Chemical composition and seasonal variation of acid deposition in Guangzhou, South China: Comparison with precipitation in other major Chinese cities

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A north-to-south decreasing trend in the neutralization capacity of precipitation in China.

A B S T R A C T

With the aim of understanding the origin of acid rains in South China, we analyzed rainwaters collected from Guangzhou, China, between March 2005 and February 2006. The pH of rainwater collected during the monitoring period varied from 4.22 to 5.87; acid rain represented about 94% of total precipitation during this period. The rainwater was characterized by high concentrations of SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+. SO_4^{2-} and NO_3^-, the main precursors of acid rain, were related to the combustion of coal and fertilizer use/ traffic emissions, respectively. Ca^{2+} and NH_4^+ act as neutralizers of acid, accounting for the decoupling between high SO_4^{2-} concentrations and relatively high pH in the Guangzhou precipitation. The acid rain in Guangzhou is most pronounced during spring and summer. A comparison with acid precipitation in other Chinese cities reveals a decreasing neutralization capacity from north to south, probably related to the role and origin of alkaline bases in precipitation.

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1. Introduction

Rapid economic growth in China over the past 30 years has been accompanied by an increase in air pollution that has evolved into one of the country's major environmental problems. A representative example of such pollution is that of the Pearl River Delta region in South China, where acid rain accounts for more than 90% of total annual precipitation (Xu et al., 2001a). Precipitation is a good proxy for atmospheric chemistry because it can scavenge and incorporate both the gases and aerosol particles present in the air. It is also well known that acid rain affects the soil, aquatic ecosystems, and forests (Menz and Seip, 2004); consequently, ongoing research into the chemical composition of precipitation is vital in terms of evaluating air quality and the mechanism of acidification in rainwater.

Previous monitoring studies carried out in the Pearl River Delta region have sought to characterize the chemical composition of acid precipitation (Chen et al., 1990; Seip et al., 1999; Tanner and Wong, 1999; Xu et al., 2001a). 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; however, most of these reports were reconnaissance studies, and similar such studies are rare in the international literature. In particular, the provenance of pollutants and mechanisms of pollutant transportation remain poorly constrained. It also remains puzzling why precipitation from different regions in China show contrasting acidity despite their similar chemistry. For example, rainwater throughout China mainly consists of Ca^{2+}, NH_4^+, SO_4^{2-}, and NO_3^-, yet the acidity of precipitation is weaker in north China (Beijing, Tang et al., 2005; Lanzhou, Zhang, 1996; Qinghai province, Zhang et al., 2003) than in the south (Chongqing, Zhang et al., 1996; Guiyang, Han and Liu, 2005; Guangzhou, this study). It is also apparent that Chinese acid rains are compositionally distinct from those in Europe and North America (Gilliland et al., 2002; Fowler et al., 2005; Zimmermann et al., 2006), probably reflecting different types of air pollution. There exists a clear and urgent need for a more detailed understanding of the dynamics of precipitation chemistry in various regions of China. The outcomes of such an investigation would be of value to planners and decision-makers in their attempts to curb the effects of acid rain.

To gain new insights into rainwater composition in China, we collected rainwater samples at two monitoring sites in Guangzhou during 47 rain events from March 2005 to February 2006. We then analyzed the pH of the samples and the concentrations of 13 major

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ions. The objectives of this contribution are to: (1) describe the chemistry of precipitation in Guangzhou; (2) explain the precipitation chemistry by examining emissions of acid rain precursors, as well as sea salt and neutralizing components; and (3) compare the chemistry of precipitation in Guangzhou with that recorded in other regions of China.

2. Methods

2.1. Location and sampling

Guangzhou City (113.3°E, 23.2°N), the primary city of South China, is located upon the Pearl River Delta about 60 km from the Pearl River Estuary. The city covers an area of 7434 km² and has a population of over 10 million. The region is subjected to a typical Asian monsoon climate: mild springs with frequent, light rainfall; hot and humid summers with strong southwesterly monsoon breezes from the sea; and relatively cool and dry autumns and winters influenced by northeastern monsoonal winds from northern China (Ding and Chan, 2005; Wang et al., 2005).

