09)	16.33 (3.42)	0.52 (0.15)	1.77 (0.63)	4.69 (1.75)	78.70 (8.78)	35.91 (17.16)	37.48 (7.07)
20–40	4.27 (0.15)	5.03 (1.11)	0.63 (0.49)	0.57 (0.27)	0.84 (0.22)	0.18 (0.19)	7.78 (0.91)	0.36 (0.05)	1.55 (0.15)	4.68 (1.50)	73.68 (25.00)	30.15 (14.35)	23.04 (6.42)
40–60	4.25 (0.13)	5.49 (1.53)	1.35 (0.63)	0.51 (0.18)	0.83 (0.23)	0.14 (0.07)	3.94 (1.54)	0.29 (0.07)	1.32 (0.19)	5.91 (3.60)	65.15 (16.96)	48.02 (79.07)	19.76 (6.61)

<sup>a</sup>Data except for the metal elements were cited from Liu *et al.* [2008]. Standard deviations are in parentheses ( $n = 10$ ).

was made from impermeable and transparent plastic sheets with the top being opened. The light intensity in the chamber was 97% of the full light. The three different layers (0–20, 20–40, and 40–70 cm depth) soil used to fill the belowground part was collected from a nearby evergreen broad-leaved forest after harvesting. Eight one- to two-year-old seedlings grown in a nursery for each of the native and dominated six species (*Castanopsis hystrix*, *Syzygium hancei*, *Pinus massoniana*, *Schima superba*, *Acmena acuminatissima*, and *Ormosia pinnata*) were transplanted in each chamber without damaging the roots. There was no significant difference in the routine parameters of soils and plants among the initial chambers. The initial soil chemical properties were presented in Table 1. The detailed description about the experimental design was shown in Liu *et al.* [2011, 2013].

## 2.2. Treatments of CO<sub>2</sub> Enrichment and N Addition

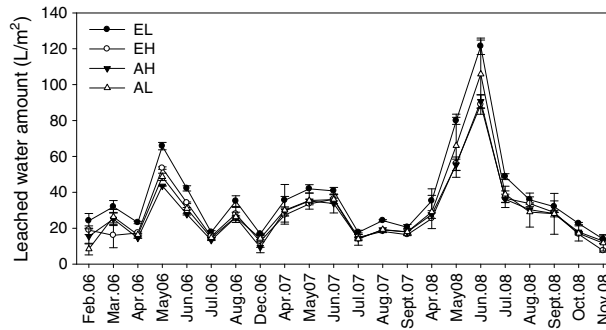
From April 2005, the chambers were randomly exposed to four treatments with two levels of CO<sub>2</sub> concentrations (ambient CO<sub>2</sub> and elevated CO<sub>2</sub>) and two levels of N additions (without N fertilizer and with N fertilizer). Three chambers received an elevated CO<sub>2</sub> (approximately 700  $\mu\text{mol mol}^{-1}$ ) and high N addition (NH<sub>4</sub>NO<sub>3</sub>-N applied at 100 kg N ha<sup>-1</sup> yr<sup>-1</sup>) (EH), three chambers received an elevated CO<sub>2</sub> treatment (EL), two chambers received a high N addition (AH), and finally, two chambers acted as a control (without elevated CO<sub>2</sub> and high N addition) (AL). The purity of NH<sub>4</sub>NO<sub>3</sub> was  $\geq 99.0\%$  with major elements (K, Na, Ca, Mg, Al, and Mn)  $\leq 0.001\%$ . The elevated CO<sub>2</sub> treatment was achieved by supplying additional CO<sub>2</sub> from a tank until the CO<sub>2</sub> concentration was approximately 700 ppm in the chambers. The high N addition was achieved by spraying seedlings once a week with a total amount of NH<sub>4</sub>NO<sub>3</sub>-N at 100 kg N ha<sup>-1</sup> yr<sup>-1</sup>. All chambers received the same wind speed by a fan and 600 mm extra tap water for irrigating the seedlings per year. The detailed treatments could be found in Liu *et al.* [2011, 2013].

## 2.3. Sample Collection and Measurement

Initial soil parameters were measured at the time of soil collection. Samples from each collected soil layer were sieved (<2 mm) and mixed thoroughly by hand. Soil pH was determined with a glass electrode in the supernatant after shaking for 2 h and sedimentation in a beaker for 24 h in deionized CO<sub>2</sub>-free water. The soil to H<sub>2</sub>O ratio was 1:2.5. After acid digestion, total K, Na, Ca, Mg, Cu, Mn, Zn, and Pb were measured using inductively coupled plasma atomic emission spectroscopy (Optima-2000 Dual View (DV), PerkinElmer USA). Total P concentration was analyzed colorimetrically [Anderson and Ingram, 1989], organic C was determined following Walkley Black's wet digestion method [Nelson and Sommers, 1982], and total N was measured using the micro Kjeldahl method [Jackson, 1964]. After soil was extracted by oxalic acid and ammonium oxalate, total Al was measured by inductively coupled plasma atomic emission spectroscopy.

