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Wet deposition of nitrogen and sulfur in Guangzhou, a subtropical area in South China

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Abstract With the aim of understanding the seasonal distribution of deposition fluxes of nitrogen (N) and sulfur (S) in South China, a main acid deposition region in China, precipitation samples were collected and analyzed from Guangzhou area, between March 2005 and February 2006. The estimated wet deposition of N (including ammonium nitrogen (NH_4-N) and nitrate nitrogen (NO_3-N)) and S (sulfate sulfur (SO_4-S)) during the monitoring period were 40.47 kg N ha^{-1} and 65.29 kg S ha^{-1}, respectively. The average deposition of NH_4-N was ~1.5 times of the NO_3-N deposition, suggesting that the reduced and oxidized N depositions were comparable in the study area. The S and N depositions in the rainy season were greater than those in the dry season, showing great seasonal variation, which was consistent with both the distribution of precipitation and the period of fertilizer application for agriculture. The N and S wet deposition fluxes in Guangzhou were greater than those in Beijing and Zhengzhou, located in the northern China, but comparable to the level of Chongqing, located in the southwestern China, another major acid deposition region. The atmospheric N and S depositions in these cities from north to south were affected by both intensive agricultural and industrial activities.

Keywords Nitrogen deposition · Sulfur deposition · Seasonal variation · Precipitation · Guangzhou

Abbreviations

N	nitrogen
S	sulfur
NH_4-N	ammonium nitrogen
NO_3-N	nitrate nitrogen
SO_4-S	sulfate sulfur

A concise and informative title: Wet deposition of nitrogen and sulfur deposition in Guangzhou, China.

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Introduction

The interest in nitrogen and sulfur deposition is increasing because of their importance as two nutrient resources and major components of acid

deposition within the overall global N and S cycle. The biodiversity and productivity of natural ecosystems (such as forests, grasslands, and water bodies) are sensitive to N or S inputs from the atmosphere (Puxbaum and Gregori 1998; Luo et al. 2002; Matson et al. 2002). Atmospheric N or S deposition refers to the process which airborne nitrogenous or sulfurous compounds are deposited on the earth's surface via wet or dry deposition. The N and S cycle in ecosystem are deeply affected by anthropogenic activities, including fossil fuel combustion, fertilizer, use and animal husbandry. For example, the current total atmospheric inorganic N deposition in Europe and North America range as 1–75 kg N ha^{-1} $year^{-1}$ and 3–32 kg N ha^{-1} $year^{-1}$, respectively, which was considered to be greater than that in preindustrial times (Goulding et al. 1998; Holland et al. 1999; Nadelhoffer 2001).

In China, the largest developing country, the consumed N fertilizers and fossil fuel have increased dramatically since the 1980s. The estimation showed that China consumed fertilizer N at a rate of more than 24 Tg $year^{-1}$ in recent years, accounting for about 30% of the total amount in the world (Anonymous 1998–2004). Most N fertilizers in China are urea and ammonium bicarbonate, which are susceptible to NH_3 volatilization. However, due to the rapid increase in domestic animal production over the past 30 years, the amount of NH_3 volatilization from wastes of domestic animals is even higher than that from fertilizer use (Bouwman et al. 2002). Furthermore, the increased NO_x and SO_2 emissions are expected due to the rapid growth in energy consumption over the whole country. For example, the number of motor vehicles increased dramatically from 6.2 million in 1990 to 36.0 million in 2003 (Larssen et al. 2006). In China, coal and oil generate 69% and 23% of the energy production, respectively, and at the same time their combustion contribute to both NO_x and SO_2 emission, which are the main precursors of NO_3-N and SO_4-S in precipitation (Larssen et al. 2006; Aas et al. 2007; Quan et al. 2008). In the Guanzhong Plain of Shanxi province, North China, a region of intensive agriculture, the N deposition averaged as 16.3 kg N ha^{-1} $year^{-1}$ with 80% being NH_4-N (Li and Li 1999). In Jiangxi province, East China, a region of acid deposition, the S deposition was estimated to be 103 kg S ha^{-1} $year^{-1}$. In Sichuan province, Southwest China, a major region of acid deposition in China, the S deposition was higher than that in East China, ranging from 43 to 591 kg S ha^{-1} $year^{-1}$ (Chen 1993).