Rain samples were collected at two monitoring sites in Guangzhou (Fig. 1): on the rooftop of the Herbarium Building in the South China Botanical Garden, and on the rooftop of the Administration Building at the Guangzhou Institute of Geochemistry, Chinese Academy of Science. Both sites were located ~20 m above the ground surface and ~500 m from the nearest road. There were no buildings greater than 30 m in height around the two sample sites.

A polyethylene bucket (inner diameter, 40 cm) with a polyethylene lid was used to collect the rain samples. Before sampling, the bucket was cleaned with tap water and rinsed thoroughly several times with distilled water until the water conductivity was ~2 μS cm⁻¹. To prevent contamination by dry deposition, the collector was covered by the lid, which was removed prior to each rain event. Rainwater was collected in a 500 ml polyethylene bottle that had been filled with pure water for at least 24 h prior to use and then washed two or three times with rainwater sample. pH was measured in the field using a portable Thermo ORION pH meter, which was calibrated before each measurement using standard pH 4.00 and 6.86 buffer solutions. The amount of rainfall was measured using a tipping-bucket rain gauge.

Rain samples were collected during 47 rain events from March 2005 to February 2006. The average temperature in Guangzhou during the study period was 23.2 °C, and the total sampled precipitation was 1755.3 mm, accounting for 91.5% of the total rainfall (1918.5 mm). The rain events were concentrated at certain times of the year due to the influence of the Asian monsoon. Precipitation was concentrated from March to August 2005, with this period recording over 93.5% of the total rainfall during the monitoring period. Only one event was recorded during each of January and February of 2006, and two during each of September and December of 2005. The rainfall amount during these events was

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

insufficient to enable analysis of the samples. No rain events were recorded during October and November of 2005.

2.2. Sample analyses

Once collected, the samples were filtered through hydrophobic cellulose acetate membrane filter paper of 0.45 μm pore size (diameter, 13 mm), and were analyzed within 1 week. All membranes were cleaned before use with 10 ml of Milli-Q ultra pure water. The filtrate was divided into two aliquots: the first (1 ml) was diluted to 10 ml with 9 ml Milli-Q ultra pure water, and the second (15 ml) was used for analyses of anions and cations. Because the rainwater samples contained high concentrations of Ca^{2+} and SO_4^{2-}, they were diluted to enable measurements by ion chromatography (IC). All samples were stored in a refrigerator at 4 °C until analysis.

The concentrations of eight anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, CH_3COO^-, $HCOO^-$, and $C_2O_4^{2-}$) and five cations (NH_4^+, Na^+, K^+, Mg^{2+}, and Ca^{2+}) were measured by IC (the detection limits of anions and cations were lower than 0.05 and 0.1 μmol l^{-1}, respectively). NO_2^- and CH_3COO^- were only detected in five samples, $HCOO^-$ in seven samples, and $C_2O_4^{2-}$ in six samples; consequently, these anions are not considered in this paper. The relative standard deviation (RSD) for all ions was 0.5–2.5%. Concentrations of H^+ were obtained from pH values.

The volume-weighted mean (VWM) concentrations of major ions ($\overline{C}$) of the every precipitation event at the two sampling sites were calculated using the formula $\overline{C} = (\sum_{i=1}^n C_i Q_i)/(\sum_{i=1}^n Q_i)$, where Q_i is the rainfall amount (mm) and C_i is the measured concentration (μeq l^{-1}) of a given anion or cation. The monthly and yearly VWM concentrations of ions (Table 1) were calculated according to the data for a given month or for the entire monitoring period.

2.3. Calculation of sea-salt contributions

Given that Guangzhou is located close to the South China Sea, we estimated the marine contribution to various ion species in precipitation by calculating their respective sea-salt fractions (SSFs) according to Rahn (1975a,b), Kulshrestha et al. (1996), and Das et al. (2005). The SSF of a component of interest (X) is given by $SSF_x = (ref)_{rainwater} \times (X/ref)_{seawater}$; the non-sea-salt fraction of X is given by $NSSF_x = X_{rainwater} - (ref)_{rainwater} \times (X/ref)_{seawater}$, where $X_{rainwater}$ is the concentration of component X in the rainwater and ref is an appropriate reference element. To measure the degree of enrichment of certain elements in precipitation relative to their marine abundances, the enrichment factor (EF) was calculated as $EF_x = (X/ref)_{rainwater}/(X/ref)_{seawater}$. The premise behind the evaluation was the assumption that all ref were of marine origin. Marine contributions to various ions were calculated using sodium as a tracer for sea salt and the known ionic ratios in seawater (Millero, 1970), as in previous studies (Kulshrestha et al., 1996; Das et al., 2005). The results of this analysis are listed in Table 2.

