

Seasonal Dry Deposition and Canopy Leaching of Base Cations in a Sub-tropical Evergreen Mixed Forest, China

Gong Zhang, Guang-ming Zeng, Yi-min Jiang, Chun-yan Du, Guo-he Huang, Jia-mei Yao, Mei Zeng, Xi-lin Zhang and Wei Tan

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We evaluated the dry deposition and canopy leaching fluxes of base cations in the growing and the dormant seasons using the Na-ratio method based on the 4-year (2000–2003) monitoring data in Shaoshan subtropical evergreen mixed forest, China. The dry deposition of base cations in the growing seasons was lower than that in the dormant seasons, while the canopy leaching of base cations was higher in the growing seasons than that in the dormant seasons. The precipitation quantity and H⁺ significantly impacted the canopy leaching processes. The annual canopy leaching of K⁺, Ca²⁺ and Mg²⁺ accounted for 88, 46 and 38% of net throughfall flux, respectively. The canopy retention of proton (H⁺ and NH₄⁺) is close to the canopy leaching of base cations calibrated by weak acids, indicating that the canopy cations leaching is neutralizing acid precipitation.

Keywords bulk precipitation, throughfall, dry deposition, canopy exchange, base cations, evergreen forest

Authors' addresses G. Zhang and Jiang, College of Environmental Science and Engineering, Hunan University, Hunan Province, Changsha 410082, P.R. China, and Hunan Environmental Protection Bureau, Hunan Province, Changsha, 410076, P.R. China; G.M. Zeng, Du, Huang, M. Zeng, X.L. Zhang and Tan, College of Environmental Science and Engineering, Hunan University, Hunan Province, Changsha 410082, P.R. China; Yao, Xiangya Hospital, Central-south University, Hunan Province, Changsha 410008, P.R. China **E-mail** zgming@hnu.cn

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1 Introduction

During the past two decades throughfall analyses used to estimate dry deposition and canopy exchanges and total atmospheric deposition in the forest ecosystems have been attached great concerns (Lovett and Lindberg 1986, Lindberg et al. 1990, Hamburg and Lin 1998, Fan et al. 1999, Zeng et al. 2005). These studies have increased our understanding of the factors affecting throughfall chemistry and flux, including nutrient input via wet deposition (Feng et al. 2001), evaporation of water by canopies (Zhang et al. 2006a), wash-off of the dry substances atmospherically deposited on leaf surface (Lindberg et al. 1986) and uptake and absorption of the nutrients from rainwater (Butler and Likens 1995, Fan et al. 1999, Campo et al. 2000, Zhang et al. 2006b). The relative importance of these factors varies among chemical species, forest types and climatical conditions (Lovett and Lindberg 1986, Puckett 1990, Baumler and Zech 1997). Monitoring forested throughfall may be a useful technique to estimate the amount of dry deposition to the forest stands provided that i) the pollutants are not taken up irreversibly by the canopy and ii) canopy leaching of compounds taken up by roots and transported to the leaves is negligible (Parker 1983, Lindberg et al. 1990, Christ et al. 1995). Numerous methods have been used to measure or calculate dry deposition on forest canopies, with multiple regression models (Lovett and Lindberg 1986, Lovett et al. 1996, Fan and Hong 2001) and the Na-ratio approach, which is the most widely used (Bredemeier 1988). Both have been successfully applied to a variety of forests in the temperate region (Johannes et al. 1986, Draaijers and Erisman 1995), but few of the methods have been used in subtropical or tropical forests (Lin et al. 2000, Fan and Hong 2001, Zeng et al. 2005).

Base cation depletion induced by atmospheric deposition has a major detrimental effect on nutrient cycling and forest health (Likens et al. 1996, Lawrence et al. 1999). Base cations are not only essential to plant growth but the critical components for buffering acid deposition in the soil and canopy. Cation leaching from forest canopy affects physiological processes, damages flowering and dormancy patterns, and makes plants more vulnerable to diseases and the effects of

freezing (Tukey 1970, DeHayes et al. 1999, Luoranen et al. 2005).

Although base cations leaching from canopies are well documented for temperate forests (Turner and Van Broekhuizen 1992, Cappellato et al. 1993, Draaijers et al. 1994, Erisman et al. 2002), little is known about it in subtropical forests (Lin et al. 2000, 2001, Fan and Hong 2001, Zeng et al. 2005). Lin et al. (2001) reported that base cations in subtropical forests were more vulnerable to be leached than in temperate forests because of low base saturation in soil, high humidity and relatively short dry period between rain events.