In South China, previous studies on the Pearl River Delta region have sought to characterize the chemical composition of acid precipitation (Seip et al. 1999; Tanner and Wong 1999; Xu et al. 2001). These studies revealed that the precursors of acid rain were mainly SO_2 and NO_x derived from the combustion of fossil fuel and traffic emissions, and NH_4^+ in precipitation was a neutralizer for rainwater acidity, derived mainly from agriculture (Larssen and Carmichael 2000; Larssen et al. 2006). However, the research on deposition of NH_4-N, NO_3-N, or SO_4-S to surface land and water bodies and comparison with other Chinese regions are very limited in the international literature, which is important to understand the air–land/air–ocean exchange between Pear River Delta and South China Sea.

Guangzhou (113.23° E, 23.16° N) is located upon the Pearl River Delta about 60 km from the Pearl River Estuary. The region is subjected to a typical Asian monsoon climate characterized by a rainy season from March to September (spring and summer) and a dry season from October to February of next year (autumn and winter). In this study, we studied N and S deposition in the process of precipitation. Our objectives were to: (1) determine the amount and seasonal distribution of N and S wet deposition in Guangzhou area and (2) compare their wet deposition fluxes with those in other regions in China.

Materials and methods

Location and sampling

The urbanization process has speeded up in Pearl River Delta, South China since 1980s. Guangzhou is the primary city in Pearl River Delta, surrounded by many other cites, such as Dongguan, Foushan, Zhongshan, and Huizhou. Due to the

development of urbanization, most rural sections of Guangzhou have been changed into semi-urban areas, which are connected with the adjacent cities. The semi-urban sections have been developed into a representative area of Guangzhou. Therefore, one monitoring site was established in Guangzhou suburb (113.35° E, 23.18° N, Fig. 1), which was located on the rooftop of the Herbarium Building in the South China Botanical Garden. The site was located ~20 m above the ground surface and ~600 m from the nearest road. There were no buildings greater than 30 m in height around the monitoring site.

A self-designed polyethylene bucket (inner diameter, 40 cm) with a polyethylene lid was used to collect the rainwater. Before sampling, the bucket was cleaned thoroughly several times with distilled water until the water conductivity was ~2 μS cm^{-1}. To collect the wet deposition, the collector lid was removed manually about 1 h earlier before each rain event in daytime. If the rain event was at wee hours, the lid was removed at 22:00 to avoid missing the rainfall. We used the self-designed collector only for collecting more rainwater sample for analysis. During the experiment period, we hired a technician to take responsibility for collecting rainwater samples. The rainwater was sampled in a 500 ml polyethylene bottle, which was cleaned with distilled water prior to use and then rinsed three times with rainwater.