2.4. Neutralization factor

Some base ions found in precipitation (e.g., Ca^{2+} and NH_4^+) act as buffers for the acidity of rainwater. To estimate the neutralization capacity of each alkaline compound, the neutralization factor (NF) was calculated using the equation (Kulshrestha et al., 1995) $NF_x = X/(SO_4^{2-} + NO_3^-)$, where X is the compound of interest.

Table 2
Monthly percentage of marine contribution to the composition of precipitation and yearly enrichment factors (EFs) of major ions with respect to seawater

Percent (%)	2005.3	2005.4	2005.5	2005.6	2005.7	2005.8	2006.1	2006.2	Yearly EFs
Cl^-	100	91.4	100	100	91.8	74.0	84.3	37.8	1.0
SO_4^{2-}	1.7	0.9	1.4	0.7	1.4	1.0	1.2	1.2	91.9
Mg^{2+}	68.9	39.6	46.2	47.8	26.6	50.9	33.0	48.6	2.2
K^+	7.3	4.8	3.7	3.4	2.4	6.7	5.2	1.6	23.2
Ca^{2+}	0.6	0.5	0.8	0.9	0.4	0.7	0.3	0.2	160.0
F^-	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	4526.1

NO_3^- and NH_4^+ are not calculated due to the lack of data in seawater.

3. Results

3.1. Acidity of precipitation

The monthly average pH values varied from 4.22 to 5.87, with a full-year average of 4.49 (Table 1). The frequency of acid rain (pH < 5.6; Charlson and Rodhe, 1982) as a proportion of total rainfall was 87.4%, indicating the severe acid rain status of Guangzhou. Specifically, about 50% of precipitation had a pH of less than 4.5, ∼30% of precipitation had a pH of 4.5–5.0, and ∼12% of precipitation had a pH greater than 6.0 (Fig. 2). Of note, pH values during the rainy season (April–August) were lower than those during the dry season (January–March). This pattern is the reverse of that observed in Beijing and Chongqing (Zhang et al., 1996; Tang et al., 2005).

3.2. Ionic composition of precipitation

In an analysis such as ours, the balance between anions with cations must be assessed to ensure the reliability of the analytical data and assess whether any ions have been overlooked. This is of particular concern because HCO_3^- cannot be analyzed by IC. Data are generally considered acceptable if the concentration ratio of the sum of measured anions to the sum of measured cations in rainwater samples is within the range of 1 ± 0.25 (Keene et al., 1986). The strong correlation observed in the present study between total anions concentration and total cations concentration ($R^2 = 0.98$) suggests that all the major components in the sampled precipitation were measured, thereby ensuring the quality of the data.

Table 1
Rainfall, pH and the volume-weighted mean concentrations of ions (μeq l^{-1}) of the precipitation in Guangzhou