The objectives of this study are 1) to evaluate the base cations concentrations and fluxes in bulk precipitation and throughfall in the growing and the dormant seasons, 2) to quantify the dry deposition and canopy leaching of base cations in precipitation and throughfall and their contribution to net throughfall flux, and 3) to compare the dry deposition of base cations with the canopy leaching in the two periods in Shaoshan forest, a subtropical evergreen mixed forest, in central-south China.

2 Materials and Methods

2.1 Study Site

Shaoshan forest with two-layer canopy structure is located in Hunan province, central-south China (27°87'N, 112°91' E, 260–350 m above sea level, a.s.l.) (Fig. 1). The stand is about 150 km from the capital city of Hunan province, Changsha city, and 30 km from the nearest city, Xiangtan city, where experiences acid rain pollution induced by sulfur dioxide emissions from local industrial sources, with an annual sulfur deposition of 3–5 g S m⁻² year⁻¹. According to the physiological status of the vegetation and the characteristics of the local climate, we group the months into two general periods, the growing and the dormant seasons. Owing to the influence of the monsoon from the Pacific and Indian Oceans, the climate of Hunan is humid subtropics monsoon type which is characterized by abundant but unevenly distributed rainfall (>70% of annual rainfall in the growing seasons). The dominating wind direc-

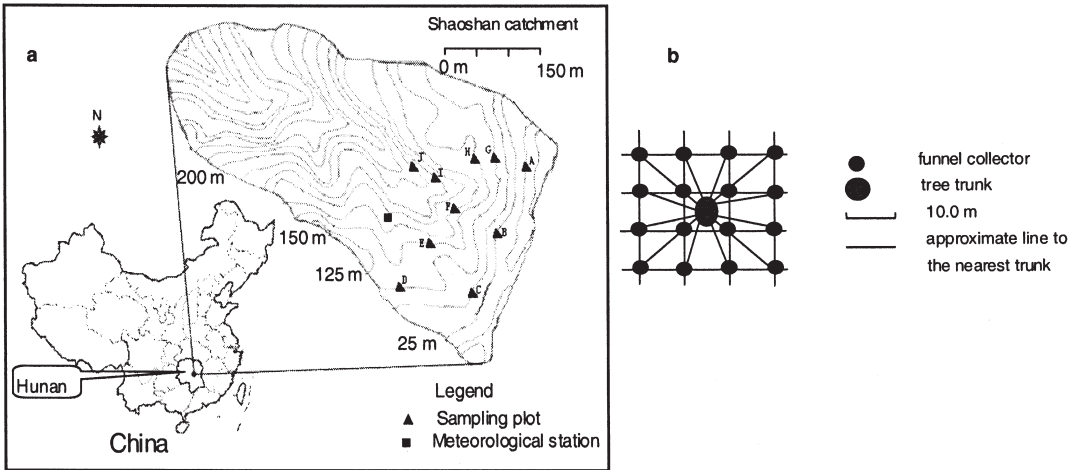


Fig. 1. Location and dispositions of the 10 plots (a) and layout of throughfall collector in each plot (b).

tion in summer is South-east and that in winter is North-west in Shaoshan forest. Relative humidity varies from 80% in the dormant seasons to 90% in the growing seasons. The highest absolute temperature of 39 °C is assigned to the growing seasons and the -2 °C to the dormant seasons. Between the observed 4 years annual rainfall ranged from 1200 to 2000 mm with an average of 1550 mm and annual temperature varied from 15.0 to 17.0 °C with an average of 17.6 °C in Shaoshan forest.

The projected top-canopy coverage of the stand is about 82% and sub-canopy (shrub canopy) coverage of the stand is 41%. The dominant tree species (diameter at breast height (DBH) ≥ 10 cm and 20–40-year-old) in top-canopy layer within the study plot are China fir (*Cunninghamia lanceolata*), massoniana (*Pinus massoniana*), camphor wood (*Cinnamomum camphora*), and bamboos (*Phyllostachys pubescens*). The four species make up approximate 98% of the density and 96% of the relative dominance of the top-canopy layer in the study stand. The shrub species (DBH of 1–8 cm and 10–20-year-old) is dominated by camellia (*Camellia japonica*), oleander (*Nerium indicum*) and holly (*Euonymus japonicus*), Ternstroemia (*Ternstroemia gymnanthera*). The vegetation is with the obvious two-layer canopy, i.e. the tall arbor and the lower shrub canopy layers. The

top-canopy layer, with an approximate height of 10–20 m, is dominated by the crowns of the four species, while the shrub layer, which ranges from approximate 0.8–3.0 m in height, is comprised of the crowns of all tree species found within the plot.

