Atmospheric Environment 64 (2013) 242–250

Contents lists available at SciVerse ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric deposition and canopy exchange of anions and cations in two plantation forests under acid rain influence

Weijun Shen [a,*], Huili Ren [a], G. Darrel Jenerette [b], Dafeng Hui [c], Hai Ren [a]

[a] CAS Key Laboratory of Vegetation Restoration and Management of Degraded Ecosystems, South China Botanical Garden, Chinese Academy of Sciences, 723 Xinke Rd., Tianhe District, Guangzhou 510650, China

[b] Department of Botany and Plant Sciences, Center for Conservation Biology, University of California Riverside, Riverside, CA 92521, USA

[c] Department of Biological Sciences, Tennessee State University, Nashville, TN 37209, USA

HIGHLIGHTS

► Sulfate is the major acidic anion while calcium and ammonium are the major neutralizing cations.
► Ion concentrations are enhanced by 1.4–20-fold after passing through plantation canopies.
► Coarser-textured tree leaves and barks are more capable of retaining acidic precursors.
► Acid rain is more severe in dry than in wet seasons.

ARTICLE INFO

Article history:
Received 18 July 2012
Received in revised form
4 October 2012
Accepted 9 October 2012

Keywords:
Atmospheric deposition
Acid rain
Canopy exchange
Plantation forest

ABSTRACT

Acid deposition as a widely concerned environmental problem in China has been less studied in plantation forests compared to urban and secondary forests, albeit they constitute 1/3 of the total forested areas of the country. We measured the rainwater amount and chemistry outside and beneath the canopies of two widely distributed plantations (*Acacia mangium* and *Dimocarpus longan*) in the severe acid rain influenced Pearl River Delta region of southeastern China for two years. Our results showed that the frequency of acid rain was 96% on the basis of pH value <5.6. The volume-weighted mean (vwm) pH was 4.62 and higher in the dry (Oct.–Mar.) than in the wet (Apr.–Sep.) seasons. The major acidic anion was sulfate with vwm concentration of 140 μeq l^{-1} and annual deposition flux of 110.3 kg ha^{-1} yr^{-1}. The major neutralizing cations were calcium (94.8 μeq l^{-1} and 28 kg ha^{-1} yr^{-1}) and ammonium (41.2 μeq l^{-1} and 11.7 kg ha^{-1} yr^{-1}). Over 95% of these major acidic anions and neutralizing cations were derived from anthropogenic and terrestrial sources as a result of industrial, agricultural and forestry activities. Plantation canopy had marked impacts on rainwater chemistry, with the measured anion and cation concentrations being significantly enriched in throughfall (TF) and stemflow (SF) rainwater by 1.4 (for NO_3^-) to 20-fold (for K^+) compared to those in bulk precipitation (BP). Dry deposition generally contributed about 13–22% of the total deposition while canopy leaching mainly occurred for K^+ (>88%) and NH_4^+ (10–38%). The two tree species showed distinct impacts on rainfall redistribution and rainwater chemistry due to their differences in canopy architecture and leaf/bark texture, suggesting that species-specific effects should not be overlooked while assessing the acid deposition in forested areas.

1. Introduction

With the rapid industrialization and accompanying increase in energy consumption, anthropogenic emissions of sulfur dioxide (SO_2) and nitrogen oxides (NO_x) have been increasing rapidly in China in the past three decades (Larssen and Carmichael, 2000; MEPC, 1996–2010). High emissions of these acidic precursors have turned southern China into the third-largest producer of acid rain in the world following northeastern US and central Europe (Cao et al., 2009; Larssen et al., 1999; Rodhe et al., 2002). Now about 40% of China's territory is affected by acid rain and the affected areas are still expanding, although the intensity is decreasing slightly (Zhang et al., 2010). Being recognized as one of the most serious environmental problems in China, acid rain has been extensively studied to quantify its spatial and temporal distribution patterns, identify the dominant sources, and assess the impacts on

* Corresponding author. Tel.: +86 20 37252950; fax: +86 20 37252615.
E-mail address: shenweij@scbg.ac.cn (W. Shen).

1352-2310/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2012.10.015

natural/semi-natural ecosystems and human societies (Aas et al., 2007; Cao et al., 2009; Hao et al., 2000; Huang et al., 2009; Larssen et al., 2006; Li and Gao, 2002; Seip et al., 1999).

However, most of the nationwide official acid rain monitoring stations established by the Ministry of Environmental Protection of China (MEPC), China Meteorological Administration (CMA) and the individual study sites were situated in urban areas (Cao et al., 2009; Hao et al., 2000; Huang et al., 2009; Xu et al., 2001; Zhang et al., 2007, 2010). Forest areas have been less studied under the context of acid deposition. Among the studies on acid deposition in forest areas, most of them (e.g., the Sino-Norwegian IMPACTS projects) were for natural or secondary forests (Aas et al., 2007; Larssen and Carmichael, 2000; Tang et al., 2001; Vogt et al., 2006), very few have been in plantation forests. This is in spite of the fact that China has the world's largest area of plantation forests (61.68 million hm^2) that account for ~1/3 of the China's total forest area (SFAC, 2010). Therefore, there is a strong need to investigate more representative forest sites and address the potential impacts of long-range transported air pollution from urban to rural areas (Aas et al., 2007).

Moreover, most previous acid deposition studies in China focused on the distribution of precipitation pH and acidic anions in wet-only or bulk deposition. But dry deposition has been found to be considerable and often greater than wet deposition in China (Aas et al., 2007; Larssen and Carmichael, 2000; Larssen et al., 2006; Vogt et al., 2006). Wet or bulk deposition values thus may greatly underestimate total deposition in forest areas. One approach to overcome this is to measure the total deposition (i.e., the integrated dry and wet deposition) via the collection of throughfall under tree canopies. But the use of throughfall as total deposition may be problematic as well because of the canopy exchange of ions. As rainwater passes through forest canopy, the concentrations of most ion species (e.g., K^+, Ca^{2+}, and Mg^{2+}) may be enhanced substantially by foliar leaching and washing-off of dry deposited solutes, but some (e.g., NH_4^+ and NO_3^-) may be reduced by leaf uptake (Balestrini et al., 2007; Levia and Frost, 2003; Lovett and Lindberg, 1984; Parker, 1983). Enrichment of base cations in throughfall may neutralize much of the acidity in bulk precipitation. Understanding the mechanisms of canopy exchange of acidic anions and base cations in addition to pH and sulfate is thus of great importance for evaluating the amount of total and dry deposition (Aas et al., 2007; Draaijers et al., 1996; Tobon et al., 2004; Vogt et al., 2006).