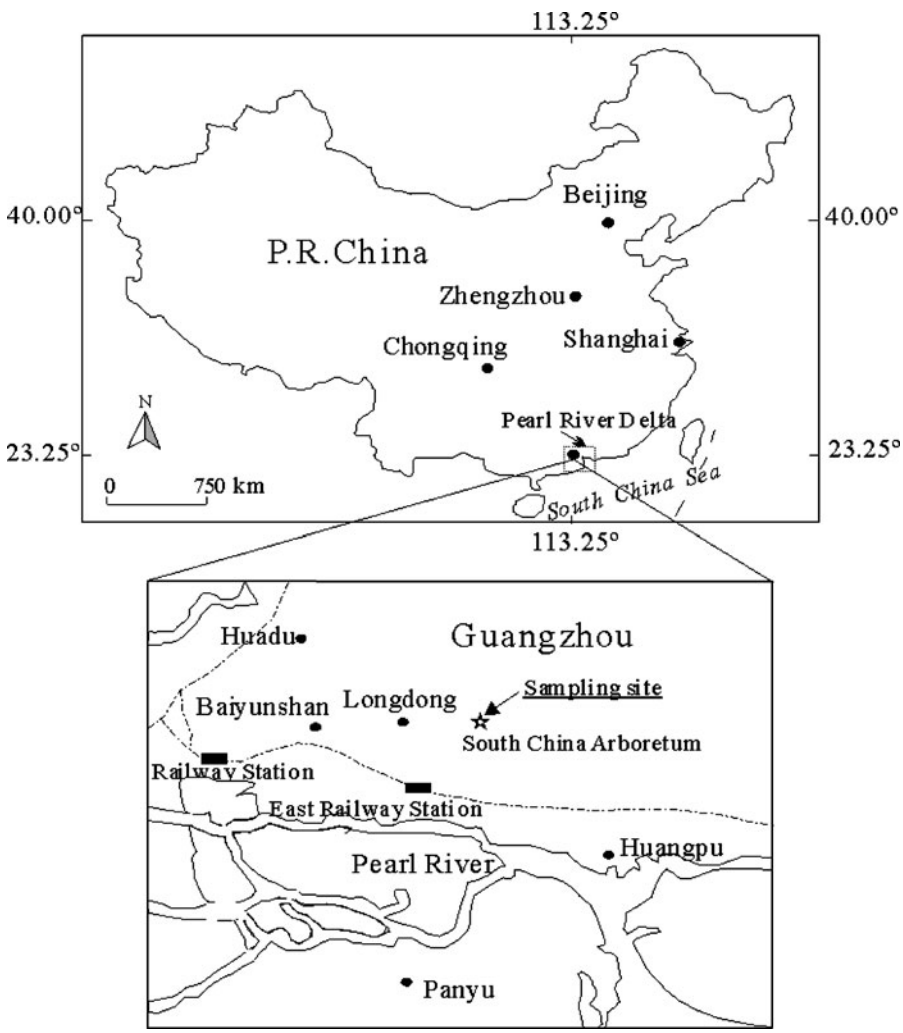

Fig. 1 Location of the monitoring site in Guangzhou in Pearl River Delta (South China)

Sample analysis

For each rain event, the rainwater pH value was measured in the field using a portable Thermo ORION pH meter, which was calibrated using standard pH 4.00 and 6.86 buffer before each measurement. The amount of rainfall was measured using a tipping bucket rain gauge. Once collected, the rainwater samples were transported to the laboratory and filtered through the hydrophobic membrane filter paper of 0.45 μm pore size. All samples were stored in a refrigerator at 4°C and were analyzed within 1 week.

According to the previous studies, the main ions in the rainwater in the many cities of China are NO_3^-, NH_4^+, SO_4^{2-}, and Ca^{2+} (Xu et al. 2001; Tang et al. 2005; Huang et al. 2008). The N and S deposition fluxes were often many researchers' discussion emphasis when they discussed the wet deposition (Liu et al. 2003, 2006). It is probably related to that they are directly or indirectly related to acidity of soil and water. In this study, four main ions were measured by ion chromatography (Dionex, ICS 90, America), and the detection limits of anions and cations were lower than 0.05 and 0.1 μmol L^{-1}, respectively. The relative standard deviation for all ions was within 2.0%. In addition, to assess the balance between the main anions and cations, the equivalent concentration ratio of the measured anions ($\sum -$) to cations ($\sum +$) were calculated for each rainwater sample.

Calculation of N and S deposition

The concentrations of NH_4-N, NO_3-N, SO_4-S, and Ca^{2+} were analyzed for every rain event. Their monthly and annually volume-weighted mean (VWM, $\overline{C}$) concentrations were calculated according to the data from a given month or the entire monitoring period. The VWM concentrations were calculated using the formula:

$$\overline{C} = \left(\sum_{i=1}^{n} C_i Q_i\right) \Big/ \left(\sum_{i=1}^{n} Q_i\right) \quad (1)$$

where Q_i is the rainfall amount (mm) of the precipitation event i, C_i is the measured concentration (mg L^{-1}), and n is the number of precipitation events.