Species	Month								Annual VWM[a]
	2005.3	2005.4	2005.5	2005.6	2005.7	2005.8	2006.1	2006.2	
F^-	13.3 (0.5)	11.8 (8.9)	10.1 (1.6)	10.3 (0.8)	18.4 (29.4)	11.5 (2.5)	28.4 (29.4)	4.6 (6.4)	12 (8.7)
Cl^-	34.1 (14.7)	24.2 (42.7)	24.7 (2.4)	9.6 (2.4)	20.5 (11.8)	22.3 (10.4)	71.1 (61.0)	23.8 (15.9)	21 (12.1)
NO_3^-	38.9 (9.2)	56.3 (60.0)	52.3 (13.0)	43.0 (14.9)	88.0 (85.9)	37.9 (13.1)	366.7 (73.5)	70.4 (1.6)	52 (40.5)
SO_4^{2-}	385.4 (17.2)	274.4 (30.2)	241.4 (22.7)	122.4 (31.6)	296.1 (39.7)	172.2 (43.7)	547.0 (111.5)	81.3 (15.9)	202 (57.9)
Ca^{2+}	376.8 (58.9)	163.6 (42.7)	152.8 (15.1)	67.1 (18.0)	184.8 (42.5)	93.8 (31.3)	713.8 (136.4)	183.8 (217.2)	131 (92.4)
K^+	15.2 (4.2)	8.6 (7.0)	15.9 (12.4)	9.0 (4.5)	14.5 (27.5)	4.7 (2.2)	21.6 (23.9)	10.8 (12.7)	9 (7.1)
Mg^{2+}	16.9 (2.5)	10.9 (13.6)	13.3 (0.3)	6.7 (1.4)	13.8 (12.8)	6.4 (1.3)	35.6 (26.5)	3.6 (2.6)	9 (10.0)
Na^+	51.3 (52.3)	19.1 (37.5)	27.1 (9.3)	14.1 (5.0)	12.2 (32.0)	14.2 (11.2)	51.7 (45.0)	7.8 (3.1)	18 (21.4)
NH_4^+	94.3 (9.0)	103.2 (50.4)	58.1 (6.3)	38.3 (10.8)	120.7 (64.7)	55.0 (8.6)	136.3 (13.1)	16.8 (7.3)	66 (20.2)
H^+	1.3 (5.3)	46.7 (12.7)	49.1 (14.5)	59.8 (9.6)	27.7 (13.5)	31.9 (9.9)	2.6 (7.3)	1.5 (6.2)	32 (10.3)
Sum (anion)	471.7	366.7	328.5	185.3	423.0	243.9	1013.2	180.1	286
Sum (cation)	555.8	352.1	316.3	195.0	373.7	206.0	961.6	224.3	265
Total ions	1027.5	718.8	644.8	380.3	796.7	449.9	1974.8	404.4	551
pH	5.87	4.33	4.31	4.22	4.56	4.50	5.58	5.81	4.49
Number of sample[b]	5	12	8	7	5	5	2	3	
Rainfall (mm)[c]	111.1	179.2	372.0	501.5	121.2	361.5	9.5	99.3	

The data in parentheses are one stand deviation.
[a] Volume-weighted mean concentrations: calculated according to the collected rainfall of every precipitation events during the monitoring period.
[b] Number of sample collected and analyzed.
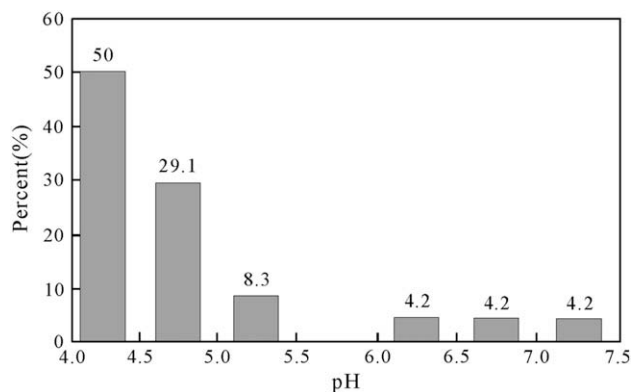[c] The rainfall amount sampled during the monitoring period.

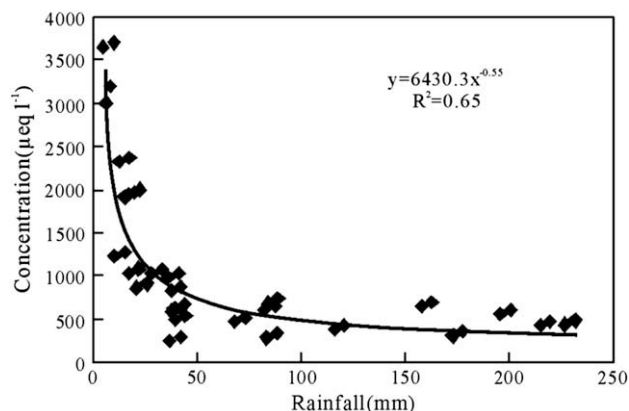**Fig. 2.** Frequency distribution of pH measured in the field.

Fig. 3. Relationship between rainfall amount and total ionic concentrations.