In this study, we chose two types of plantation forests, a legume tree acacia (*Acacia mangium*) plantation and a fruit tree longan (*Dimocarpus longan*) plantation to quantify the dry and wet deposition rates, analyze the dominant sources, discriminate the canopy exchange processes, and compare the canopy effects on rainwater chemistry between the two plantations. These two types of plantation forests are widely distributed in the Pearl River Delta region in the Guandong province, southeastern China. With more than 90% of the precipitation events having pH values less than 5.6, this region has been identified as one of the most severe acid rain affected areas in China (Cao et al., 2009; Huang et al., 2009; Xu et al., 2001). The fast-growing *A. mangium* tree was introduced from Australia into this region to provide timber and protect the heavily eroded hilly land from erosion because of its ability of nitrogen fixation and adaptation to poor soil conditions. Now the *A. mangium* and other *Acacia* spp. plantations have become one of the three most common plantation forests in Guandong province besides eucalyptus and massoniana pine (Liu and Liu, 2008). Longan is one of the most common and unique fruits in southeast China, with the distribution area of about 460 × 10^3 hm^2 and accounting for about 11% of all the fruit tree plantations in the region (Yu et al., 2010). Studying the atmospheric deposition in the acacia and longan plantations may provide valuable information for regional assessment of acid deposition and insights into understanding the interactions between acid deposition and vegetation canopy.

2. Material and methods

2.1. Site description

The study plantations are located at the Heshan National Field Research Station (Heshan-NFRS) of Forest Ecosystems (112°54′E, 22°41′N), Heshan City, Guangdong province, southeast China. This site is characterized by a typical subtropical monsoon climate. The mean annual temperature is 21.7 °C, with the maximum mean monthly air temperature of 29.2 °C in July and the minimum of 12.6 °C in January. The mean annual precipitation is 1700 mm, nearly 80% of which falls in the wet season from April through September. The soil is an oxisol developed from sandstone, with a pH of about 4.2. The study area is typical of the region with low hills with peak elevation of 98 m and small watersheds with area of about 3–100 ha (Shen et al., 2011). Fog rarely occurs at this site and input of occult precipitation is assumed to be negligible. With about the same age and after about 20 years of development, the acacia plantation had larger leaf area index (LAI), stem density, mean height, basal diameter, and soil organic matter accumulation than the longan plantation (Table 1). This is partly due to the ecophysiological nature of the two species and partly due to the management practices imposed on them.

2.2. Rainwater collection and calculation

Bulk precipitation (BP), throughfall (TF) and stemflow (SF) were measured and sampled in two years from January 2006 to December 2007. The amount of BP was monitored continuously by an automatic meteorological station (M520, Vaisala, Finland) mounted on an open hill top about 100 m from the two study plantations. The rainfall amount was also measured manually using three 20 cm diameter rain gauges (ARM-1, Shanghai Meteorological Instrument Factory Co., Ltd., China) that were placed nearby the weather station to provide a calibration on the automatically recorded bulk precipitation amount. Three bulk precipitation samples for chemical analysis were taken from the containers of the three ARM-1 rain gauges on a biweekly basis. The containers were pre-washed with dilute (5%) HCl and thoroughly rinsed with deionized water after each sampling.

Throughfall was measured and collected using the same type of rain gauges. Four rain gauges were randomly placed in each of the

Table 1
Stand and soil characteristics of the acacia and longan plantations at the Heshan National Field Research Station for forest ecosystems.

Parameter	Acacia (*A. mangium*)	Longan (*D. longan*)
Stand parameters		
Canopy range (m^2)	5.1 × 5.0	7.4 × 7.2
Leaf area index (m^2 m^{-2})	3.94	3.25
Stand age (yrs)	23	21
Stem density (n ha^{-1})	853	526
Mean height (m)	13.2	8.0
Diameter at breast high (cm)	19.9	21.5
Soil parameters		
Litter fall (g DM m^{-2} yr^{-1})[a]	1026.3	470.2
C_{org} (%; 0–20 cm)[b]	2.37	1.97
N_{tot} (%; 0–20 cm)[b]	0.1	0.07
P_{tot} (%; 0–20 cm)[b]	0.015	0.039
pH[b]	4.43	5.8

C_{org}: organic carbon, N_{tot}: total nitrogen, P_{tot}: total phosphorus.
[a] Shen et al., 2011.
[b] Li et al., 2005.

three 20 × 20 m^2 permanent observation plots in each plantation, resulting in 12 throughfall sampling points for each plantation. Each rain gauge was fixed to the top of a 1.5 m high stake of stainless steel to avoid splash contamination. The accumulated material in the rain gauge was removed weekly. The rainfall containers of the rain gauges were pre-washed with dilute (5%) HCl and thoroughly rinsed with deionized water after each sampling. Throughfall volume was measured with a graduated cylinder and samples were taken biweekly with clean 100-ml polythene. Throughfall per unit area (i.e., 1 ha) was corrected by subtracting 0.24% and 0.19% stem areas for the acacia and longan plantations, respectively. All the four samples at each plot were pooled into a composite sample and thus resulted in 3 composite samples for chemical analysis for each plantation.

Stemflow was measured on 3 representative trees belonging to three DBH classes (<15 cm, 15–25 cm, and >25 cm) within each of the three permanent observation plots. Stemflow collars consisted of a 25-mm-diameter high quality polyethylene plastic hose slit longitudinally and sealed to the trunk in an upward spiral pattern with galvanized iron staples and neutral silicon sealant. The lower unsplit section of hose directed stemflow into a 25-l dark inert plastic container on the forest floor. Container was emptied and accumulative stemflow volume was measured on a biweekly basis as well. The total stemflow per unit area was calculated by multiplying the mean stemflow volumes for each DBH class with the number of trees in that class. Stemflow samples for chemical analysis were also collected on a biweekly basis. Three samples in each plot were mixed to give a composite sample for chemical analysis and therefore there were three samples for chemical analysis for each plantation. Stemflow containers were also pre-washed with dilute (5%) HCl and thoroughly rinsed with deionized water after each sampling.

2.3. Chemical analysis and quality control

Bulk precipitation, throughfall and stemflow samples were stored on ice in coolers and transported to the institute laboratory at Guangzhou about 80 km from the Heshan-NFRS within two days. Samples were filtered through 0.45 μm polypropylene membranes and stored in a refrigerator at a temperature lower than 4 °C preserving their chemical properties intact until analysis. pH and conductivity were measured within 48 h after field sampling. The concentrations of major ions were measured as soon as possible after sampling, generally within two weeks. NH_4^+ and NO_3^- concentrations were determined by a flow injection analyzer (QuickChem FIA+ 8000, Lachat Instruments, USA), SO_4^{2-} by the barium sulfide turbidity method, HPO_4^{2-} by the phosphoantimonylmolybdenum blue spectrophotometric method, and K^+, Na^+, Ca^{2+}, Mg^{2+} by an inductive coupled plasma emission spectrometer (Optima 2000DV, Perkin–Elmer, USA). In some cases, total P and HPO_4^{2-} concentrations were under the limit of detection, especially during the wet season months with relatively large amount of rainfall amount and low concentration. We excluded those cases during our calculation of volume-weighted mean (vwm) concentrations for TP and HPO_4^{2-}.