Leaching water sample collection started in 2006 in the second year of the treatment applications and continued for three years. Soil leachates were collected at the bottom of the chamber below ground walls in stainless steel boxes. During the dry season, they were collected after each rainfall. During the wet season, they were collected once a week. Each time, the exact volume of total leachates was measured and 100 ml per box was collected for chemical analysis.

The concentrations of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, Cu<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> in the leachates were measured using the inductively coupled plasma atomic emission spectroscopy (Optima2000). NO<sub>3</sub><sup>-</sup>-N was determined by the phenol disulfonic acid spectrophotometric method [Nicholas and Nason, 1957] and NH<sub>4</sub><sup>+</sup>-N by the indophenol blue spectrophotometric method [Horn and Squire, 1966]. The P concentration was measured by the stannous chloride method (American Public Health Association Standard Methods,



**Figure 2.** Monthly volumes over 3 years of exposure to various CO<sub>2</sub> and N treatments. Error bars are standard deviations ( $n = 9$  for EL and EH and  $n = 6$  for AH and AL). Treatments are: AL = control, AH = high N treatment, EL = elevated CO<sub>2</sub> concentration treatment, and EH = elevated CO<sub>2</sub> concentration treatment + high N treatment. Data were cited from Liu *et al.* [2011]

20th ed., 4–145, Method 4500-P D, 1998). In order to determine element and ions input from rainfall, rain water was collected in an open area near the chambers and submitted to the same analyses as for leachates.

#### 2.4. Data Analysis

Data analyses were carried out using the Statistics Analysis System (SAS) software (SAS Institute Inc., Cary, NC, U.S.). For each variable, the normality of the distribution was tested by a Shapiro–Wilk test. We chose  $\alpha$  equal to 0.05. Analyzed data consisted of concentrations and amounts of ions in the leachates, amount

of leaching water. Monthly leaching water volumes were calculated by adding each individual amount of leaching water during the whole month. Monthly ion leached was calculated by adding each individual ion concentration measurement factored by their respective amount of leaching water. Standardized average monthly ion concentrations in the leachates for the supporting information were calculated by dividing monthly ion amounts by monthly volumes of the leachates. Annual net loss amounts were calculated by adding monthly amounts, but minus the element inputs from the precipitation. Data were analyzed for each year separately. The mixed linear model was used to examine the effects of the CO<sub>2</sub> treatments (ambient or 700 ppm), the N treatment (ambient or high addition), and precipitation and their interactions on the ion concentrations in each collected leachates. The effect of the chambers nested inside the CO<sub>2</sub> and N treatments was added to the above model as a random variable. In order to know the effects of CO<sub>2</sub> and N treatments on annual volumes of leaching water and annual net loss amount of ions, one-way analysis of variance were used. When the effects were significant, they were further analyzed using Tukey’s multiple comparison honestly significant difference test. Additionally, simple correlations were performed on the whole set of data using the Pearson correlation coefficients.

### 3. Results

#### 3.1. Leaching Water Volume

The volumes of leaching water showed the greater amounts during the wet season (from April to September) than the dry season, which was consistent with the rainfall amounts during the whole experiment period (Figures 1 and 2). There had been highest annual water leaching amounts in 2008, followed by 2006, and then 2007. The high CO<sub>2</sub> treatment increased the leaching water volumes, while the high N treatment reduced the volumes (Table 2). Compared to the control treatment, the volumes of leachates were 69%, 18%, and 20% greater in the EL treatment in 2006, 2007, and 2008, respectively. There was a strongly interactive effect of the high CO<sub>2</sub> and N treatment on leachate volume ( $P < 0.01$  in 2006 and  $P < 0.001$  in 2007 and 2008). In 2006, the water volumes in the leachates were in the order: EL > EH > AH > AL. However, in both 2007 and 2008, the greatest water volumes were found in the EL chambers, followed by AL, and finally the AH and EH treatments, indicating that with time, the N treatment had significantly negative effects on the leaching amount of soil water.

#### 3.2. Base Cations in the Leaching Water

The base concentrations of K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> in the leachates varied throughout the whole experiment period (see Figure S1 in the supporting information). The CO<sub>2</sub> treatment, N treatment, and precipitation and their interactions all affected significantly base cation concentrations (Table 3). The CO<sub>2</sub> treatment increased the base cation concentrations, while N treatment decreased the base cation concentrations. There was a positive relationship between the Ca<sup>2+</sup> and Mg<sup>2+</sup> concentrations ( $R^2 = 0.41$  and  $P < 0.05$ ). It was also found that the Mg<sup>2+</sup> and Ca<sup>2+</sup> concentrations were positively correlated to the Na<sup>+</sup> concentrations ( $R^2 = 0.35$  and  $R^2 = 0.47$ , respectively,  $P < 0.05$ ).