The VWM concentrations of the major ionic species for the entire monitoring year were in the following order (Table 1): SO_4^{2-} > Ca^{2+} > NH_4^+ > NO_3^- > H^+ > Cl^- > Na^+ > F^- > Mg^{2+} > K^+ (μeq l^{-1}). The annual total anions and cations in the sampled Guangzhou precipitation were 3212 and 3185 μeq l^{-1}, respectively. Specifically, sulfate occurred in the highest concentrations, with a full-year average of 202 μeq l^{-1}. Ca^{2+} and NH_4^+ were the predominant cations, with full-year average concentrations of 131 and 66 μeq l^{-1}, respectively. These levels are similar to those obtained in other major cities in China (Table 3), but are significantly higher than those reported for cities in Europe and North America. For example, the concentration of Ca^{2+} in Guangzhou rainwater is as high as 130.6 μeq l^{-1}, compared with just 5.4–71.4 μeq l^{-1} within precipitation in Europe and North America (Gilliland et al., 2002; Topçu et al., 2002; Fowler et al., 2005; Zimmermann et al., 2006).

3.3. Relationship between rainfall amount and precipitation chemistry

The observed ionic concentrations show a decreasing trend with increasing precipitation amount (Fig. 3). For example, little precipitation was recorded during January (9.5 mm), but this month recorded the highest concentration of ions (1974.8 μeq l^{-1}). In contrast, ionic concentrations were lowest (380.3 μeq l^{-1}) during June, which recorded the largest rainfall amount (501.5 mm). Overall, the concentrations of ions in Guangzhou precipitation decrease exponentially with increasing rainfall, as reported in previous studies (Liu et al., 2006; Shimamura et al., 2006), although one exception to this trend is February, which recorded relatively little rainfall (99.3 mm) and low ionic concentrations (404.4 μeq l^{-1}). This anomaly may reflect a reduction in anthropogenic activities during February because of the long national holidays (Spring Festival and the Festival of Lanterns) that occur during this month.

3.4. Temporal variations in ionic concentrations

The following three main features are apparent from monthly average ionic concentrations in precipitation at Guangzhou (see Table 1).

(1) During the rainy season (April–August), SO_4^{2-} is the dominant ion; however, Ca^{2+} becomes dominant during the dry season (January–March). In general, precipitation is acidic when the concentration of SO_4^{2-} is greater than that of Ca^{2+}, and vice versa.
(2) The concentration of H^+ in precipitation is relatively low during the dry season compared with the rainy season. Other ions tend to show the reverse trend, except for data for February.
(3) We observed remarkable seasonal variations in precipitation chemistry, with acid rain being more pronounced during spring and summer than during autumn and winter. It is interesting to note that this seasonal variation is the reverse of that observed at Chongqing (Southwest China) and Beijing (North China), where the pH in rainwater is lower during winter than during summer (Zhang et al., 1996; Tang et al., 2005).

4. Discussion

4.1. Dilution effect of rainwater on precipitation chemistry

The relationship observed between rainfall amount and precipitation chemistry indicates that rainwater has a dilution effect on precipitation chemistry. An important contribution to the ions in rainwater is floating particles in the air. The dilution effect is less pronounced during small rainfall events than during large events. This explains why ionic concentrations are significantly higher during small rainfall events compared with large events. The precipitation chemistry may also be partially dependent on the residence time of floating particles in air. During the dry season,

Table 3
Main ion concentrations (μeq l^{-1}), pH and the buffering capacity of precipitation in some major Chinese cities

Cities	Period	SO_4^{2-}	NO_3^-	Ca^{2+}	NH_4^+	$\frac{Ca^{2+}+NH_4^+}{SO_4^{2-}+NO_3^-}$	pH	Estimated pH[a]	Difference pH[b]	Reference
Beijing (116.4°E, 39.9°N)	2001–2003	248.9	84.1	191.2	234	1.28	6.01	3.37	2.64	Yang et al. (2004)
Zhengzhou (113.07°E, 34.48°N)	1999	139.6	46.3	113.8	188.9	1.63	6.41	3.52	2.89	Zhao et al. (2001)
Shanghai (121.48°E, 31.23°N)	1999	95.0	40.4	95.0	80.6	1.30	5.92	3.75	2.17	Xu et al. (2000)
Chongqing (106.30°E, 29.30°N)	2002	338.0	41.8	285.5	138.3	1.12	4.89	3.36	1.53	Zhou et al. (2003)
Kunming (102.7°E, 25.05°N)	2000	199.2	13.2	111.9	51.6	0.77	4.94	3.76	1.18	Zhu (2003)
Guangzhou (113.3°E, 23.2°N)	2005–2006	202.2	51.8	130.6	66.2	0.77	4.49	3.64	0.85	This study

[a] Estimated pH: use the ($H^+ + Ca^{2+} + NH_4^+$) as the H^+ to estimate the original acidity of precipitation.
[b] Difference pH: use measured pH to subtract the estimated pH.

floating particles persist in the air for a relatively long period, thereby accumulating to relatively high levels. Consequently, their incorporation during small rainfall events gives rise to high ionic concentrations in rainwater during the dry season. In contrast, frequent precipitation during the rainy season flushes particles from the air, thereby minimizing ion concentrations in rainwater.