2.2 Sampling and Laboratory Analysis

A wet-only collector from MISU (Meteorological Institution, Stockholm University) was placed on a tower (10 m height) adjacent to the throughfall plots. The wet deposition samples were weekly collected and analyzed. For the 10 plots in the forest stand, 3 plots were located in the lower parts of the catchment (25–50 m a.s.l.), 5 in the middle of the catchment (75–100 m a.s.l.) and 2 in the upper parts (125–170 m a.s.l.) (Fig. 1a). At each studied plot, 16 throughfall collectors in 4 parallel lines with 4 collectors are installed 2–2.5 m from each other, avoiding trunks (Fig. 1b). The throughfall collectors are placed under vegetation canopies and 1.0 m above the forest ground. The throughfall collector is made of a plastic bottle (2 l), a plastic funnel (d=11.5 cm), a connector with a filter (nylon screen) and a mounting equipment. The collectors were opaque and kept in the dark. A filter was placed in the mouth of

each funnel to prevent water samples from contamination. The fiber plugs were replaced by a new one and the collectors were rinsed twice by distilled water after weekly collection. 16 throughfall samples within one plot were mixed and weighed. Chemical analysis of throughfall is done at monthly intervals in pooled samples. Pooled samples are stored in the refrigerator at 4 °C and filtered (0.45 µm membrane filter) prior to analysis.

SO₄²⁻, NO₃⁻ and Cl⁻ were analyzed as described in NS-EN ISO 10304-1 (1992), and Na⁺ and NH₄⁺ were analyzed as in ISO 14911 (1998) by ion chromatography (Dionex-320 system). Ca²⁺, Mg²⁺ and K⁺ were analyzed as described in NS-EN ISO 9963-1 (1994), using flame atomic absorption spectroscopy (SH-3800). Conductivity was measured as described in ISO 7888 (1985) by electrometry and pH measured as in ISO 10523 (1994) by potentiometry in unfiltered solutions at 25 °C.

Quality of the data on wet-deposition samples (precipitation and throughfall) is assured according to the requirements of EMEP manual for continuously active sampling and chemical analysis (EMEP 1996). Reproducibility was checked by replicated analysis (n=5) of rain samples at different concentrations. The results showed that the repeatability for NH₄⁺, Ca²⁺, Mg²⁺, SO₄²⁻ was <2%, for NO₃⁻ and Cl⁻ it was 3% and for K⁺ it was 6%. The quality of the analytical data was checked by comparing the measured conductivity with the conductivity calculated from concentration of all measured ions and their specific conductivities. If the differences were less than 20% we consider that the major ions had been analyzed.

2.3 Calculation

Differences in ion concentrations and fluxes between precipitation and throughfall and among the seasons were examined using one-way analysis of variance (SPSS10.0 for Windows).

The data series of this study were the averaged values of the same season in the four observed years. They represented the synthesis of the same time section in the studied years in Shaoshan forest and were calculated according to:

$$\bar{X}_i = \frac{1}{4} \sum_{j=1}^4 X_{ij} \quad (3)$$

where X is the given ion (Ca²⁺, Mg²⁺, K⁺, SO₄²⁻, NO₃⁻, NH₄⁺, Cl⁻), i is the season, and j is the j th year of the four studied years.

Na-ratio method (canopy budget model) (Ulrich 1983, Draaijers and Erisman 1995) was applied to estimate dry deposition and canopy leaching of base cations. The Na-ratio method assumes that almost all (>90%) of the throughfall Na⁺ which is in excess of that in bulk precipitation can be attributed to dry deposition because Na⁺ concentration in foliage are very low (Parker 1983). The dry deposition of base cations (DD_{BC}) and canopy leaching of base cations (CL_{BC}) can be obtained from Eqs. 1 and 2:

$$DD_{BC} = \frac{TF_{Na} - PD_{Na}}{PD_{Na}} \times PD_{BC} \quad (1)$$

where TF_{Na} denotes the throughfall flux of Na, PD_{Na} is the precipitation deposition of Na. PD_{BC} is the precipitation deposition flux of base cations.