**Table 2.** The Annual Volumes of Leaching Water and Annual Net Loss Amounts of Ions<sup>a</sup>

Parameters		2006				2007				2008			
		EL	EH	AH	AL	EL	EH	AH	AL	EL	EH	AH	AL
Water *10 <sup>-4</sup>	means	281 <sup>b</sup>	215 <sup>c</sup>	170 <sup>d</sup>	166 <sup>e</sup>	181 <sup>b</sup>	147 <sup>d</sup>	150 <sup>d</sup>	153 <sup>c</sup>	390 <sup>b</sup>	294 <sup>d</sup>	299 <sup>d</sup>	326 <sup>c</sup>
	SD	39.9	26.7	34.1	13.8	16.4	16.2	16.1	13.0	32.4	38.3	21.1	67.0
K <sup>+</sup>	means	22.2 <sup>b</sup>	15.9 <sup>c</sup>	8.5 <sup>d</sup>	6.9 <sup>d</sup>	8.1	6.4	6.1	4.9	9.2	7.2	8.8	8.5
	SD	5.3	2.5	2.1	2.1	3.6	1.7	0.6	1.7	4.5	2.9	2.4	2.4
Na <sup>+</sup>	means	67.4 <sup>b</sup>	35.2 <sup>c</sup>	14.6 <sup>d</sup>	11.5 <sup>d</sup>	26.6 <sup>b</sup>	10.7 <sup>c</sup>	7.6 <sup>c</sup>	6.8 <sup>c</sup>	69.3 <sup>b</sup>	24.5 <sup>c</sup>	13.4 <sup>c</sup>	18.7 <sup>c</sup>
	SD	15.7	7.1	3.1	2.6	12.0	2.8	1.6	1.9	37.5	6.2	1.5	2.6
Ca <sup>2+</sup>	means	171 <sup>b</sup>	114 <sup>c</sup>	65 <sup>d</sup>	64 <sup>d</sup>	106 <sup>b</sup>	62 <sup>c</sup>	62 <sup>c</sup>	54 <sup>c</sup>	241 <sup>b</sup>	137 <sup>c</sup>	113 <sup>c</sup>	128 <sup>c</sup>
	SD	48.6	27.7	15.0	15.3	42.6	20.3	17.6	13.3	74.8	43.0	21.8	15.9
Mg <sup>2+</sup>	means	8.21 <sup>b</sup>	6.07 <sup>c</sup>	1.52 <sup>d</sup>	1.70 <sup>d</sup>	1.04 <sup>b</sup>	0.56 <sup>c</sup>	0.39 <sup>c</sup>	0.31 <sup>c</sup>	9.01 <sup>b</sup>	4.31 <sup>c</sup>	3.58 <sup>c</sup>	4.03 <sup>c</sup>
	SD	2.38	1.83	0.49	0.48	0.59	0.33	0.16	0.09	3.97	2.50	1.22	0.53
Al <sup>3+</sup>	means	0.13	0.17	0.26	0.20	0.00 <sup>c</sup>	0.02 <sup>bc</sup>	0.05 <sup>b</sup>	0.03 <sup>bc</sup>	0.02 <sup>d</sup>	0.11 <sup>c</sup>	0.30 <sup>b</sup>	0.18 <sup>c</sup>
	SD	0.10	0.18	0.34	0.18	0.00	0.04	0.05	0.04	0.00	0.11	0.23	0.14
Cu <sup>2+</sup>	means	0.00	0.00	0.00	0.00	0.00 <sup>c</sup>	0.00 <sup>c</sup>	0.00 <sup>b</sup>	0.00 <sup>bc</sup>	0.01 <sup>c</sup>	0.02 <sup>c</sup>	0.04 <sup>b</sup>	0.03 <sup>bc</sup>
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01
Mn <sup>2+</sup>	means	0.00	0.01	0.01	0.01	0.02	0.00	0.03	0.01	0.02 <sup>c</sup>	0.01 <sup>c</sup>	0.04 <sup>b</sup>	0.02 <sup>c</sup>
	SD	0.00	0.01	0.01	0.02	0.01	0.00	0.03	0.01	0.06	0.00	0.01	0.01
Pb <sup>2+</sup>	means	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn <sup>2+</sup>	means	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	SD	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NH <sub>4</sub> <sup>+</sup> -N	means	0.00	0.01	0.01	0.00	0.03	0.03	0.02	0.03	0.03	0.02	0.02	0.02
	SD	0.04	0.01	0.07	0.02	0.02	0.02	0.01	0.03	0.02	0.01	0.02	0.01
NO <sub>3</sub> <sup>-</sup> -N	means	2.01 <sup>d</sup>	6.29 <sup>b</sup>	3.01 <sup>c</sup>	0.97 <sup>d</sup>	1.25 <sup>c</sup>	2.00 <sup>b</sup>	0.82 <sup>c</sup>	0.74 <sup>c</sup>	3.53 <sup>c</sup>	7.02 <sup>b</sup>	3.71 <sup>c</sup>	2.12 <sup>c</sup>
	SD	0.98	1.30	1.27	0.90	0.54	0.31	0.24	1.97	0.37	3.01	1.50	0.54
Soluble PO <sub>3</sub> *10 <sup>3</sup>	means	4.35 <sup>b</sup>	3.31 <sup>bc</sup>	3.00 <sup>bc</sup>	2.51 <sup>c</sup>	0.68 <sup>d</sup>	4.03 <sup>b</sup>	2.14 <sup>c</sup>	1.28 <sup>c</sup>	2.88 <sup>c</sup>	4.62 <sup>b</sup>	3.10 <sup>c</sup>	1.90 <sup>d</sup>
	SD	0.00	0.00	0.00	0.00	0.33	2.43	1.24	0.54	0.28	3.97	1.75	1.06