4.2. Source of chemical components in precipitation

As the composition of rainwater is determined by the scavenging of both gases and particles in the air, the concentration of ions in precipitation could reflect the composition of the atmosphere through which it falls. As indicated in many previous studies (Kelly et al., 2002; Terada et al., 2002; Hu et al., 2003; Laudon et al., 2004; Rogora et al., 2004; Das et al., 2005), there are three main sources of the gas and particles found in precipitation: terrestrial, marine, and anthropogenic. The intensity of pollution is largely reflected in the relative contributions of terrestrial and anthropogenic sources.

It is possible that sea salts had a strong influence on precipitation chemistry in the present study, as Guangzhou is situated adjacent to the South China Sea. The SSF of Cl^- accounts for 37.8–100% of its monthly VWM amount (Table 2); equivalent values are 26.6–68.9% for Mg^{2+}, <10% for K^+, and just <2% for SO_4^{2-}, Ca^{2+}, and F^-. These results suggest that Cl^- in the rainwater is mainly derived from the sea. About half of the Mg^{2+} can be attributed to a marine source, meaning that an additional source is required to explain the remaining Mg^{2+} in the precipitation. The SSFs of the other four ions (K^+, SO_4^{2-}, Ca^{2+}, and F) are very low (<10%), suggesting an origin other than a marine source. These results also indicate that the effect of the contribution of sea salt to the acidity of precipitation in Guangzhou is very small, as the marine contribution to SO_4^{2-} and Ca^{2+} in rainwater is small (<2%).

The precipitation in Guangzhou is characterized by high concentrations of sulfate, NO_3^-, and alkaline bases. Specifically, SO_2 is almost entirely derived from anthropogenic sources. It has been considered elsewhere that the extensive use of coal and oil is a major cause of acid rain in China (Xu et al., 2001a; Larssen et al., 2006); indeed, the combustion of coal accounted for ~70% of the energy production in China in 2004 (SEPA, 2004). In particular, the strong correlations observed between the frequency of acid rain and (i) yearly coal consumption and emissions of (ii) NO_x and (iii) SO_2 in Guangzhou ($R^2 = 0.83$, 0.73, and 0.79, respectively; Chen, 1990; Xu et al., 2001b) strongly suggest that fuel combustion and traffic emissions play a central role in the development of acid rain in Guangzhou.

Ca^{2+} is mainly derived from alkaline dust, which has many potential sources, including windblown dust and anthropogenic sources such as industrial and construction activities. The main source of NH_3 supplied to the atmosphere is considered to be agriculture (Larssen et al., 2006), although in the present study NH_3 concentrations may be directly related to the burgeoning construction industry in the region. The Pearl River Delta is one of the most rapidly developing areas in the world, and Guangzhou City has been expanding since the 1980s. The land uses and industrial processes in the region have resulted in not only greater amounts of NH_3 but also more alkaline dust transported from the soil to the air. In other words, the high concentrations of Ca^{2+} observed in Guangzhou precipitation are largely derived from local sources, with only a minor contribution by desert dust transported over large distances.

4.3. Acid neutralization in Guangzhou precipitation

As demonstrated above, SO_2 and NO_X are the main precursors of acid rain in Guangzhou. If all of the SO_4^{2-} and NO_3^- in precipitation is

assumed to occur as free acids, the corresponding pH value of the precipitation in Guangzhou, as calculated by adding the VWM equivalent concentrations of NH_4^+ and Ca^{2+} to the measured H^+ concentration, would be 3.64 (Table 3), which is 0.85 less than the measured value. Therefore, the measured concentration of hydrogen ions within precipitation is not a measure of the original acidity, but most likely reflects the acidity after neutralization by atmospheric bases (Galloway et al., 1987; Larssen and Carmichael, 2000).