The CL_{BC} is estimated by the difference between throughfall of base cations (TF_{BC}), DD_{BC} and PD_{BC} as:

$$CL_{BC} = TF_{BC} - DD_{BC} - PD_{BC} \quad (2)$$

Dry deposition and canopy exchange are the key processes in regulating the net throughfall flux (NTF) (Lovett and Lindberg 1986). Net throughfall flux of base cations (NTF_{BC}) is estimated from the difference between throughfall and bulk precipitation fluxes.

The effect of acidity ([H⁺]) and precipitation quantity (P) on net canopy effect (NCE) was examined using simple linear regression (NCE = a [H⁺] + $b P$). NCE of base cations fluxes is assumed to equal to CL_{BC} in our study. When there is no precipitation to wash-off dry deposited materials and to move materials in and out the canopy, the intercept of the models should be zero.

3 Results

3.1 Precipitation and Throughfall Chemistry

Volume weighted mean seasonal and annual concentrations of base cations, H^+ , and weak acid in bulk precipitation and throughfall are listed in Table 1. The relatively low Na^+ content indicated little oceanic influence on precipitation chemistry. The most abundant cation in bulk precipitation was Ca^{2+} , followed by H^+ , Mg^{2+} and K^+ . Ca^{2+} accounted for 30.7% and 46.3% of cations in precipitation in the growing seasons and the dormant seasons, respectively. Ca^{2+} content in precipitation in the growing seasons was much lower than that in the dormant seasons, with $51.2 \pm 3.2 \mu mol l^{-1}$ in the growing seasons and $116.7 \pm 9.4 \mu mol l^{-1}$ the dormant seasons. It should be noted that weak acid (w.a.) was increased from $19.6 \pm 3.4 \mu mol l^{-1}$ in bulk precipitation to $79.0 \pm 7.2 \mu mol l^{-1}$ in throughfall in the growing periods and from $25.7 \pm 3.3 \mu mol l^{-1}$ in bulk precipitation to $35.5 \pm 4.1 \mu mol l^{-1}$ in throughfall in the dormant periods.

Cation concentrations in throughfall were significantly enriched relative to precipitation (Table 1). Although the highest concentration in throughfall was Ca^{2+} , the most enriched in throughfall was K^+ . Concentrations of K^+ increased from $15.5 \pm 2.8 \mu mol l^{-1}$ in precipitation to $90.1 \pm 8.4 \mu mol l^{-1}$ in throughfall in the growing times and from $5.7 \pm 0.7 \mu mol l^{-1}$ to $62.0 \pm 6.5 \mu mol l^{-1}$ in the dormant times, respectively (Table 1). The enrichment of Mg^{2+} and Na^+ in throughfall was low relative to bulk precipitation in the dormant seasons.

About 78% of H^+ in precipitation was retained by the canopy, dropping from $122 \pm 11.2 mmol m^{-2} year^{-1}$ in precipitation to $27 \pm 3.7 mmol m^{-2} year^{-1}$ in throughfall (Table 2), with a corresponding increase in pH from 4.2 in precipitation to 5.0 in throughfall.

3.2 Net Throughfall Flux (NTF)

The negative net throughfall flux (NTF) of H^+ indicated the retention by the canopies, whereas the positive NTF of base cations and w.a. implied their leaching from the canopy. The negative NTF of H^+ occurred both in the growing period ($-56.1 mmol m^{-2}$) and the dormant ($-38.3 mmol m^{-2}$). NTF_{BC} in the growing seasons were significantly higher than the dormant seasons except Mg^{2+} (Table 2). NTF of w.a. was about two times higher in the growing seasons than that in the dormant seasons. Canopy leaching of K^+ accounted for 88% of NTF of K^+ , which was higher than that of 46% of the canopy leaching of Ca^{2+} in NTF of Ca^{2+} and 38% of canopy leaching of Mg^{2+} in NTF of Mg^{2+} .

To better understand the chemical transformation during passage through the canopies and to identify the factors regulating the NTF, we examined the Spearman correlation coefficients between NTF and precipitation quantity. We obtained the positive coefficients ($p < 0.01$) between P and NTF of Ca^{2+} , Mg^{2+} , K^+ , and w.a. in the growing seasons and the dormant seasons as well as the negative coefficients of H^+ in the both two periods (Table 3). As shown in Table 3,

Table 1. Seasonal and annual precipitation-weighted mean values of solutes ($\mu mol l^{-1}$) of bulk precipitation (BP) and throughfall (TF) at Shaoshan forest during the observed periods.