<sup>a</sup>Data about annual volumes of leaching water were cited from Liu *et al.* [2011]. Treatments with different superscript letter are significantly different from each other ( $p > 0.05$ ) in the same year. Unit: L ha<sup>-1</sup> yr<sup>-1</sup> for water, kg ha<sup>-1</sup> yr<sup>-1</sup> for the others.

<sup>b</sup>AL = control.

<sup>c</sup>AH = high N treatment.

<sup>d</sup>EL = elevated CO<sub>2</sub> concentration treatment.

<sup>e</sup>EH = elevated CO<sub>2</sub> concentration treatment + high N treatment.

The monthly leached amounts of base cations also varied over the three years. Greater monthly leached amounts for the base cations were found in the EL chambers followed by EH chambers, and then the chambers with treatments of AH and AL (Figure 3). For K<sup>+</sup> and Na<sup>+</sup>, there were more leaching amounts in 2006 than the other sampling years, while for Ca<sup>2+</sup> and Mg<sup>2+</sup>, greater leaching amounts in 2008 than in the other years (Table 2). The CO<sub>2</sub> treatment affected significantly the amounts of basic cations in the leachates (Figure 3). Compared to the other treatments, the EL treatment showed the greatest amounts of base cations in the leachates (Table 2). The total loss of base cation (K<sup>+</sup>+Na<sup>+</sup>+Ca<sup>2+</sup>+Mg<sup>2+</sup>) in the chambers with EL treatment was higher than that of the control by 220%, 115%, and 106% in 2006, 2007, and 2008, respectively.

The N treatment did not directly affect the base cation loss in the leachates. However, there was significant interaction of N treatment and CO<sub>2</sub> treatment on the base cation loss. Lower base cation losses were found in EH treatment than those in the EL treatment (Table 2 and Figure 3). The Mg<sup>2+</sup> leached amount was positively related to the Ca<sup>2+</sup> and Na<sup>+</sup> leached amounts ( $R^2 = 0.84$  and  $R^2 = 0.75$ , respectively,  $P < 0.05$ ).

### 3.3. Inorganic N and Soluble P in the Leaching Water

The NH<sub>4</sub><sup>+</sup>-N concentrations in the leachates were low in all the treatments, and there were no detectable leaching losses in some months (Figure S2). The NH<sub>4</sub><sup>+</sup>-N concentrations were related to the N treatments, the interactions of CO<sub>2</sub> and N treatment, as well as precipitation (Table 3). The NO<sub>3</sub><sup>-</sup>-N concentrations in leachates were significantly positively affected by both CO<sub>2</sub> and high N treatments ( $P < 0.001$ ) (Table 3). Precipitation also affected significantly the NO<sub>3</sub><sup>-</sup>-N concentrations. Soluble P concentrations were very low in leachates (Figure S2). They also showed a significant response to the CO<sub>2</sub>, N treatment, and precipitation (Table 3).

The monthly leached amounts of NH<sub>4</sub><sup>+</sup>-N and NO<sub>3</sub><sup>-</sup>-N varied through the whole study period (Figure 4). It showed no differences for annual net loss amounts of NH<sub>4</sub><sup>+</sup>-N among different treatments in all the 3 years.

**Table 3.** Effects of CO<sub>2</sub> Treatment (C), N Treatment (N), Precipitation, and Their Interactions on Concentrations of Elements in Leachates<sup>a</sup>

Variables	Year	C	N	C*N	Precipitation	C* Precipitation	N* Precipitation
K <sup>+</sup>	2006		*	***	***		
	2007	***		*	***	*	
	2008	***	***		***	***	***
Na <sup>+</sup>	2006	***		***			
	2007	***	***	***	**		*
	2008	***	***	***	***	***	***
Ca <sup>2+</sup>	2006						
	2007	**	*	**	**		
	2008	***	***	***	***	***	***
Mg <sup>2+</sup>	2006	*					
	2007	***		*	***		
	2008	***	***	***	***	***	***
Al <sup>3+</sup>	2006						
	2007	**	**		**		
	2008	***	***	***	***	***	***
Cu <sup>2+</sup>	2006						
	2007	***	***		***	*	
	2008	***	***	**	***		
Mn <sup>2+</sup>	2006		*		***		**
	2007		***		**	**	*
	2008	**	***	***	***		
N-NH <sub>4</sub> <sup>+</sup>	2006	***		**	***		
	2007		***	*	***	*	*
	2008		*	***	***	***	***
N-NO <sub>3</sub> <sup>-</sup>	2006		***	***	***	*	***
	2007	***	***	***	***		
	2008	***	***	***	***	***	***
Soluble P	2006	***	***		***	***	**
	2007	***	***	***	***	*	**
	2008	*	***		*	***	

<sup>a</sup>Asterisks indicate the level of significance (no asterisk = not significant).