The monthly wet deposition of NH_4-N, NO_3-N, SO_4-S, and Ca^{2+} (WD, in kg N or S ha^{-1} was calculated by the formula:

$$\mathrm{WD} = 10^{-2} \sum_{i=1}^{n} C_i' Q_i \quad (2)$$

where n is the number of precipitation events in a given month, and C_i' is the N, S, or Ca^{2+} concentration in rainwater (mg N or S L^{-1}).

Results and discussion

Rainfall and pH

At the monitoring site, the rain samples were collected during 57 rain events from March 2005 to February 2006. Forty-six rain events occurred in the rainy season and eleven rain events occurred in the dry season. Influenced by the Asian monsoon, the precipitation was concentrated over a period from March to August 2005 (1,816.7 mm), being 91.5% of the total rainfall during the entire monitoring period (1,986.4 mm). In the dry season, only four and one rain event occurred in September and December of 2005, respectively, in which the rainfall amount was not sufficient for conducting the routine analysis. No rain event took place in October and November 2005. There were six rainfall events in January and February 2006, and the total rainfall was 148.8 mm. In Guangzhou area, there are many showers in the rainy season. It is very often that there was a strong shower in a monitoring site, but no one drop in other monitoring site nearby (such as 3 km away). There is an official rain gauge, which is about 4 km away from the monitoring site. We used the rainfall data measured by ourselves, and used the official data as reference. In this study, the annual rainfall at suburban monitoring site was measured to be 1,986.4 mm, which was very comparable with the official data, 2,032.4 mm.

The pH values varied between 4.18 and 7.26, with an average of 4.83. The frequency of acid rain (pH < 5.6) was 87.5% during the monitoring period, and the acid deposition mainly occurred

in the rainy season. These results showed that the rainfall in Guangzhou area has apparently seasonal variation. The high frequency of acid rain implied a threat to the quality of ecological environment.

Concentration and deposition distribution of N and S

In this study, the equivalent concentration ratio of $\sum -/\sum +$ varied from 0.90 to 1.18, indicating that the measurements were reliable. According to the calculation using formula (1) and (2), the results of NH_4-N, NO_3-N, SO_4-S, and Ca^{2+} concentrations and deposition in this study and other major Chinese regions were listed in Table 1 and Table 2, respectively. As shown in Table 1, the monthly VWM concentrations of total N (NH_4-N + NO_3-N) in precipitation ranged from 1.72 to 4.61 mg N L^{-1} and averaged at 2.33 mg N L^{-1}. The monthly VWM concentrations of SO_4-S ranged from 2.28 to 7.72 mg S L^{-1} and averaged at 4.10 mg S L^{-1}. Molar ratios of NH_4/NO_3 in rainwater ranged from 0.51 to 2.29 over all the monitoring months, suggesting the reduced and oxidized N (NH_4-N and NO_3-N) depositions were comparable to each other in the study area. The monthly VWM concentrations of Ca^{2+}, considered as the main basic ion in rainwater (Larssen and Carmichael 2000), ranged from 2.36 to 11.70 mg L^{-1} and averaged at 4.64 mg L^{-1}.

The monthly NH_4-N and NO_3-N deposition were at close level. The monthly N deposition in precipitation ranged from 1.71 to 11.03 kg N ha^{-1}, with an annual deposition of 40.47 kg N ha^{-1}. The monthly S deposition ranged from 2.26 to 13.94 kg S ha^{-1}, with an annual deposition of 65.29 kg S ha^{-1}. These results showed that the annual N deposition in Guangzhou was greater than that in Guanzhong Plain of Shanxi province (16.3 kg N ha^{-1}; Li and Li 1999), located in northwestern China, and the annual S deposition was comparable with that in Sichuan province (3–32 kg N ha^{-1}; Chen 1993), located in southwestern China. The monthly wet deposition of Ca^{2+} in this study ranged from 4.07 to 13.57 kg ha^{-1}, with a total amount of 64.28 kg ha^{-1}.