The volume-weighted mean concentrations of major ions were calculated using the equation $VWMC_i = \sum_{j=1}^{n} C_{ij}W_j / \sum_{j=1}^{n} W_j$, where C_{ij} is the *i*-solute concentration in BP, TF or SF during the *j*-event, W_j is the amount of BP, TF or SF in a given event. Element fluxes were calculated by multiplying vwm ion concentrations with rainwater volumes per unit area. The quality of chemical analysis was partly assessed by the conductivity and ion balance method. The ion balance in 80% of the BP samples showed a good agreement, with the percentage difference between the sum of anions and the sum of cations being generally less than 4%. For TF and SF samples, approximately 50–70% of them appeared to fulfill the requirement that the percentage difference is less than 25% (de Vries et al., 2007; Keene et al., 1986). Due to the very little rainfall in some dry season months, we were not able to collect sufficient and high quality TF and SF samples for chemical analysis. Data for January were therefore absent. In total, we were successful in taking samples for chemical analysis in 31 occasions (or sampling dates) during the two years.

2.4. Assessment of dry deposition and canopy exchange

We applied the canopy budget model developed by Ulrich (1983) to estimate the dry deposition (DD) and canopy exchange (CE) in throughfall and stemflow. In the model, Na was assumed not to be influenced by canopy exchange processes and treated as a tracer element. The dry deposition fluxes of the cations (Ca^{2+}, Mg^{2+}, K^+, NH_4^+) were therefore calculated using the following equation:

$$DD_i = BP_i \cdot f_{DD} = BP_i \cdot \frac{TF_{Na} + SF_{Na} - BP_{Na}}{BP_{Na}}$$

where DD_i was the dry deposition flux (kg ha^{-1} yr^{-1}) of cation *i*, BP_i was the bulk precipitation flux (kg ha^{-1} yr^{-1}) of cation *i*, f_{DD} was the dry deposition factor, TF_{Na} and SF_{Na} were the throughfall and stemflow fluxes (kg ha^{-1} yr^{-1}) of Na respectively, and BP_{Na} was the bulk precipitation flux of Na (kg ha^{-1} yr^{-1}). In the model, it was also assumed that canopy exchange of NO_3^- and SO_4^{2-} was negligible. Therefore, the dry deposition fluxes of these two ions were equal to their net throughfall fluxes. After calculation of DD, canopy exchange for element *i* (CE_i) was calculated using the mass balance approach (Lovett and Lindberg, 1984): $CE_i = NTF_i - DD_i$, where NTF was the net throughfall flux calculated by subtracting BP flux from the sum of TF and SF fluxes.

2.5. Statistical analysis

The non-parametric Wilcoxon two-sample test was used to detect the statistical differences between the amounts of different rainwater types (e.g., TF vs. BP), the ion concentrations in different types of rainwater (e.g., $[SO_4^{2-}]$ in TF vs. BP), and the two plantation types (acacia vs. longan). The relationship between TF and BP and the correlation between different ion species (e.g., Ca^{2+} and SO_4^{2-}) were analyzed using the Spearman correlation analysis. All statistics were computed using SAS and the significance level was set at $\alpha < 0.05$.

3. Results and discussion

3.1. Canopy impacts on rainwater fluxes

The bulk precipitation in 2006 (2172.7 mm) was nearly double of that in 2007 (1167.3 mm). About 86% and 92% of the total annual rainfall fell in the wet-season months from April through September in 2006 and 2007, respectively. On average, the proportions of TF to BP were 89.9% and 83.2% and those of SF to BP were 4.3% and 6.8% for the acacia and longan plantations, respectively. The canopy interceptions were therefore 5.8% for the acacia and 10% for the longan plantation. The Spearman correlation analysis showed that both TF and SF of the two plantations were positively correlated with BP ($r \geq 0.7824$ and $p < 0.0001$), particularly with respect to TF (Fig. 1).

The Wilcoxon two-sample test showed that the TF proportion for the acacia plantation was significantly higher than that for the longan plantation ($p < 0.0001$), but the SF proportion of the acacia

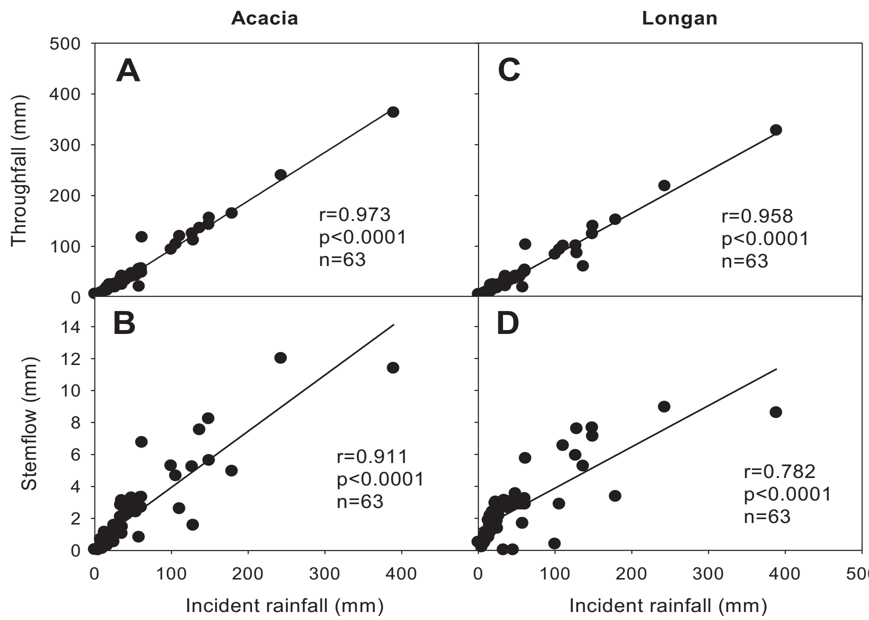

Fig. 1. Linear correlations between throughfall/stemflow and bulk precipitation in the acacia and longan plantations. *r* is the Spearman correlation coefficient. *p* is the significance value. *n* is the sample size.

plantation was significantly lower ($p < 0.0001$). Such rainfall partitioning differentiation between the two plantations may be explained by their differences in canopy structure and tree architecture. At stand level, smaller crown size and larger canopy gaps in the acacia plantation (see Table 1) allowed more rainfall to pass through its canopy and resulted in greater TF yield; whereas greater DBH and projected crown area in the longan plantation (see Table 1) benefited the generation of SF (Crockford and Richardson, 2000; Pypker et al., 2011). At the individual tree level, tree species with erectophile branching pattern and smooth bark can produce much larger SF volumes than those with plagiophile branching pattern and rougher bark (Andre et al., 2008; Levia and Frost, 2003). The smoother bark and more orthotropic branching angle of longan trees might therefore contribute to the greater SF yield in the longan plantation than the acacia plantation.

3.2. Bulk deposition and origin of ions

The pH values of individual BP samples varied from 3.56 to 5.94 with the vwm pH of 4.62 for the study site (Table 2). About 96% of the rainwater samples had pH values less than 5.6 below which acid rain is defined. Based on the ranking of acid rain in terms of pH values (Bashkin, 2003), the rainfall at the study site was moderately to strongly acidic. A comparison between urban and rural sites (Table 3) showed that the rainfall pH values were generally <5.0 in the Pearl River Delta region and higher at rural (>4.5) than urban sites (<4.5), indicating that acid rain was more severe in urban than in rural areas of the region.