\**P* < 0.05.

\*\**P* < 0.01.

\*\*\**P* < 0.001.

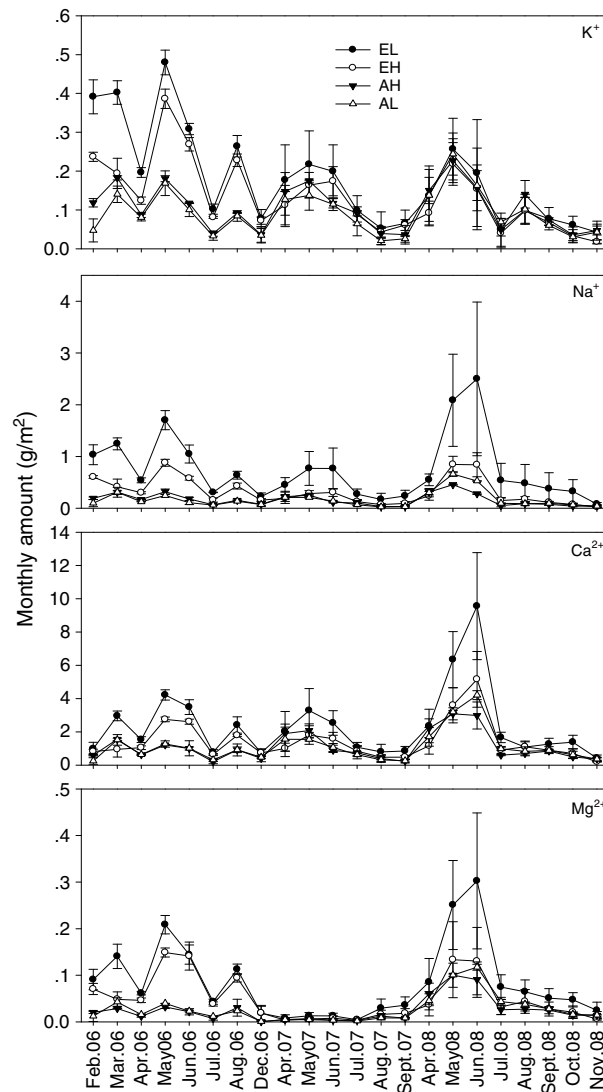
However, the CO<sub>2</sub> treatment, the N treatment, and their interactions all affected the leached amounts of NO<sub>3</sub><sup>-</sup>-N. Compared to the other treatments, the EH treatment showed the greatest amount of NO<sub>3</sub><sup>-</sup>-N in the leachates, while the control showed the lowest amount. For soluble P, it was related to both CO<sub>2</sub> and N treatments. The highest leached amount of soluble P was found in the EL treatment in 2006, while the highest ones were detected in the EH treatment in both 2007 and 2008. The annual net P leaching losses were 4.03, and 4.62 g ha<sup>-1</sup> y<sup>-1</sup> in the EH treatment in 2007 and 2008, respectively, which were 215% and 143% higher than those of the control (Table 2).

### 3.4. Metal Cations in the Leaching Water

Except for Al<sup>3+</sup>, metal cation concentrations (Cu<sup>2+</sup>, Mn<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup>) were low in all the treatments and varied throughout the whole experimental period (Figure S3). We could not detect the concentrations of Pb<sup>2+</sup> and Zn<sup>2+</sup> for most of the sampling times, and hence, there were no observations in the effects of both CO<sub>2</sub> and N treatments on them. With time, the concentrations of Al<sup>3+</sup>, Cu<sup>2+</sup>, and Mn<sup>2+</sup> were found to be related to the CO<sub>2</sub> treatment, N treatment, and precipitation (Table 3). However, unlike the base cations, they were decreased by the CO<sub>2</sub> treatment, but increased by the N treatment.

Great differences existed among different months for the metal cation leached amount. Greater amounts of metal cations leached in 2008 than other years (Figure 5). In 2006, all the metal cation leached amounts were not affected by the treatments. However, the leached amounts of Al<sup>3+</sup> and Mn<sup>2+</sup> were decreased by the CO<sub>2</sub> treatment but increased by the N treatment in 2008. Compared to the control, the net loss of Al<sup>3+</sup> and Mn<sup>2+</sup> in the high N treatment increased 100% and 67%, respectively (Table 2). For Cu<sup>2+</sup>, the high N treatment also showed the highest leaching loss in 2008, while the EL treatment showed the lowest leached amounts in these 2 years.