Characteristics of seasonal variations in N and S deposition

With respect to the monthly N and S deposition in precipitation, the following four main features were apparent (see Fig. 2a–c and Table 1).

1. The N and S concentrations in rainwater decreased dramatically with increased rainfall, particularly when the rainfall was lower than 30 mm (Fig. 2a–c), which was consistent with previous studies (Liu et al. 2006; Shimamura et al. 2006). Their monthly mean concentrations in the rainy season were apparently lower than that in typical dry month, January 2006 (Table 1).
2. The monthly N and S deposition fluxes in the rainy season were larger than those in the dry season, showing strong seasonal variation.
3. The concentration and deposition flux of NH_4-N were larger than those of NO_3-N in the rainy season, but the trend was opposite in the dry season.
4. The monthly deposition of Ca^{2+} in the rainy season was higher than that in the dry season.

Factors affected the seasonal variation of N and S deposition

The negative correlation between rainfall and N or S concentrations indicated that the chemistry of precipitation was significantly affected by rainwater mainly via dilution, i.e., a large amount of rainfall could dilute the ion concentration in rainwater (Lee et al. 2000). The suspended particle in the air is an important contribution to NH_4-N, NO_3-N, and SO_4-S in rainwater. The dilution effect on the heavy events was much pronounced than on the light rainfall events. This explained why N and S concentrations of small rainfall events (<30 mm) were much higher than those of the large events (>60 mm; Fig. 2a–c). Furthermore, the chemistry of precipitation may partially depend on the residence time of suspended particles in the air (Lee et al. 2000). The residence time of the suspended particles persist in the air tended to be longer during the dry season, thereby leading to an accumulation of higher concentrations. Consequently,

Table 1 Wet deposition of NO_3-N, NH_4-N, SO_4-S, Ca^{2+}, and their standard deviation (in parentheses) in Guangzhou

	Mean	Rainfall	N, S and Ca^{2+} concentration (mg l^{-1})						N, S and Ca^{2+} precipitation (kg ha^{-1})				
	pH	(mm)	NO_3-N	NH_4-N	SO_4-S	Ca^{2+}	Total N	NH_4/NO_3	NO_3-N	NH_4-N	SO_4-S	Ca^{2+}	Total N
Mar. 2005 ($n = 6$)	5.10	132.0	0.97 (0.13)	1.77 (0.13)	5.92 (0.28)	6.50 (1.28)	2.74 (0.26)	1.82	1.28 (0.17)	2.34 (0.17)	7.82 (0.37)	8.57 (1.69)	3.62 (0.34)
Apr. 2005 ($n = 12$)	4.47	211.2	0.70 (0.14)	1.16 (0.15)	3.32 (1.68)	3.06 (0.62)	1.86 (0.29)	1.66	1.48 (0.30)	2.45 (0.32)	7.02 (3.55)	6.46 (1.31)	3.93 (0.62)
May 2005 ($n = 8$)	4.22	383.1	0.86 (0.18)	1.03 (0.09)	3.00 (0.36)	2.84 (0.24)	1.89 (0.27)	1.20	3.29 (0.69)	3.95 (0.34)	11.47 (1.38)	10.89 (0.92)	7.24 (1.03)
Jun. 2005 ($n = 7$)	4.38	574.6	0.73 (0.20)	1.19 (0.15)	2.43 (0.51)	2.36(0.46)	1.92 (0.35)	1.63	4.20 (1.15)	6.83 (0.86)	13.94 (2.93)	13.57 (2.64)	11.03 (2.01)
Jul. 2005 ($n = 7$)	4.42	140.4	1.02 (0.20)	1.48 (0.53)	4.97 (1.44)	4.16 (0.56)	2.50 (0.73)	1.45	1.43 (0.28)	2.07 (0.74)	6.97 (2.02)	5.83 (0.79)	3.50 (1.02)
Aug. 2005 ($n = 6$)	4.56	375.4	0.58 (0.11)	1.33 (0.12)	3.20 (0.70)	2.43 (0.44)	1.91 (0.23)	2.29	2.19 (0.41)	4.97 (0.45)	11.99 (2.63)	9.11 (1.65)	7.16 (0.86)
Jan. 2006 ($n = 2$)	6.90	49.5	2.47 (1.03)	2.14 (0.18)	7.72 (2.18)	11.70 (1.57)	4.61 (1.71)	0.87	1.22 (0.51)	1.06 (0.09)	3.82 (1.08)	5.78 (0.78)	2.28 (0.60)
Feb. 2006 ($n = 4$)	7.16	99.3	1.14 (0.12)	0.58 (0.10)	2.28 (0.25)	4.11 (1.10)	1.72 (0.22)	0.51	1.13 (0.12)	0.58 (0.10)	2.26 (0.25)	4.07 (1.09)	1.71 (0.22)
Monthly average			1.06 (0.32)	1.27 (0.23)	4.10 (0.82)	4.64 (0.68)	2.33 (0.55)	1.20	2.03 (0.45)	2.93 (0.38)	8.16 (1.77)	8.04 (1.36)	4.96 (0.83)
Total monthly		1965.5 (do not include the sum rainfall of Sep.–Dec. 2005, 20.9 mm)							16.22 (3.63)	24.25 (3.08)	65.29 (14.20)	64.28 (10.87)	40.47 (6.71)