The predominant acidic precursor was SO_4^{2-} with vwm concentration of 140.1 μeq l^{-1} (Table 2), which was close to those at other rural and suburban sites in the region but much less than those at urban Guangzhou (Table 3). Unlike at the urban sites, NO_3^-

Table 2
Volume-weighted mean ion concentrations (μeq l^{-1}) in bulk precipitation (BP), throughfall (TF) and stemflow (SF) samples ($n = 31$) collected in the acacia and longan plantations.

		pH	TN	NO_3^-	NH_4^+	TP	HPO_4^{2-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
BP	2006	4.57	74.9	3.57	34.9	0.53	0.18	135.7	60.2	5.7	47.9	6.52
	2007	4.67	172.2	4.64	47.6	0.80	0.28	144.5	129.4	17.5	47.3	15.1
	Mean	4.62	123.6	4.11	41.2	0.66	0.23	140.1	94.8	11.6	47.6	10.8
Acacia												
TF	2006	5.01	67.1	3.96	61.1	0.93	0.35	220.3	75.9	29.3	64.2	92.5
	2007	5.35	313.7	4.27	113.6	1.52	0.76	311.3	176.1	38.5	59.9	122.4
	Mean	5.15	190.4	4.12	87.3	1.23	0.56	265.8	126	33.9	62.0	107.4
SF	2006	3.86	154.1	7.38	141.7	0.61	0.55	502.2	144.7	37.6	73.3	100.8
	2007	3.67	641.1	11.6	197.5	1.73	1.15	763.5	207.5	41.0	47.4	112.2
	Mean	3.76	397.5	9.51	169.6	1.17	0.85	632.9	176.1	39.3	60.3	106.5
Longan												
TF	2006	5.10	69.0	3.07	45.3	2.70	0.51	143.7	71.2	16.0	80.8	101.2
	2007	5.65	268.6	4.47	87.7	7.45	3.71	265.6	181.9	24.9	39.8	171.8
	Mean	5.37	168.8	3.77	66.5	5.08	2.11	204.7	126.6	20.4	60.3	136.5
SF	2006	4.92	98.8	5.15	74.7	3.78	1.26	363.4	159.1	72.9	79.6	175.9
	2007	4.97	305.0	5.96	124.7	6.59	4.12	367.6	164.9	79.4	25.8	224.3
	Mean	4.92	201.9	5.55	99.7	5.19	2.69	365.5	162.0	76.1	52.7	200.1

Table 3
Concentrations of major ions (μeq l^{-1}) and pH values of bulk precipitation reported in the Pearl River Delta region.

Location		Period	pH	SO_4^{2-}	NO_3^-	NH_4^+	Ca^{2+}	Reference
Heshan	Rural	2006–2007	4.62	140.1	4.11	41.2	94.8	This study
Dinghushan	Rural	2009	4.90	NR[a]	13.5	40.4	128.2	Zhang et al., 2010
Liuxihe	Rural	2003	4.57	86	9.0	13.0	41.0	Aas et al., 2007
Guangzhou	Urban	2006	4.49	163.3	53.4	70.6	103.6	Cao et al., 2009
Guangzhou	Urban	2005–2006	4.49	202.2	51.8	66.2	130.6	Huang et al., 2009
Guangzhou	Urban	1998–1999	4.39	200.0	7.5	64.2	105.4	Xu et al., 2001
Guangzhou	Suburban	1998–1999	4.37	138.9	6.8	63.6	58.5	Xu et al., 2001
Guangzhou	Urban	Early 1990s	NR	231.0	20.1	103.0	164.8	Li and Gao, 2002
Guangzhou	Suburban	Early 1990s	NR	121.0	18.6	91.9	108.2	Li and Gao, 2002

[a] NR = Not reported.

was not the major acidic precursor at our study site, with its concentration being over 10 times less than those of the urban Guangzhou (Table 3), reflecting the decreasing contribution of traffic emissions of NO_x from urban Guangzhou to rural Heshan.

The most abundant base cation in BP was Ca^{2+} with vwm concentration of 94.8 μeq l^{-1} (Table 2). The secondary abundant cations were NH_4^+ and Na^+, with their vwm concentrations being 41.2 and 47.6 μeq l^{-1}, respectively (Table 2). In terms of the neutralization factor (NF), defined as $[X]/([SO_4^{2-}]+[NO_3^-])$ with [X] being the vwm concentration of cation X, Ca^{2+}, NH_4^+, Mg^{2+}, and K^+ had NF values of 0.66, 0.29, 0.08 and 0.07, respectively, further indicating that Ca^{2+} and NH_4^+ were the predominant acid neutralizing agents. In comparison of the major cation concentrations between the rural and urban sites, both Ca^{2+} and NH_4^+ concentrations were smaller in rural area (Table 3), reflecting less intense industrial, construction, and fertilization activities in the rural area. It is worth to point out that eucalyptus plantations, besides rice paddies and fruit tree stands, were widely distributed in the nearby region. Heavy fertilization was often adopted to gain fast growth and more economic income. We suspect that such agricultural and forestry activities might contribute a large portion to the emissions of NH_3 and therefore NH_4^+ deposition in the study area.

To identify the origin of an ion in BP, enrichment factor (EF) for the ion species was computed using Na^+ and Ca^{2+} as the reference ions for marine and continental sources, respectively (see Table 4 for calculations of EF). The relative contributions from marine and terrestrial sources were further calculated as the percent reciprocal of EF for a considered ion. The relative contribution from anthropogenic source was calculated as the difference between 100% and the sum of marine and soil contributions. Based on the EF and relative contribution values listed in Table 4, the majority (~95%) of SO_4^{2-} and NO_3^- were from anthropogenic sources; Ca^{2+} and K^+ (91%) were mainly from terrestrial sources; Mg^{2+} and Na^+ were mainly from marine sources (Table 4). As SO_2 derived from fossil fuel combustion has been recognized as the most important precursor of acid deposition in China (Larssen et al., 2006; Li and Gao, 2002), a potentially important source of SO_2 at our study site might come from the "ceramic capital" Foshan city, which is about 30 km away from the study site and notorious for its air pollution resulting from the ceramic industry. The high Ca^{2+} concentration at the study site might mainly comes from local alkaline dust that derived from industrial and road construction, mining activities, and long-distance transported windblown dust (Huang et al., 2009; Xu et al., 2001). The Spearman correlation coefficient (SCC) analysis also showed that SO_4^{2-} was significantly correlated with NH_4^+ (SCC = 0.900, $P < 0.01$) and Ca^{2+} (SCC = 0.743, $p < 0.01$), which was

Table 4
Sources of elements in bulk precipitation.

	NO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
Seawater $[X/Na^+]$ ratio[a]	–	0.125	0.044	0.227	1.000	0.022
Rainwater $[X/Na^+]$ ratio	–	3.354	1.996	0.296	1.000	0.251
EF_{marine}	–	26.83	45.36	1.30	1.000	11.41
Soil $[X/Ca^{2+}]$ ratio[a]	0.002	0.019	1.000	0.561	0.569	0.504
Rainwater $[X/Ca^{2+}]$ ratio	0.049	1.681	1.000	0.148	0.501	0.126
EF_{soil}	23.46	89.40	1.000	0.264	0.881	0.250
Marine fraction (%)	–	3.70	–	76.8	100	8.80
Soil fraction (%)	4.30	1.10	100	23.2	–	91.2
Human fraction (%)	95.7	95.2	–	–	–	–

[a] Reference seawater [X/Na] and soil [X/Ca] ratios are from Cao et al. (2009); [X] is the vwm concentration of considered ion. EF stands for enrichment factor and is calculated by dividing the rainwater $[X/Na^+]$ ratio or $[X/Ca^{2+}]$ ratio by the reference seawater $[X/Na^+]$ ratio or soil $[X/Ca^{2+}]$ ratio for marine or soil sources, respectively. Dash (–) means not available.