**Figure 3.** Monthly amounts of base cations in leachates over 3 years of exposure to various CO<sub>2</sub> and N treatments. Error bars are standard deviations ( $n = 9$  for EL and EH and  $n = 6$  for AH and AL). Treatments are: AL = control, AH = high N treatment, EL = elevated CO<sub>2</sub> concentration treatment, and EH = elevated CO<sub>2</sub> concentration treatment + high N treatment. Data in 2006 were cited from Liu *et al.* [2008]

*et al.*, 2011]. Moreover, the soil in the high CO<sub>2</sub> treatment showed greater moisture contents in our experiment. Enhanced soil moisture could induce important secondary effects on soil ecological processes, such as the stimulation of soil microbial processes, which leads to increased rates of litter decomposition and nutrient mineralization [Niklaus *et al.*, 1998]. Greater net annual cation losses by leaching in the elevated CO<sub>2</sub> treatment in our experiment were the results of higher cation concentrations and greater volumes of leachates. The greater leaf nutrient contents found in our previous study in the chambers exposed to the high CO<sub>2</sub> treatment should be the results of the higher nutrient concentration in the soil water in these chambers [Li *et al.*, 2012].

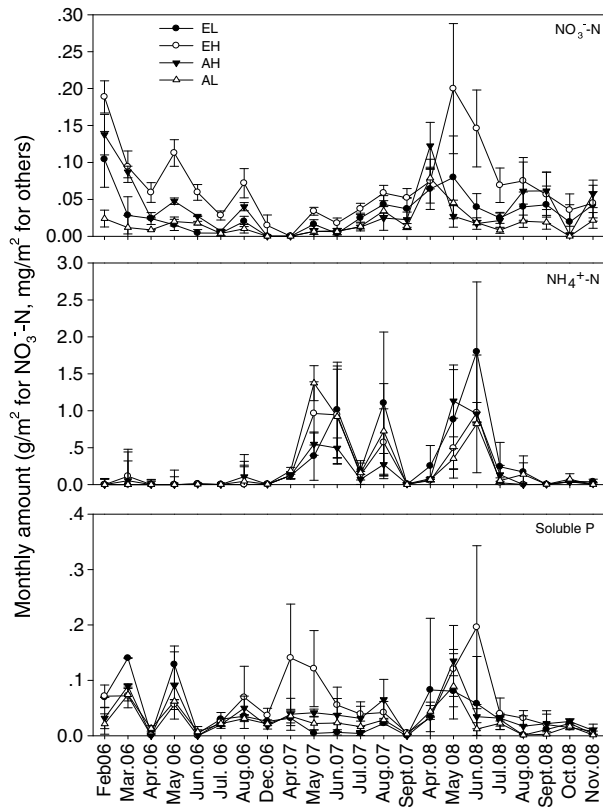
Experimental results of the effects of high CO<sub>2</sub> on soil NO<sub>3</sub><sup>-</sup>-N is controversial. It was reported that elevated CO<sub>2</sub> concentration decreased [Torbert *et al.*, 1996; Hagedorn *et al.*, 2005;], increased [Korner and Arnone, 1992; Niklaus *et al.*, 2001; Garcia-Palacios *et al.*, 2012], and had no effect [Williams *et al.*, 2003] on NO<sub>3</sub><sup>-</sup>-N concentration in the soil solution. The differences in the observed effects of elevated CO<sub>2</sub> on leachate NO<sub>3</sub><sup>-</sup>-N may be due to the nature of soils used, climatic conditions, or soil microbial activities

## 4. Discussion

### 4.1. The Effects of CO<sub>2</sub> Treatment on Soil Ion Leaching

High atmospheric CO<sub>2</sub> concentrations in the EL treatment resulted in a shift of the leaching pattern imposed by the rainfall toward greater leaching rates. This led to greater annual leaching volumes in the EL treatment during the whole experiment period, compared with those in the control. Increased leaching volumes in the EL treatment were probably related to the decrease of other water outputs such as lower transpiration due to CO<sub>2</sub>-induced stomatal closure [Gedney *et al.*, 2006]. Indeed, EL treatment showed the highest soil moisture contents [Deng *et al.*, 2010]. The elevated CO<sub>2</sub>-increased soil moisture was also found in other sites, which led to increased water drainage [Nelson *et al.*, 2004].