The relationship between acidity and the components in the sampled precipitation reveals a relatively strong correlation between H^+ and $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ ($R^2 = 0.45$), whereas a weak correlation is generally found between H^+ and other components (values of R^2 calculated with respect to Mg^{2+}, Na^+, F^-, and Cl^- are 0.22, 0.18, 0.21, and 0.21, respectively). This observation indicates that Ca^{2+} and NH_4^+ act as neutralizers to acids in the precipitation. This interpretation is further supported by the strong linear correlation between $(H^+ + NH_4^+ + Ca^{2+})$ and $(SO_4^{2-} + NO_3^-)$ ($R^2 = 0.94$). In addition, the neutralization factor is 0.51 for Ca^{2+}, 0.26 for NH_4^+, and very small values for other bases such as Mg^{2+} (0.035). Therefore, Ca^{2+} and NH_4^+ are the dominant neutralization substances; the degree of neutralization by other base cations can be regarded as negligible. The role of alkaline elements in acid neutralization has previously been emphasized by Larssen and Carmichael (2000).

The difference between the observed pH values in Guangzhou precipitation and their 'original' pH values prior to neutralization can be taken as another index of the buffering capacity of bases in rainwater. The estimated 'original' pH values are relatively constant regardless of the season, varying between 3 and 4. This may be due to the relatively constant nature of emissions of acidic precursors (SO_2) into the air at Guangzhou. This finding also implies that acid pollutants such as SO_2 and NO_x are mainly sourced locally, with only minor contributions from pollutants transported over long distances. The difference between original and observed pH values is larger during the dry season (2.15–2.55) than during the rainy season (0.44–1.09), reflecting the relatively high buffering capacity of base ions in rainwater during the dry season. This finding may reflect the relatively high concentration of base cations in precipitation during the dry season (Table 1).

4.4. Comparison with precipitation in other Chinese cities

To gain an insight into the state of air pollution in mainland China and regional variations in rain acidity, we compared the chemistry of precipitation among major cities in China (from north to south: Beijing, Zhengzhou, Shanghai, Chongqing, Kunming, and Guangzhou). Despite finding similar overall rainwater chemistry among the different cities (Table 3), we found the following temporal and spatial variations, for which possible triggers are discussed.

4.4.1. Seasonal variations
The rainwater in China shows remarkable seasonal variations in pH, but the nature of this variation is distinct in different cities. In Guangzhou, acid rain mainly occurs during the rainy season, with the pH increasing during the dry season (Table 1). This trend is the reverse of that observed in Chongqing (Southwest China) and Beijing (North China), where acid rain is more of a problem during winter than spring and summer (Zhang et al., 1996; Tang et al., 2005). These spatial differences may imply different generation mechanisms of acid rain in different parts of China.

In Southwest China, large cities such as Chongqing are commonly situated within valleys. The limited nature of air circulation in such regions is not favorable for the transport and diffusion of locally emitted SO_2. Consequently, pollutants tend to

accumulate in the lower atmosphere, entering rainwater when precipitation is formed. This interpretation is supported by the similar $\delta^{34}S$ values found between atmospheric SO_2 aerosol and SO_2 particles produced during coal combustion in Southwest China (Zhang et al., 1995). Therefore, the seasonal variations in precipitation chemistry in Southwest China may be directly related to the extent of local consumption of coal, which is greater in winter than in summer. The extensive use of coal leads to increased emissions of SO_2, resulting in turn in a reduction in the pH of rainwater. A similar interpretation is relevant to Beijing, where heating requirements in winter lead to a considerable increase in coal consumption. The contrast in precipitation chemistry among different seasons is further enhanced by dust storms, which are common in late spring and summer, transporting significant amounts of alkaline bases into the air. In summary, high coal consumption during winter leads to a decrease in the pH of rainwater, whereas the occurrence of dust storms during spring and summer leads to an increase in pH.

The explanation detailed above involving seasonal variations in coal consumption cannot explain the trend observed in Guangzhou, as the pH of rainwater in winter is higher than that in summer. In fact, coal consumption in Guangzhou remains essentially stable over the year due to the subtropical climate of the city. The Ca^{2+} contents (and also $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$) in Guangzhou rainwater during winter and autumn are significantly higher than those during spring and summer. It is likely that the high pH of precipitation during winter is due to the increased neutralizing capacity of base cations.