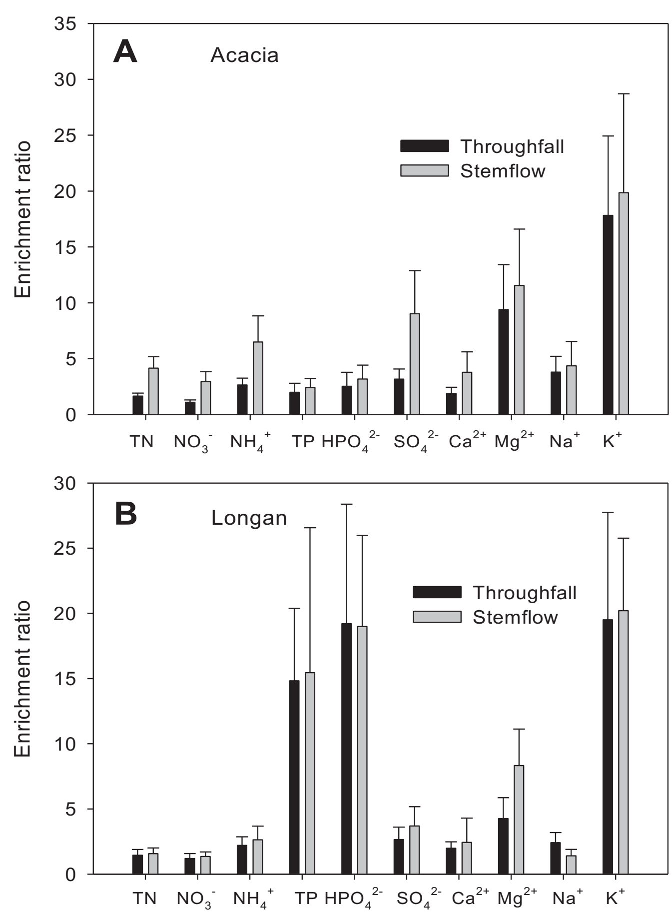

Fig. 2. Enrichment ratios of ion concentrations for the throughfall and stemflow of the acacia (A) and longan (B) plantations. Error bars are confidence intervals at level $\alpha = 0.05$.

consistent with the finding from the IMPACTS project that the main components in the airborne particles are $(NH_4)_2SO_4$ and $CaSO_4$ in south China (Aas et al., 2007).

3.3. Canopy impacts on rainwater chemistry and deposition fluxes

After passing through the plantation canopies, element concentrations in rainwater were significantly enriched in TF and SF compared with those in BP (P values mostly <0.01), with the exceptions that P (TP and HPO_4^{2-}) concentrations were not significantly altered by the acacia canopy and N (TN and NO_3^-) concentrations were not significantly altered by the longan canopy. As a result of changes in ion concentrations, throughfall pH was significantly enhanced in both plantations ($P < 0.001$); whereas stemflow pH was significantly reduced in the acacia ($P < 0.001$) but not significantly altered in the longan plantation ($P = 0.099$; Table 2). Although both element concentration and pH were modified by plantation canopies, SO_4^{2-} was still the most abundant anion with vwm concentration varying from 204.7 μeq l^{-1} in longan TF to 632.9 μeq l^{-1} in acacia SF (Table 2). Ca^{2+} and NH_4^+ were still the dominant cations in acacia TF and SF but K^+ became the dominant cation in longan TF and SF (Table 2), indicating that different tree species had different influences on rainfall chemistry.

To quantify the modification of plantation canopy on rainwater chemistry, we calculated the enrichment ratio for each of the 10 measured elements by dividing the element concentration in TF (or SF) by the element concentration in BP and presented the results in Fig. 2. K^+ concentration was altered the most among all elements analyzed, with an increment of about 20-fold in TF and SF of both plantations. Mg^{2+}, Na^+, NH_4^+ and SO_4^{2-} also showed relatively large enrichment of about 10-fold, particularly in acacia SF. For most other elements, the enrichment ratios were less than 5. In general, element concentrations followed the order of SF > TF > BP (Table 2). The longer canopy residence time and greater leachability of bark tissue for SF than for TF were thought to be responsible for such a chemical concentration gradient (Levia and Herwitz, 2000). In comparison of the two plantations, the enrichment of element concentration was mostly larger in acacia than in the longan plantation. Especially with respect to SO_4^{2-}, its concentrations in acacia TF and SF were nearly double of those in longan TF and SF (Table 2). This might have caused the soil pH value of 1.4 unit lower in the acacia than in the longan plantation (Table 1). The coarser-textured acacia leaf and bark tissues might be more efficient in capturing and retaining the atmospheric deposits and therefore resulted in the greater enrichment for the acacia plantation (Levia and Frost, 2003; Pryor and Barthelmie, 2005).

The enrichment of element concentrations directly resulted in the enhancement of total deposition fluxes under plantation canopies (Table 5). The total deposition of SO_4^{2-} was nearly double its bulk deposition in the acacia plantation and 22% greater in the longan plantation, further demonstrating that acid deposition would be greatly underestimated in forested areas if only looking at the bulk deposition (Aas et al., 2007). Relative to the bulk deposition, the total Ca^{2+} deposition under the acacia and longan canopies were also increased by 31% and 14%, respectively. Our measurements showed the bulk N deposition was 25.2 kg ha^{-1} yr^{-1}, which was moderately high compared with the regional N deposition rates of 16.2–38.2 kg ha^{-1} yr^{-1} (Fang et al., 2011). Inorganic N (NO_3^- and NH_4^+), particularly NH_4^+, composed of the majority (62.5–78.2%) of the total N deposition, which was enhanced by 44% and 10%

Table 5
Mean annual deposition and canopy exchange fluxes (kg ha^{-1} yr^{-1}) for the acacia and longan plantations.