The four cations, K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>, were measured in higher concentrations in the leachates from the chambers exposed to the high CO<sub>2</sub> treatment. Under elevated atmospheric CO<sub>2</sub>, increased plant growth and soil respiration have been detected [Deng *et al.*, 2010; Zhao *et al.*, 2011]. Carbonic acid, which is a byproduct of soil and root respiration, can accelerate the weathering of silicates and carbonates, and thus release greater amounts of Si and base cations in the soil solution [Bernier *et al.*, 1983; Liu *et al.*, 2011]. Increased inorganic C leaching was previously found in our experiment which supported this result and led to higher pH values in the soil solution [Liu



**Figure 4.** Monthly amounts of inorganic N and soluble P concentrations in leachates over 3 years of exposure to various CO<sub>2</sub> and N treatments. Error bars are standard deviations ( $n = 9$  for EL and EH and  $n = 6$  for AH and AL). Treatments are: AL = control, AH = high N treatment, EL = elevated CO<sub>2</sub> concentration treatment, and EH = elevated CO<sub>2</sub> concentration treatment + high N treatment. Data in 2006 were cited from Liu et al. [2008]

leaching amount of base cations in the chambers exposed to elevated CO<sub>2</sub> treatment in the experiment also supports this.

**4.2. The Effects of N Treatment on Soil Ion Leaching**

High N addition caused a decrease in leachate volume, and this decrease became more obvious with time. This is the consequence of a better tree growth following N fertilization [Zhao et al., 2011; Liu et al., 2011]. During the low rainfall months, the volume of leachates showed reduced differences among the treatments because less water was available for leaching due to increased plant water use.

Previous studies showed that high N deposition would often accelerate soil basic cation leaching [Foster et al., 1989; Gbondo-tugbawa and Driscoll, 2003; Watmough and Dillon, 2003]. However, the N treatment did not directly affect the base cation loss in the leachates in our study. This is because high N treatment generated greater plant growth in the experiment, [Zhao et al., 2011], which required more nutrients [Li et al., 2012], and led to an overall reduction of nutrient leaching rates.

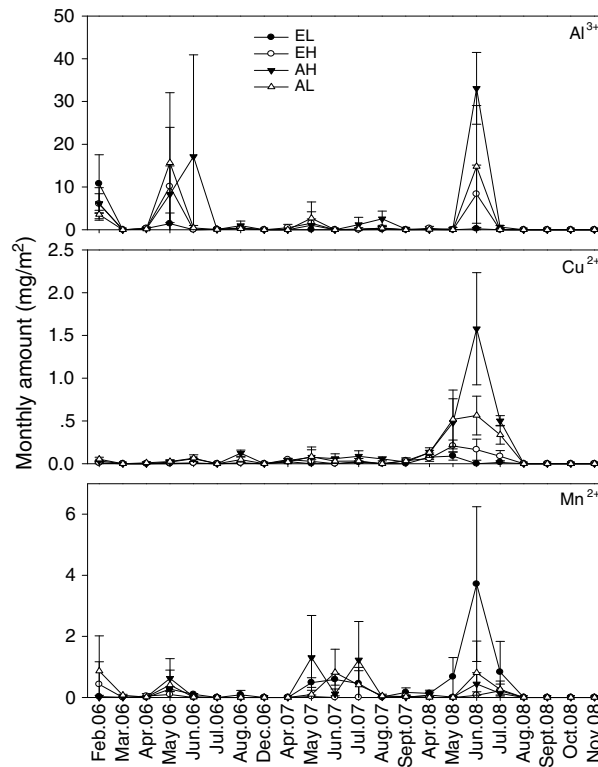
High N addition increased the leaching of inorganic N. This is quite reasonable as the N deposition is extremely high around Guangzhou City near the experimental site. In 2006, the wet N deposition of about 56 kg ha<sup>-1</sup> yr<sup>-1</sup> in our experimental site was found [Liu et al., 2008]. Although high N addition accelerated root uptake of N nutrient in the high N treatment, not all the additional N was absorbed by tree growth in the high-N treatment chambers. The excess inorganic N was then lost by leaching.

Although the N treatment increased metal (Al<sup>3+</sup>, Cu<sup>2+</sup>, and Mn<sup>2+</sup>) concentration in both 2007 and 2008, only the leached amounts of Al<sup>3+</sup> and Mn<sup>2+</sup> were significantly increased by the N treatment in 2008 as the N treatment decreased the amount of leachate. It was reported that N addition would often mobilize heavy

[García-Palacios et al., 2012]. The greater NO<sub>3</sub><sup>-</sup>-N concentration in the soil leachate induced by elevated CO<sub>2</sub> was shown in our own observation, which is consistent with that from Korner and Arnone [1992] as both studies were under the subtropical climatic conditions and used similar soils.