The "n" in parentheses is the number of rain event

Table 2 Annual mean concentration and wet deposition of NO_3-N, NH_4-N, and SO_4-S in major Chinese cities (from north to south)

	Period	Rainfall	N and S concentration (mg l^{-1})				N and S deposition (kg ha^{-1})				Reference
		(mm)	SO4-S	NO3-N	NH4-N	NH_4/NO_3	SO_4-S	NO_3-N	NH_4-N	Total N	
Beijing (116.46° E, 39.92° N)	2001–2003	453.7	3.98	1.18	3.28	2.78	18.07	5.34	14.86	20.21	Yang et al. (2004)
Zhengzhou (113.07° E, 34.48° N)	1999	528.5	2.23	0.65	2.64	4.08	11.80	3.43	13.98	17.40	Zhao et al. (2001)
Shanghai (121.48° E, 31.23° N)	2005	1,071.2	3.19	0.70	1.13	1.62	34.21	7.47	12.10	19.57	Huang et al. (2008)
Chongqing (106.30° E, 29.30° N)	2002	1,236.8	5.41	0.59	1.94	3.31	66.89	7.24	23.95	31.18	Zhou et al. (2003)
Guangzhou (113.23° E, 23.16° N)	2005–2006	1,986.4	4.10	1.06	1.27	1.20	65.29	16.22	24.25	40.47	This study

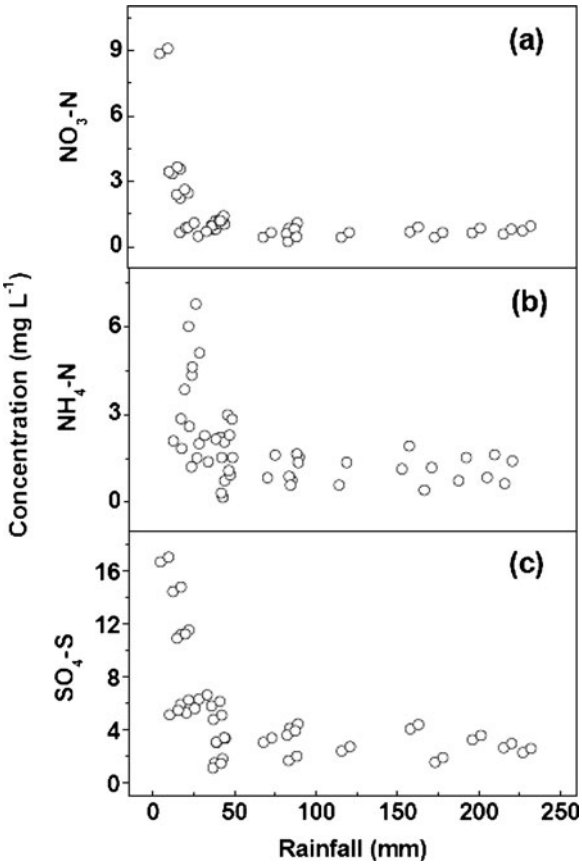

Fig. 2 Relationship between rainfall and concentration of **a** NO_3-N, **b** NH_4-N, and **c** SO_4-S