		TN	NO_3^-	NH_4^+	TP	HPO_4^{2-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+
BP[a]	2006	22.7	4.78	13.6	0.35	0.19	140.8	26.1	1.50	23.8	5.50
	2007	27.8	3.30	9.87	0.28	0.15	79.9	29.9	2.45	12.5	6.78
	Mean	25.2	4.05	11.7	0.32	0.17	110.3	28.0	1.99	18.1	6.14
Acacia											
TF[b]	2006	18.8	4.90	22.0	0.57	0.33	211.4	30.4	7.11	29.5	72.2
	2007	47.8	2.88	22.3	0.51	0.40	162.5	38.4	5.08	15.0	52.0
	Mean	33.3	3.89	22.1	0.54	0.37	186.9	34.4	6.10	22.2	62.1
SF[c]	2006	2.10	0.45	2.49	0.02	0.03	23.5	2.82	0.44	1.64	3.84
	2007	4.19	0.34	1.66	0.03	0.03	17.1	1.94	0.23	0.51	2.05
	Mean	3.14	0.39	2.07	0.02	0.03	20.3	2.38	0.34	1.07	2.94
TD[d]	Mean	36.4	4.28	24.2	0.56	0.40	207.2	36.8	6.44	23.3	65.1
NTF[e]		11.2	0.24	12.5	0.25	0.22	96.9	8.79	4.46	5.15	58.9
DD[f]		7.15	1.15	3.33	0.09	0.05	31.3	7.93	0.56	5.15	1.74
CE[g]		4.03		9.15	0.15	0.17		0.86	3.89		57.2
DD/TD%		19.7	26.8	13.8	16.0	12.3	15.1	21.6	8.72	22.1	2.68
CE/TD%		11.1		37.8	26.8	42.5		2.3	60.4		87.9
Longan											
TF[a]	2006	17.7	3.48	15.0	1.53	0.45	126.4	26.2	3.56	34.0	72.5
	2007	33.5	2.47	14.1	2.06	1.59	113.6	32.5	2.69	8.14	59.8
	Mean	25.6	2.98	14.5	1.79	1.02	120.0	29.3	3.13	21.1	66.2
SF[b]	2006	1.37	0.32	1.34	0.12	0.06	17.3	3.17	0.88	1.82	6.83
	2007	2.88	0.25	1.52	0.14	0.13	11.9	2.23	0.65	0.40	5.92
	Mean	2.13	0.28	1.43	0.13	0.10	14.6	2.70	0.77	1.11	6.37
TD[c]	Mean	27.7	3.26	15.9	1.93	1.12	134.7	32.0	3.89	22.2	72.5
NTF[d]		2.52	−0.79	4.23	1.60	0.94	24.4	4.05	1.91	4.05	66.4
DD[e]		5.63	0.90	2.62	0.07	0.04	24.6	6.24	0.44	4.05	1.37
CE[f]		−3.11		1.61	1.53	0.91		−2.20	1.47		65.0
DD/TD%		20.3	27.7	16.4	3.69	3.41	18.3	19.5	11.3	18.3	1.89
CE/TD%				10.1	79.3	81.3			37.8		89.7

[a] BP = bulk precipitation.
[b] TF = throughfall.
[c] SF = stemflow.
[d] TD = total deposition flux as the sum of TF and SF.
[e] NTF = net throughfall flux as the difference between TD and BP.
[f] DD = dry deposition.
[g] CE = canopy exchange.

under the acacia and longan canopies, respectively. Phosphorus (TP and HPO_4^{2-}) deposition was small at the study site and generally less than 1 kg ha^{-1} yr^{-1}. Na^+ deposition (~20 kg ha^{-1} yr^{-1}) was relatively larger compared to Mg^{2+} (<~7 kg ha^{-1} yr^{-1}), indicating the considerable contribution from the South China Sea. The total K^+ deposition under plantation canopies was enhanced the most – nearly ~10 times of its bulk deposition, reflecting the high mobility of this element in plant tissues (Levia and Frost, 2003; Pypker et al., 2011).

The relative contributions of canopy leaching and dry deposition to the total deposition differed among ion species and between plantation types (Table 5). The acidic anions (SO_4^{2-} and NO_3^-) and

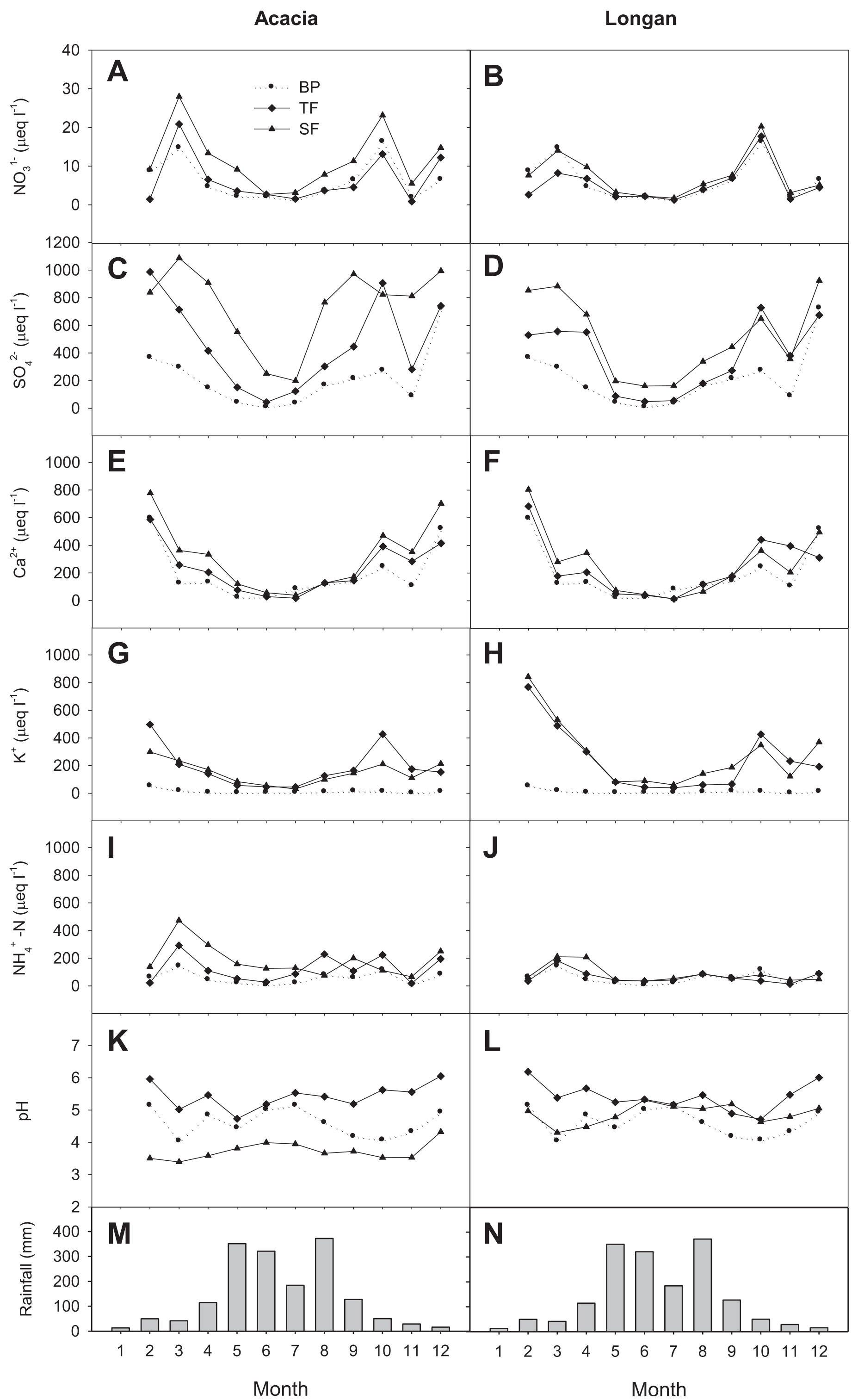

Fig. 3. Monthly variation of volume-weighted mean ion concentrations in bulk precipitation (BP), throughfall (TF), and stemflow (SF) of the acacia (left panel) and longan (right panel) plantations. For comparison, monthly rainfall is presented at the bottom of the graph as well.