		H ₂ O (mm)	H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Weak acid
Growing seasons	BP	970	59.2 (5.1)	51.2 (3.2)	30.0 (2.1)	11.0 (1.3)	15.5 (2.8)	19.6 (3.4)
	TF	780	1.7 (0.8)	170.5 (11.1)	70.1 (6.9)	20.9 (2.6)	90.1 (8.4)	79.0 (7.2)
Dormant seasons	BP	820	76.5 (8.5)	116.7 (9.4)	43.0 (6.3)	10.0 (2.1)	5.7 (0.7)	25.7 (3.3)
	TF	710	34.3 (3.1)	243.4 (15.0)	98.5 (8.7)	18.7 (3.2)	62.0 (6.5)	35.5 (4.1)
Annual	BP	1790	67.9 (6.0)	83.5 (7.5)	36.4 (4.9)	10.6 (2.9)	10.7 (1.9)	22.4 (3.5)
	TF	1490	18.0 (3.8)	207.3 (10.6)	84.3 (5.6)	19.8 (3.4)	76.0 (6.7)	57.3 (5.8)

Note: Significant difference ($p < 0.05$) between precipitation and throughfall (calculated on an event basis). Standard errors are given in parentheses.

Table 2. Mean seasonal and annual fluxes ($\text{mmol m}^{-2} \text{ season}^{-1}$) of bulk precipitation (BP), throughfall (TF), net throughfall fluxes (NTF), dry deposition (DD), and canopy exchange (CE) calculated using Na-ratio method at Shaoshan forest.

		H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Weak acid
Growing seasons	BP	57.4 (8.7)	49.7 (6.7)	29.1 (3.4)	10.6 (3.8)	15.0 (2.9)	19.0 (3.1)
	TF	1.3 (0.3)	134.0 (8.6)	55.1 (5.4)	16.4 (2.1)	70.8 (6.3)	62.6 (7.4)
	NTF	-56.1 (4.6)	84.3 (7.1)	26.0 (2.4)	5.8 (1.1)	55.8 (5.7)	43.6 (4.9)
	DD	31.4 (5.1)	27.2 (4.2)	15.9 (3.5)	5.8 (1.1)	8.2 (2.4)	7.4 (1.9)
	CE	-87.5 (8.4)	57.1 (5.3)	10.1 (2.6)	0	47.6 (5.4)	36.2 (4.2)
Dormant seasons	BP	62.7 (5.4)	95.7 (7.2)	35.3 (2.6)	8.2 (1.7)	4.7 (0.8)	21.1 (2.6)
	TF	24.4 (3.1)	172.8 (12.6)	69.9 (5.3)	13.3 (2.5)	44.0 (3.7)	25.2 (4.1)
	NTF	-38.3 (4.3)	77.1 (6.8)	34.6 (5.9)	5.1 (0.8)	39.3 (3.4)	14.1 (2.6)
	DD	17.8 (2.8)	59.4 (4.7)	21.9 (3.5)	5.1 (0.8)	2.9 (0.5)	7.6 (2.3)
	CE	-56.1 (4.9)	17.7 (3.1)	12.7 (2.6)	0	36.4 (3.6)	6.5 (1.8)
Annual	BP	121.5(11.2)	149.4 (13.4)	65.2 (4.8)	18.8 (2.4)	19.1 (2.8)	40.1 (6.2)
	TF	26.8 (3.7)	310.4 (19.5)	125.8 (9.2)	29.7 (3.5)	106.2 (9.5)	87.8 (7.9)
	NTF	-94.7 (8.6)	161.4 (12.6)	60.6 (7.6)	10.9 (2.6)	95.1 (6.5)	57.7 (6.4)
	DD	49.1 (5.6)	86.6 (7.5)	37.8 (5.1)	10.9 (2.6)	11.1 (2.1)	15.0 (3.1)
	CE	-143.8 (9.1)	74.8 (6.8)	22.8 (4.3)	0	84.0 (5.9)	42.7 (5.3)

Note: Differences between precipitation and throughfall fluxes are significant for all cations seasonally and annually ($p < 0.001$ calculated on a paired event basis using paired t test). Standard errors are given in parentheses.

Table 3. Spearman correlations between precipitation (P) and net throughfall flux (NTF) of ions in growing and dormant seasons in Shaoshan forest.