the combined effect of a great dilution factor and a greater residence time of suspend particles during the small rainfall events would give high ionic concentrations in precipitation, such as in the dry season. In contrast, frequent precipitation during the rainy season flushed particles from the air, therefore, lowering the ion concentrations in rainwater. This explained the occurrence of the highest concentrations of NH_4-N, NO_3-N, SO_4-S, and Ca^{2+} in the dry season in this study.

The N, S (NH_4-N, NO_3-N, and SO_4-S), and Ca^{2+} deposition in precipitation in the rainy season were higher than those in the dry season, which must be affected by the seasonal variation in emissions and meteorology in Guangzhou.

As reported in the previous studies, atmospheric NH_3 (the major precursor of NH_4-N in rainwater) mainly came from N fertilizers and domestic animal production, and the majority of atmospheric NO_x and SO_2 (the major precursors of NO_3-N and SO_4-S in rainwater) originated from industrial emission (e.g., vehicles and electricity plants through coal or oil combustion) and natural production (e.g., lighting; Liu et al. 2003, 2006; Larssen et al. 2006). In the case of Guangzhou, combustion for space heating is not required since it locates in the subtropical zone. Therefore, fossil fuel combustion acts as a relatively stable

contribution for NO_x and SO_2 in air, rather than a seasonally dependent source.

It was noticed that the seasonal variation of inorganic N and S deposition fluxes in precipitation were closely related to N management of local agriculture and rainfall events in different seasons. For example, at the beginning of the rainy season (March), all agriculture activities started and relatively larger amount of fertilizers were applied, resulting in a relatively larger NH_4/NO_3 ratio (1.82). In the rainy season, the arable lands were cultivated, and the levels of applied N fertilizers and temperature (17.2–29.9°C) were high, leading to more NH_3 emission from surface land or water bodies into air. Furthermore, the major rainfall took place in the rainy season accounted for more than 90% of annual precipitation in this study. Semi-continuous washing by rainfall efficiently increased the N and S deposition. In the dry season, rainfall events were infrequent, and the emitted N from surface land and water bodies were relatively small due to the little application of N fertilizers and low temperature, which were the reasons for the deposition fluxes of N and S in the winter were low. It was interesting to note that the inorganic N and S concentrations in February were much lower than those in January. This anomaly may reflect a reduction in anthropogenic activities because of the long national holidays (Spring Festival and the Festival of Lanterns) in this month.

The source of Ca^{2+} in Guangzhou is likely related to the coal combustion, cement production, and construction (Larssen et al. 2006). The Ca^{2+} deposition in the dry season was apparently lower than that in the rainy season, suggesting that the rainfall is an important factor affecting the wet deposition of Ca^{2+}.

To sum up, the depositions of inorganic N and S in precipitation showed a consistency with the seasonal variation of rainfall, suggesting that the Asian monsoon played a vital role.

Comparison with precipitation in other major Chinese cities

To gain a better insight of the regional variations of inorganic N and S deposition in precipitation in the scope of mainland China, we compared the annual deposition of NH_4-N, NO_3-N, and SO_4-S in rainwater among major cities in China (from north to south: Beijing, Zhengzhou, Shanghai, Chongqing, and Guangzhou) as shown in Table 2.

Annual NH_4-N, NO_3-N, and SO_4-S deposition fluxes in rainwater in Guangzhou and Chongqing (southern cities) were apparently higher than those in Beijing and Zhengzhou (northern cities). For an example, annual NO_3-N and SO_4-S deposition in Guangzhou were about two and three times more than those in Beijing, respectively, which was consistent with the rainfall ratio of two regions.