two base cations (Ca^{2+} and Na^{+}) were mainly from BP or wet deposition (>70%); dry deposition accounted for 20–30% and canopy leaching was meager. Contrastingly, K^{+} was predominantly (~90%) from canopy leaching while wet and dry deposition only contributed about 10%. Canopy leaching was also considerable (40–60%) for Mg^{2+} in both plantations with dry deposition contributing about 10% and the rest from wet deposition. The relative contributions of wet deposition, dry deposition, and canopy leaching for NH_4^{+} and P elements (TP and HPO_4^{2-}) were more species-specific, but in general acacia canopy leached out more N and longan more P and K. Coincidently, we found that P and K contents were also higher in longan leaf litter and N content was higher in acacia leaf litter in a previous study (Shen et al., 2011). We therefore suspect that the quantity of these elements leached out from the plantation canopies was positively related to the element contents in tree leaves. But this hypothesis needs to be further examined by measuring the throughfall chemistry and corresponding leaf nutrient contents with respect to more vegetation types.

3.4. Seasonality

As the study site experienced distinct dry and wet seasons, rainwater chemistry also showed clear seasonal patterns. Fig. 3 depicts the monthly variation of pH, rainfall, and the vwm concentrations of the major ions (SO_4^{2-}, NO_3^{-}, Ca^{2+}, K^{+}, and NH_4^{+}). In general, ion concentrations and pH in rainwater (BP, TF, and SF) were higher in dry-season months (Oct.–Mar.) than in wet-season months (Apr.–Sep.), with their peak concentrations appearing in the late dry season (i.e., Nov.–Jan.; Fig. 3). Contrastingly, ion deposition fluxes showed just the opposite seasonal variation patterns as ion concentrations, being larger in wet-season months than in dry-season months (data not shown), mainly because rainwater volume predominantly determined the magnitude of ion fluxes and the seasonal variation pattern of ion fluxes therefore generally tracked the variation of rainwater amount. For the same reason, the deposition fluxes of most elements were greater in 2006 with much more rainfall (c.a., 1100 mm) than in 2007 (Table 5), albeit the element concentrations were all larger in 2007 than in 2006 (Table 2).

The seasonal variation patterns of ion concentrations observed at our rural plantation site was similar to those observed at urban Guangzhou. For example, it has been reported that the Ca^{2+} contents in Guangzhou rainwater were significantly higher during the drier autumn and winter than those during the wetter spring and summer, and pH values were also higher in dry than in wet seasons (Huang et al., 2009; Xu et al., 2001). The higher dry-season pH values in the region were therefore likely due to the increased neutralizing capacity of base cations (e.g., Ca^{2+}) in the alkaline dust that were easier to be incorporated into and accumulated in the air during the dry season. In contrast, during the wet season, soil dust emissions were reduced due to the relatively wet surface. Moreover, the dilution effects on ion concentrations and pH values could also be considerable due to frequent rainfall wash-off in the wet season. The slightly higher pH values during the summer months (Jun.–Aug.) than in late spring and early autumn (Fig. 3K, L) indicated that the wash-off of acidic precursors was more pronounced during these very rainy months.

4. Conclusions

By measuring the rainwater amount and chemistry in two years, we found that the rainwater at the study site was moderately to strongly acidic. Sulfate was the major acidic precursor mainly derived from anthropogenic sources such as fossil fuel combustion for power and transportation. Calcium and ammonium were the major neutralizing agents mainly derived from terrestrial sources as a result of construction, agricultural and forestry activities. The marine contribution was also considerable to some base cations such as Na^{+} and Mg^{2+} from the South China Sea. Corresponding to the distinct rainfall seasonality, rainwater chemistry also showed clear seasonal variation patterns with higher ion concentrations and pH being observed in the dry season than in the wet season. Our comparative analysis showed that the acid rain was only slightly less severe at our rural plantation site than the urban sites in terms of pH values and ion concentrations, further demonstrating the necessity to study such environmental problems as acid and N depositions at regional scales.

Plantation canopies had marked influences on the atmospheric deposition by redistributing rainfall, enhancing pH and ion concentrations, washing off canopy-captured dry deposits, and leaching out elements from plant tissues. Distinct species-specific canopy impacts on rainwater amount and chemistry were also detected from this study that the coarser-textured acacia leaves and barks were more capable in capturing and retaining acidic precursors while the longan tissues could leach out more base cations such as K^{+}. Such differentiation of species-specific effects might further shape the chemistry of soil and stream water as soil acidity was found to be much lower in the acacia plantation than in the longan plantation (Li et al., 2005). Selection of species during the construction of plantations is therefore critically important in ameliorating the influence of environmental problems such as acid rain.

Acknowledgments

We thank Mr. Yongbiao Lin and Ms. Huilan Zhang helped with field sampling and lab analysis. We are also grateful to Dr. Yunting Fang for his constructive comments on the early draft of the manuscript. Financial supports came from the National Natural Science Foundation of China (NSFC-31130011, 31070562) and the Major State Basic Research Development Program (973 Planning Program 2011CB403206).

References

Aas, W., Shao, M., Jin, L., Larssen, T., Zhao, D.W., Xiang, R.J., Zhang, J.H., Xiao, J.S., Duan, L., 2007. Air concentrations and wet deposition of major inorganic ions at five non-urban sites in China, 2001–2003. Atmospheric Environment 41, 1706–1716.
Andre, F., Jonard, M., Ponette, Q., 2008. Influence of species and rain event characteristics on stemflow volume in a temperate mixed oak-beech stand. Hydrological Processes 22, 4455–4466.
Balestrini, R., Arisci, S., Brizzio, M.C., Mosello, R., Rogora, M., Tagliaferri, A., 2007. Dry deposition of particles and canopy exchange: comparison of wet, bulk and throughfall deposition at five forest sites in Italy. Atmospheric Environment 41, 745–756.
Bashkin, V.N., 2003. Environmental Chemistry: Asian Lessons. Kluwer Academic Publishers, New York.
Cao, Y.Z., Wang, S.Y., Zhang, G., Luo, J.Y., Lu, S.Y., 2009. Chemical characteristics of wet precipitation at an urban site of Guangzhou, South China. Atmospheric Research 94, 462–469.
Crockford, R.H., Richardson, D.P., 2000. Partitioning of rainfall into throughfall, stemflow and interception: effect of forest type, ground cover and climate. Hydrological Processes 14, 2903–2920.
de Vries, W., van der Salm, C., Reinds, G.J., Erisman, J.W., 2007. Element fluxes through European forest ecosystems and their relationships with stand and site characteristics. Environmental Pollution 148, 501–513.
Draaijers, G.P.J., Erisman, J.W., Spranger, T., Wyers, G.P., 1996. The application of throughfall measurements for atmospheric deposition monitoring. Atmospheric Environment 30, 3349–3361.
Fang, Y.T., Yoh, M., Koba, K., Zhu, W.X., Takebayashi, Y., Xiao, Y.H., Lei, C.Y., Mo, J.M., Zhang, W., Lu, X.K., 2011. Nitrogen deposition and forest nitrogen cycling along an urban–rural transect in southern China. Global Change Biology 17, 872–885.
Hao, J.M., Wang, S.X., Liu, B.J., He, K.B., 2000. Designation of acid rain and SO_2 control zones and control policies in China. Journal of Environmental Science and Health Part A – Toxic/Hazardous Substances & Environmental Engineering 35, 1901–1914.
Huang, D.Y., Xu, Y.G., Peng, P., Zhang, H.H., Lan, J.B., 2009. Chemical composition and seasonal variation of acid deposition in Guangzhou, South China: comparison