		H ⁺	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Weak acid
P in the growing seasons (mm)	r-value	-0.33	0.51	0.45	0.45	0.83	0.39
	p-value	0.71	0.01	0.01	0.01	0.01	0.004
P in the dormant seasons (mm)	r-value	-0.22	0.54	0.32	0.24	0.76	0.75
	p-value	0.71	0.05	0.01	0.01	0.001	0.05

the coefficient of base cations and w.a. in the growing seasons were higher than that in the dormant seasons, indicating that NTF of these ions were more strongly related to precipitation quantity in the growing seasons than that in the dormant seasons.

3.3 Dry Deposition and Canopy Leaching

Dry deposition (DD) of base cations accounted for 54.7% of the precipitation flux in the growing seasons and 62.1% in the dormant seasons (Table 2). DD of Ca²⁺, Mg²⁺ and K⁺ accounted

for 20, 29 and 12% of the throughfall flux in the growing seasons and 34, 32 and 7% in the dormant seasons, respectively. DD of Ca²⁺ in the dormant seasons was approximate two times that in the growing seasons. DD of Mg²⁺ in the dormant times also was significantly larger than that in the growing seasons, and DD of w.a. in dormant seasons was slightly higher than that in growing seasons. However, DD of K⁺ in the dormant seasons was lower than that in the growing seasons. The contribution of dry deposition (DD) of Ca²⁺, Mg²⁺ and K⁺ to NTF was 32, 61 and 15% in growing periods and 77, 50 and 7% in the dormant periods, respectively. The contribution of DD of

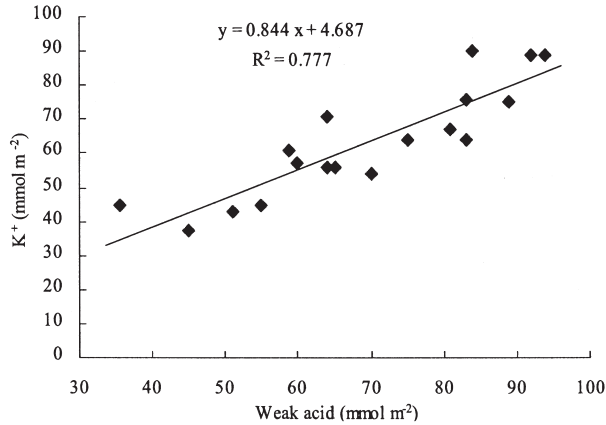


Fig. 2. Weak acid flux in throughfall compared to K^+ in throughfall in Shaoshan forest.

Table 4. Linear regression coefficients for predicting net canopy effect (NCE) using quantity (P) and acidity ($[H^+]$) of precipitation concentrations ($NCE = a [H^+] + b P$)

	Coefficient	Ca^{2+}	Mg^{2+}	K^+
Growing seasons (n=39)	<i>a</i>	9.4 (3.15) **	7.7 (2.37) *	12.6 (4.32) ***
	<i>b</i>	0.006 (0.001) ***	0.004 (0.001) ***	0.013 (0.003) ***
Dormant seasons (n=23)	<i>a</i>	8.3 (2.4) *	6.5 (2.1) **	9.1 (2.9) ***
	<i>b</i>	0.003 (0.0015) ***	0.003 (0.0012) ***	0.009 (0.002) ***

Note: *: $p \leq 0.05$; **: $p \leq 0.01$; ***: $p \leq 0.001$; Standard errors are given in parentheses.

w.a. to NTF was 17% and 54% in the growing and the dormant seasons, respectively.

The Na-ratio method presented a negative canopy leaching for H^+ , while the method presented a positive canopy effect for Ca^{2+} , Mg^{2+} , K^+ , and w.a. (Table 3). The highest canopy leaching flux of cation in the growing seasons was Ca^{2+} but the maximum in dormant seasons was K^+ , accounting for 50% and 55% of canopy leaching of base cations (CL_{BC}), respectively. Canopy leaching of w.a. amounted to 31.5 and 10.0% of CL_{BC} in the growing and the dormant seasons, respectively. As shown in Fig. 2, the throughfall flux of K^+ was positively related to throughfall flux of w.a. ($R^2=0.78$; $p < 0.01$). The NTF of weak acid was strongly related to the quantity of precipitation, as indicated by the Spearman correlation coefficient of 0.79 and 0.74 in the growing

and the dormant times, respectively.

The two predictors, $[H^+]$ and P , of the linear regression model ($NCE = a [H^+] + b P$) were positive and significant for base cations, indicating that both P and $[H^+]$ have positive effect on canopy leaching processes (Table 4).