The annual wet deposition of N and S in Guangzhou and Chongqing, two serious acid deposition areas in China, were at the same level, but the molar ratio of NH_4/NO_3 in Chongqing (3.31) was obviously greater than that in Guangzhou (1.20). This result maybe resulted from the agriculture activities in Chongqing were relatively more intensive. Shanghai and Guangzhou as important commercial cities in China, displayed relatively lower NH_4/NO_3 ratios as results of weaker agriculture activities than other cities, while the highest NH_4/NO_3 ratio appeared in Zhengzhou (4.08), an intensively agricultural regions of China. It was interesting to note that NH_4/NO_3 ratios among these major cities (1.20–4.08) are much greater than those in USA and European countries (usually <1, Goulding et al. 1998; Fahey et al. 1999), which suggests that N deposition in China is more affected by agricultural activities.

Great concerns should be raised to the observation that the NO_3-N and SO_4-S deposition in precipitation were high not only in Guangzhou and Chongqing but also in Shanghai, as illustrated in Table 2. In the 1980s and 1990s, South and Southwest China were considered as two main acid deposition regions in China, but now the acid deposition zones got enlarged. It has been reported that the annual mean pH value of rainwater in Shanghai (in East China) was 5.92 in 1999 (Xu et al. 2000) and reduced to 4.49 in 2005 (Huang et al. 2008). Furthermore, in northern China, the buffering capacity of calcareous soil

for acid deposition was larger than that of red lateritic soil in southern China. Therefore, the effect of acid deposition on the ecosystem in southern China would be more significant than in northern China.

Total atmospheric N and S deposition estimated in Guangzhou area

In this study, dry deposition of N and S were not monitored as wet deposition. Obviously, their total atmospheric deposition can be largely underestimated in Guangzhou if only wet depositions were monitored. Previous studies have pointed out the important role of dry deposition of N in North China (Liu et al. 2003, 2006). In Thessaloniki, the second most populated city of Greece, dry deposition of both N and S accounted for more than 50% of their total (wet + dry) atmospheric deposition (Anatolaki and Tsitouridou 2007). In addition, soluble organic N and S in precipitation were not measured. Many other studies have shown that organic N deposition attributed to 10–30% of wet N deposition in different regions of the world (Keene et al. 2002; Neff et al. 2002). Guangzhou locates in subtropical zone and closes with South China Sea, thus the relatively high temperature and marine source of N and S may result in more organic N and S in rainwater compared with northern regions. In Guangzhou region, if assumed that dry depositions of inorganic N and S were equivalent to their wet depositions and the soluble organic N and S accounted for 15% of their wet depositions, the annual total atmospheric N and S deposition were estimated to be ~87 kg N ha^{-1} $year^{-1}$ and ~140 kg S ha^{-1} $year^{-1}$, respectively. The estimated annual total atmospheric N deposition accounted for ~28% of annual fertilizer N applied in Pearl River Delta (~310 kg N ha^{-1} $year^{-1}$; Ye and Wang 2007).

However, the amount of N and S emitted from N fertilizers or other sources was not well known. The $\delta^{15}N$ and $\delta^{34}S$ technique may provide more detailed information for their environmental fate (Zhang et al. 1995; Gao 2002; Xiao and Liu 2002), which should be considered in the future works.

Conclusions

1. The estimated annual wet deposition fluxes of inorganic N and S in Guangzhou were 40.47 kg N ha^{-1} and 65.29 kg N ha^{-1}. Their concentrations were related to seasonal variation in emissions and meteorology, and their deposition fluxes in the rainy season were greater than those in the dry season. Asian monsoon played a vital effect for their seasonal variation.
2. The levels of inorganic N and S deposition fluxes in Guangzhou, a southern city, were higher than those in Beijing and Zhengzhou (northern cities), but were comparable to Chongqing (southwestern city). The effect of wet deposition of N and S for ecosystem in South China might be much greater than that in North China. In addition, the molar ratios of NH_4/NO_3 in rainwater in presented major cities from north to south in China ranged from 1.20 to 4.08, suggesting N deposition in China was affected by both intensive agricultural and industrial activities.

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