with precipitation in other major Chinese cities. Environmental Pollution 157, 35–41.
Keene, W.C., Pszenny, A.A.P., Galloway, J.N., Hawley, M.E., 1986. Sea-salt corrections and interpretation of constituent ratios in marine precipitation. Journal of Geophysical Research – Atmospheres 91, 6647–6658.
Larssen, T., Carmichael, G.R., 2000. Acid rain and acidification in China: the importance of base cation deposition. Environmental Pollution 110, 89–102.
Larssen, T., Lydersen, E., Tang, D.G., He, Y., Gao, J.X., Liu, H.Y., Duan, L., Seip, H.M., Vogt, R.D., Mulder, J., Shao, M., Wang, Y.H., Shang, H., Zhang, X.S., Solberg, S., Aas, W., Okland, T., Eilertsen, O., Angell, V., Liu, Q.R., Zhao, D.W., Xiang, R.J., Xiao, J.S., Luo, J.H., 2006. Acid rain in China. Environmental Science & Technology 40, 418–425.
Larssen, T., Seip, H.M., Semb, A., Mulder, J., Muniz, I.P., Vogt, R.D., Lydersen, E., Angell, V., Tang, D.G., Eilertsen, O., 1999. Acid deposition and its effects in China: an overview. Environmental Science & Policy 2, 9–24.
Levia, D.F., Frost, E.E., 2003. A review and evaluation of stemflow literature in the hydrologic and biogeochemical cycles of forested and agricultural ecosystems. Journal of Hydrology 274, 1–29.
Levia, D.F., Herwitz, S.R., 2000. Physical properties of water in relation to stemflow leachate dynamics: implications for nutrient cycling. Canadian Journal of Forest Research – Revue Canadienne De Recherche Forestiere 30, 662–666.
Li, M., Peng, S., Shen, W., Lin, Y., Liu, Z., 2005. Vegetation restoration and spatial variation of soil nutrient contents in a hill-pond landscape. Transactions of The Chinese Society of Agricultural Engineering 21, 72–75 (in Chinese).
Li, W., Gao, J.X., 2002. Acid deposition and integrated zoning control in China. Environmental Management 30, 169–182.
Liu, Z., Liu, F., 2008. Status quo of fast-growing and high-yielding timber forest base construction and developmental countermeasures. Forest Inventory and Planning 33, 110–112 (in Chinese).
Lovett, G.M., Lindberg, S.E., 1984. Dry deposition and canopy exchange in a mixed oak forest as determined by analysis of throughfall. Journal of Applied Ecology 21, 1013–1027.
MEPC, 1996. Annual Reports of Environmental Statistics. Available online at: http://zls.mep.gov.cn.
Parker, G.G., 1983. Throughfall and stemflow in the forest nutrient cycle. Advances in Ecological Research 13, 57–133.
Pryor, S.C., Barthelmie, R.J., 2005. Liquid and chemical fluxes in precipitation, throughfall and stemflow: observations from a deciduous forest and a red pine plantation in the midwestern USA. Water, Air and Soil Pollution 163, 203–227.
Pypker, T.G., Levia, D.F., Staelens, J., Van Stan, J.T., 2011. Canopy structure in relation to hydrological and biogeochemical fluxes. In: Levia, D.F., Carlyle-Moses, D., Tanaka, T. (Eds.), Forest Hydrology and Biogeochemistry: Synthesis of Past Research and Future Directions. Springer, New York, pp. 371–388.
Rodhe, H., Dentener, F., Schulz, M., 2002. The global distribution of acidifying wet deposition. Environmental Science & Technology 36, 4382–4388.
Seip, H.M., Aagaard, P., Angell, V., Eilertsen, O., Larssen, T., Lydersen, E., Mulder, J., Muniz, I.P., Semb, A., Tang, D.G., Vogt, R.D., Xiao, J.S., Xiong, J.L., Zhao, D.W., Kong, G.H., 1999. Acidification in China: assessment based on studies at forested sites from Chongqing to Guangzhou. Ambio 28, 522–528.
SFAC, 2010. Forest Resource Statistics of China 2004–2008: the Seventh National Forest Resource Inventory. State Forestry Administration of China (SFAC), Beijing.
Shen, W.J., Lin, Y.B., Jenerette, G.D., Wu, J.G., 2011. Blowing litter across a landscape: effects on ecosystem nutrient flux and implications for landscape management. Landscape Ecology 26, 629–644.
Tang, D., Lydersen, E., Seip, H.M., Angell, V., Eilertsen, O., Larssen, T., Liu, X., Kong, G., Mulder, J., Semb, A., Solberg, S., Torseth, K., Vogt, R.D., Xiao, J., Zhao, D., 2001. Integrated monitoring program on acidification of Chinese terrestrial systems (impacts) – a Chinese-Norwegian cooperation project. Water, Air and Soil Pollution 130, 1073–1078.
Tobon, C., Sevink, J., Verstraten, J.M., 2004. Solute fluxes in throughfall and stemflow in four forest ecosystems in northwest Amazonia. Biogeochemistry 70, 1–25.
Ulrich, B., 1983. Interaction of forest canopies with atmospheric constituents: SO_2, alkali and earth alkali cations and chloride. In: Ulrich, B., Pankrath, J. (Eds.), Effects of Accumulation of Air Pollution in Forest Ecosystems. Springer, Reidel, Dordrecht, pp. 33–45.
Vogt, R.D., Seip, H.M., Larssen, T., Zhao, D.W., Xiang, R.J., Xiao, J.S., Luo, J.H., Zhao, Y., 2006. Potential acidifying capacity of deposition – experiences from regions with high NH4+ and dry deposition in China. Science of the Total Environment 367, 394–404.
Xu, Y.G., Zhou, G.Y., Wu, Z.M., Luo, T.S., He, Z.C., 2001. Chemical composition of precipitation, throughfall and soil solutions at two forested sites in Guangzhou, south China. Water, Air and Soil Pollution 130, 1079–1084.
Yu, H., Zhou, C., Wan, Z., Liu, Y., Chen, H., 2010. The developmental status of lichii and longan industry of Guangdong province in 2009. Agricultural Science in Guangdong 4, 288–291 (in Chinese).
Zhang, M.Y., Wang, S.J., Wu, F.C., Yuan, X.H., Zhang, Y., 2007. Chemical compositions of wet precipitation and anthropogenic influences at a developing urban site in southeastern China. Atmospheric Research 84, 311–322.
Zhang, X., Chai, F., Wang, S., Sun, X., Han, M., 2010. Research progress of acid precipitation in China. Research of Environmental Sciences 23, 527–532 (in Chinese).