4 Discussion

4.1 Precipitation and Throughfall Chemistry

Throughfall chemistry was significantly altered relative to precipitation chemistry, which was probably due to the processes of the washed-off of materials in the air and on the leaf surfaces, the leaching or uptake of nutrients by the canopies.

DD of Ca^{2+} contributed 51.5% and 37.2% to bulk precipitation flux in the growing and the dormant seasons, respectively, which was slightly higher than that in Taiwan subtropical rain forest (Hamburg and Lin 1998, Lin et al. 2000), but similar to the temperate forests in North America (Lovett et al. 1996, Watmough and Dillon 2003). The exact origin of Ca^{2+} in precipitation is unclear at this stage but could be derived from road dust, cement factories and long-distance transported soil dust. High content of H^+ in bulk precipitation was attributed to the heavy acid rain pollution in Hunan province, with annual mean pH below 4.3 in rainwater (Jiang et al. 2004).

Base cations can be significantly leached from the canopies under acid rain in Shaoshan forest, especially Ca^{2+} and K^+ . The canopy leaching process for K^+ is mainly controlled by the precipitation quantity (Vistousek and Sanford 1986, Tukey 1970, Langusch et al. 2003). In a study on the biogeochemistry of K^+ at Hubbard Brook forest (USA), Likens et al. (1994) reported that the amount of precipitation was the only variable useful for predicting net throughfall of K^+ , while the length of dry period and rain acidity were unrelated.

4.2 Dry Deposition and Canopy Leaching

Although there are some uncertainties in using the Na-ratio method, it is a useful method to estimate the dry deposition and the canopy leaching of base cations in forests (Draaijers and Erisman 1995, Lin et al. 2000, Zeng et al. 2005). The contribution of dry deposition to NTF in the dormant seasons was higher than in the growing seasons, because the length of dry period in the dormant seasons was long relative to that in the growing periods. Moreover, about 6% of the conifers and 20% of the deciduous species in Shaoshan forest defoliated in the dormant seasons, which may increase dry substances in throughfall and forest floor.

Enrichment (TF/PD) of K^+ was 4.7 and 9.4 in the growing and the dormant seasons, which was higher than the ratio of other cations. The high contribution of CL_{K^+} to throughfall in Shaoshan forest was in agreement with other throughfall studies in temperate and (sub)tropical forests

(Balestrini and Tagliaferri 2001, Fan and Hong 2001, Lin et al. 1997, 2001). Potassium is not tightly bound in structural tissues or enzyme complexes as Ca^{2+} and Mg^{2+} , but acts as a highly mobile carrier (Draaijers et al. 1994, Campo et al. 2000). Miller and Miller (1987) found that increments of K^+ and Mg^{2+} in throughfall mainly came from foliage leaching, but Ca^{2+} derived from bulk precipitation with appreciable values of dry deposition, while canopy leaching of Ca^{2+} was almost imperceptible. But the canopy leaching of Ca^{2+} was reported in many other forests (Bredemeier 1988, Campo et al. 2000, Fan and Hong 2001). The significant canopy leaching of Ca^{2+} was observed also in the present study. Throughfall has been reported to have a major importance for potassium transfer in tropical moist forest, while litterfall represented the major flux for calcium (Martinelli et al. 2000).

The mean annual canopy retention of H^+ ($144 \text{ mmol m}^{-2} \text{ year}^{-1}$) was close to the CL_{BC} ($139 \text{ mmol m}^{-2} \text{ year}^{-1}$) which was corrected by weak acid, because the leaching of base cations associated with weak acids did not consume proton of rainfall (Draaijers and Erisman 1995). The correction may reflect the canopy buffering acidity capacity. Many laboratory experiments have demonstrated that the low acidity of the fluent can accelerate the base cations leaching from spruce needles (Fritsche 1992, Luoranen et al. 2005). Although there were some different opinions on the canopy exchange mechanisms (Turner and van Broekhuizen 1992), our observations suggested that the leaching of base cations could explain much of the observed canopy buffering process.