Assuming that Ca^{2+} in rainwater is mainly sourced from alkaline dust, we attribute the seasonal variation in precipitation chemistry observed in Guangzhou to seasonal variations in weather and dry deposition. The majority of rainfall in Guangzhou occurs during spring and summer, accounting for about 90% of annual precipitation. During the rainy seasons, soils are relatively wet, meaning that little surface dust is incorporated into the air. Semi-continuous washing by rainfall is also efficient in lowering the concentrations of alkaline particles in the atmosphere, leading to a decrease in the concentrations of base cations in rainwater and a consequent reduction in acid-neutralizing capacity. In contrast, the long residence time of floating particles in the air during the dry season can result in the accumulation of base ions, giving rise to high ionic concentrations in rainwater.

As discussed above, both the pH difference between calculated and measured values and the $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ ratio can be taken as measures of acid-neutralization capacity; consequently, the two indexes are expected to show a degree of correlation. With the exception of Beijing, the value of $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ shows a positive correlation with the pH difference ($R^2 = 0.89$; Table 3), thereby confirming the role of Ca^{2+} and NH_4^+ as acid neutralizers. Despite the relatively large difference between observed and estimated original pH values in Beijing precipitation, the value of $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ is as low as that observed at Shanghai, significantly lower than the expected values. The reason for this decoupling of the two indexes of acid neutralization for Beijing precipitation remains unknown. One potential factor is that Beijing rainwater contains high concentrations of Mg^{2+} (Tang et al., 2005), which may act as an additional neutralizer to acids.

4.4.2. North–south decreasing trend in neutralization capacity in precipitation over China

There exists a north–south decreasing trend in the neutralization capacity of base cations in rainwater within China. For example, the difference between the observed and estimated original pH values for precipitation in northern cities varies between 2 and 3, whereas it is as low as 0.85 in South China (Table 3). This decreasing trend from north to south shows a broad

correlation with a decreasing trend in $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ ($R^2 = 0.92$), reflecting a decline in the contribution of base ions to precipitation relative to acid-generating components such as SO_4^{2-} and NO_3^-. As discussed above, base ions in precipitation are most likely to be derived from alkaline dusts derived in turn from soils and deserts. Deserts in China are restricted to the northwest of the country, and transportation of desert sands is largely controlled by eastward air circulation. Hence, it is logical to infer that desert-derived dusts contribute to precipitation in South China to a lesser extent than that in North China.

It is also interesting to note that the lime content of soils in China decreases from north to south, with Ca concentrations of 4.15 ppm in soil within Shanxi province (112°E, 37°N), 2.43 ppm in soil within Henan province (113°E, 34°N), 0.13 ppm in Hubei province (114°E, 30°N), and 0.06 ppm in Guangdong province (113°E, 23°N) (CNEMC, 1990). In general, rainfall is greater in South China than in North China; consequently, the soil is relatively wet and surface dust is not readily incorporated into the air. These factors explain the observed north–south decrease in neutralization capacity within China.

5. Conclusions

(1) Rainwater in Guangzhou is characterized by high concentrations of SO_4^{2-}, NO_3^-, Ca^{2+}, and NH_4^+. The frequency of acid rain (pH < 5.6) as a proportion of total rainfall was 87.5% during the monitoring period, indicating the severe-pollution status of Guangzhou. These chemical features of Guangzhou precipitation are similar to those of rainfall in other major cities in China.

(2) SO_4^{2-} and NO_3^- are the main precursors of acid rain in Guangzhou, while Ca^{2+} and NH_4^+ act as neutralizers to acidification. SO_4^{2-} and NO_3^- are derived almost entirely from anthropogenic sources (combustion of coal and oil). Concentrations of Ca^{2+} and NH_4^+ in precipitation are affected by the burgeoning construction industry in the region and the application of fertilizer upon the Pearl River Delta. Marine sources make only a minor contribution to the acidity of rainwater in Guangzhou.

(3) Precipitation in Guangzhou displays remarkable monthly variations, with acid rain being more important during the rainy season than during the dry season. This variation is largely related to the high neutralizing capacity of base cations in rainwater during winter. The opposite seasonal trend is observed at Beijing and Chongqing, probably due to seasonal trends in the use of fossil energy.

(4) There exists a reduction in the neutralization capacity of base cations in rainwater from North China to South China, possibly related to a decline in the contribution of base ions to precipitation relative to acid-generating components such as SO_4^{2-} and NO_3^-.

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