With time, the leached amounts of Al<sup>3+</sup> and Mn<sup>2+</sup> were found to be decreased by the CO<sub>2</sub> treatment in 2008. Elevated CO<sub>2</sub> treatment would often firstly induce base cations leaching and followed by the metal cations [Liu et al., 2011]. Compared to the base cations (K<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>), Al<sup>3+</sup> and Mn<sup>2+</sup> are often held tight by the soil colloids. As the relative concentrations of the cations in soil solution helps determine the degree of adsorption, the increased leaching of base cations induced by elevated CO<sub>2</sub> treatment in our experiment led to a decreased leaching of Al<sup>3+</sup> and Mn<sup>2+</sup>. However, we assume that the CO<sub>2</sub> treatment would finally increase the leaching of these two cations when the base cations are exhausted slowly in this lateritic soil as high soil CO<sub>2</sub> is capable of displacing almost all exchangeable cations in soils [Liu et al., 2011; Duval et al., 2011]. With time, the slowly decreased





**Figure 5.** Monthly amounts of metal cations in leachates over 3 years of exposure to various CO<sub>2</sub> and N treatments. Error bars are standard deviations ( $n = 9$  for EL and EH and  $n = 6$  for AH and AL). Treatments are: AL = control, AH = high N treatment, EL = elevated CO<sub>2</sub> concentration treatment, and EH = elevated CO<sub>2</sub> concentration treatment + high N treatment. Data in 2006 were cited from Liu et al. [2008]

metal elements [Matzner and Murach, 1995; Marschner et al., 1998]. However, the greater tree growth induced by the N addition did not increase these two metal element uptakes [Li et al., 2012]. Hence, higher leached amounts of Al<sup>3+</sup> and Mn<sup>2+</sup> were found in the chambers with N addition. High N addition did not affect the leaching loss of Pb<sup>2+</sup> and Zn<sup>2+</sup> as these two elements were quite low in the soil.

### 4.3. The Interactive Effects Among CO<sub>2</sub> Treatment, N Treatment, and Precipitation on Soil Ion Leaching

There was a strong interactive effect of the high-CO<sub>2</sub> and high-N treatment on leaching water volume. Leaves exposed to elevated atmospheric concentrations of CO<sub>2</sub> often show decreased diffusive conductance [Pearson et al., 1995; Niklaus et al., 1998] and reduced stomatal conductance [Saxe et al., 1998], which would often result in reduced vapor losses per unit of CO<sub>2</sub> assimilated and translate usually into decreased rates of canopy transpiration and increased soil moisture in CO<sub>2</sub>-enriched plots [Bunce, 2004]. This was also found in our experiment [Deng et al., 2010]. Increased soil moisture would often increase leaching water volume. On the contrary, high N treatment would generate greater plant growth which would consume more soil water. Hence, the strong interactive effect of the high CO<sub>2</sub> and N treatment ( $P < 0.01$ ) on leaching water amount was found in our experiment.

In the experiment, the interactive effects of precipitation with the high CO<sub>2</sub> and N treatments on soil water chemistry were significant. This is because our study site has a typical monsoon climate with precipitation occurring from April to September. This led to the higher ion leaching occurring in the wet season (from April to September) than that in the dry season. The precipitation varied a lot among different months and hence resulted in varied ion leaching in the experiment. In subtropical China with the typical monsoon climate, the wet season is also the plant growth time. The greater plant growth in the wet season would often lead to higher water consume. Although the CO<sub>2</sub> treatment induced higher base cation loss in the experiment, the accelerated plant growth in the wet season induced by the N treatment decreased the base cation loss.

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## 5. Conclusions

In the study, we quantified the loss of major ions induced by CO<sub>2</sub> enrichment and N treatments in subtropical model forest ecosystems over 3 years, from the second year to the fourth year of exposure, to various CO<sub>2</sub> and N treatments. The total rainfall in 2006 equalled almost that in 2008. However, the leached amounts for metal ions in the chambers exposed to high N treatment were greater in 2008 than those in 2006. This suggests that the effect of high N treatment is increasing with time. The leached amount for NO<sub>3</sub><sup>-</sup>-N in all chambers was found to be increasing with time, which demonstrated that the soil was N-saturated [Fang et al., 2009]. The leaching losses of metal cations induced by high N treatment were increasing slowly over time, because the mobilization and leaching loss of metal ions were stepwise induced by high N addition. The results above suggest that the duration of exposure to N treatment affected ion loss in these model forests. We also found that the increased intensity of soil water leaching loss induced by high CO<sub>2</sub> treatment was decreasing with time, and so did the annual leached amounts of base cations. These indicate that the effect of high CO<sub>2</sub> treatment is weakening. The

result is consistent with the previous studies which showed that the effects of elevated atmospheric CO<sub>2</sub> on the forest is alleviating with time [Reich et al., 2006; Oh et al., 2007; Xu et al., 2009]. Continuous monitoring of element fluxes and soil solution composition under the high CO<sub>2</sub> and N treatments is necessary.

Our experiment showed larger losses of mineral nutrients (K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) in the model forests under elevated atmospheric CO<sub>2</sub> concentrations in subtropical China. As the lateritic soils here are nutrient-poor, nutrient limitations might reduce the response of plant growth to elevated CO<sub>2</sub> in subtropical China in the future. Atmospheric N deposition is a serious problem in southern China. High ambient N deposition has been found in our experimental site [Liu et al., 2008]. As high N deposition would often mobilize heavy metal elements [Marschner et al., 1998], the toxicity of metal elements on forest plants should be of concern in the future.

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