4.3 Effects of Weak Acid on Canopy Leaching Process

Flux of w.a. in precipitation was similar in the two separate seasons. But w.a. in throughfall in the growing seasons was much higher than that in the dormant seasons, which was attributed to the high canopy leaching of weak acid in the growth seasons. Canopy leaching of weak acid is strongly related to the tree physiology (Ulrich 1983, DeHayes et al. 1999). Potter et al. (1991) and Turner and van Broekhuizen (1992) reported

that the vegetation in growth seasons may accelerate the excretion of weak acid from the vegetation. Base cations leaching from the canopy in deciduous forests have been reported to go through two paths: one is the base cations of leaves exchange with H^+ in rainfall; the other is the base cations leach in association with the excretion of weak acids (Bredemeier 1988, Hoffman et al. 1980, Cappellato and Peters 1995, Zhang et al. 2006b). The latter is true in Shaoshan forest.

Balestrini and Tagliaferri (2001) reported the co-transportation of weak acid with K^+ out of plant cells in northern Italian alpine forest ecosystems. The similar phenomena were observed in our present study.

4.4 Effects of $[H^+]$ and Precipitation Quantity on Canopy Leaching Process

Precipitation quantity in the growing period accounts for 70–80% of annual rainfall, which may keep the canopy surface wet for a long period. Therefore, base cations of canopy are most likely to be leached in the long growth period, as indicated by the high coefficients of b for base cations in the growing seasons.

The effect of $[H^+]$ on the canopy leaching process of K^+ was the strongest both in the growing and the dormant seasons, which was indicated by the highest coefficients of a . These observations were similar to the results in Fujian fir plantations of China (Fan and Hong 2001), Taiwan subtropical rain forest (Lin et al. 2001), Hubbard Brook forest of USA (Likens et al. 1994) and other temperate forests (Potter et al. 1991, Cappellato and Peters 1995, Moreno et al. 2001).

4.5 Effects of Climate

In the dormant seasons Shaoshan forest experiences less rainfall and long dry periods relative to the growing seasons. Moreover, about 6–20% of tree species defoliate in the dormant season, normally from October to November. During the long dry period the forest canopies easily accumulate deposited dry materials. In addition, the physiological activity of trees is relatively low in the dormant seasons and internal canopy exchange

processes are also much reduced. About higher than 70% of rainfall was assigned to the growing seasons, particularly from May to July. Thus, the contribution of DD in TF in the dormant periods was significantly higher than that of CL_{BC} in TF except K^+ . Lin et al. (2001) reported that the canopy leaching of base cations in winter was as high as that in summer in Taiwan rain forest, because the meteorological conditions in winter were similar to summer. However, Shaoshan forest experienced the low canopy leaching of base cations in the dormant seasons relative to the growing seasons.

Canopy leaching and NTF in the growing seasons were higher than that in the dormant seasons except Mg^{2+} , which may be attributed to the fact that the high humidity and the frequent rainfall as well as the severe acid rain in the growing seasons accelerate the canopy leaching processes (Lin et al. 2001, Zeng et al. 2005). Zhang et al. (1996) reported decline in forest growth in southwestern China because of the base cations depletion induced by acid rain. However, Shaoshan forest, central-south China, does not show any indication of decline in forest productivity.

4.6 Uncertainties

The assumption both in the calculation of canopy exchange and the total deposition of base cations is that the particles containing Ca^{2+} , Mg^{2+} and K^+ have the same deposited efficiency as particles containing Na^+ , which may cause the underestimates of Ca^{2+} and Mg^{2+} and the overestimates of K^+ (Draaijers et al. 1994, Zeng et al. 2005, Zhang et al. 2006b). The reason is that the mass median diameters of Ca^{2+} and Mg^{2+} are probably larger than that of Na^+ , but that of K^+ smaller than Na^+ . In the present study the seasonal values may reduce the temporal variability compared with the annual ones in other forested studies in the world.

5 Conclusions

The canopy leaching of base cations in the growing periods was much higher than the canopy

leaching of base cations in the dormant periods, while the dry deposition of base cations was significantly low in the growing seasons relative to that in dormant seasons. The contribution of canopy leaching of base cations to net throughfall flux was higher than the dry deposition in the growing seasons, but that of canopy leaching of base cations to net throughfall flux was lower than dry deposition of base cations in dormant seasons. These were probably attributed to the differences in the physiological activities of trees, the species and the local weather conditions, i.e. precipitation quantity, dry period and rain intensity, etc. Although there is a continuous loss of base cations from canopies in the study forests, little indication of damage has been observed during the past decades. The mechanisms to control the nutrient cycling and to regulate the development of the forest remain unclear. Therefore, the nutrient cycling in the whole forest ecosystem and the effects of the elements on the forest productivity is needed to elucidate in the future studies in the subtropical forest.

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