

Three-decade changes in chemical composition of precipitation in Guangzhou city, southern China: has precipitation recovered from acidification following sulphur dioxide emission control?

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ABSTRACT

We examined if precipitation had recovered from acidification in Guangzhou, the third biggest city in China, and if sulphur deposition in precipitation had decreased, and to what extent if yes, following abatement strategies in sulphur dioxide (SO₂) emission and energy use implemented since 2001. SO₂ emissions were decreasing steadily since 2001, but a marked recovery of precipitation acidity occurred only since 2005; precipitation pH values decreased from 4.65 in 2001 to 4.34 in 2005 and then increased to 5.08 in 2010, while in the same period acid rain (pH < 5.6) frequency increased from 70% to 81% and then decreased to 48%. During this period, the change in pH value and sulphate concentration more reflected the patterns of SO₂ emission at provincial and national scales than at the local scale, suggesting that precipitation chemical composition was largely controlled by the emissions of pollutants from surrounding areas of the study city. Since 2001, sulphate deposition in precipitation decreased significantly (by 40%) but nitrogen deposition remained unaltered. More importantly, the current sulphur (43 kg S ha⁻¹ yr⁻¹ as sulphate) and nitrogen depositions (35 kg N ha⁻¹ yr⁻¹ as ammonium plus nitrate in 2010) were still among the highest in China. These results highlight the fact that ambient sulphur and nitrogen deposition still pose a threat to the health of both terrestrial and aquatic ecosystems. Precipitation may become more acidified in the future because the deposition of alkaline dusts containing calcium is also likely to decrease with stricter SO₂ emission control policy and reduced construction activities. Additionally, we recommend that a reduction of emissions of nitrogen and chlorine bearing pollutants is urgently required for complete control on acid deposition.

Keywords: chemical composition, precipitation, southern China, sulphur and nitrogen deposition, sulphur dioxide emission control

1. Introduction

Associated with the rapid development of the economy, acid rain (with pH < 5.6) in China has increasingly received concern since the 1980s, due to its adverse impacts on

vegetation and aquatic environments (Larssen et al., 1999; Hao et al., 2001; Zhao et al., 2009). Sulphur dioxide (SO₂) is a precursor of sulphuric acid and sulphate aerosol and a main contributor to acid rain. The anthropogenic SO₂ emission in China is of national and international concern; it has contributed to about 25% of the global inventory, more than 50% of Asia inventory and 90% of East Asia inventory since the 1990s (Streets et al., 2000; Ohara et al.,

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2007; Lu et al., 2010; Smith et al., 2011). Furthermore, the sulphur-containing air pollutants (e.g. sulphate) emitted in Asia can be transported long distances to the Northwestern Pacific region, North America and the rest of the northern hemisphere, as indicated from both model simulation (Lin et al., 2008; Osada et al., 2009; Aikawa et al., 2010) and from field experiments, for example, ACE-Asia (Huebert et al., 2003), TRACE-P (Jacob et al., 2003) and INTEX-B (Singh et al., 2009).

In order to reduce SO_2 emissions and their subsequent impacts on human health and natural ecosystems, the Chinese government has implemented several policies since 2001 (Liu et al., 2013; Wang et al., 2013). Although there is a growing body of reports showing the present-day situations on precipitation chemical composition in both urban and rural regions throughout China (Wai et al., 2005; Larssen et al., 2006; Aas et al., 2007; Zhang et al., 2007; Huang et al., 2010; Wang and Han, 2011; Li et al., 2012), to our knowledge, in China very few studies so far have addressed the long-term patterns of acid rain, N and S deposition, particularly after the policy of SO_2 emission abatement was put into effect. Some pressing questions remain unanswered. For example, has acid rain been reduced through the nationally implemented reduction of SO_2 emissions? Is the present reduction in SO_2 emission sufficient for recovery from acid rain and soil acidification? Will other pollutants, like N-bearing compounds, control rain acidity in the future?

To address those issues mentioned above, we selected Guangzhou city in southern China (China's third biggest

city) as a pilot study for characterising the current status of acidity, deposition of inorganic N (NH_4^+ plus NO_3^-) and S (SO_4^{2-}) in precipitation and their long-term changes since 1983. Specifically, we examined if precipitation in this study city had recovered from acidification and if S deposition in precipitation had decreased, and to what extent if yes, following abatement strategies in SO_2 emission and energy use implemented since 2001. To this end, we compared the current observations at four monitoring sites during the period of 2001–2010 with historical records since 1983. The results from this study will thus contribute to the understanding of how precipitation chemistry respond to the changes in the emissions of N and S pollutants to the atmosphere in southern China, which is required for both policy makers and scientific communities in order to reduce emissions, to evaluate effectiveness of the abatement strategy of SO_2 emissions on precipitation chemistry and air quality, and to assess its potential effects on terrestrial and aquatic ecosystems.

2. Methodology

2.1. Sites description

The study city, Guangzhou (112°57'–114°3'E, 22°26'–23°56'N), is the capital of Guangdong Province and is located in the Pearl River Delta (Fig. 1). The PRD region, encompassing nine major cities (Guangzhou, Foshan, Shenzhen, Zhongshan, Zhuhai, Jiangmen, Huizhou and Zhaoqing), experienced remarkable economic development

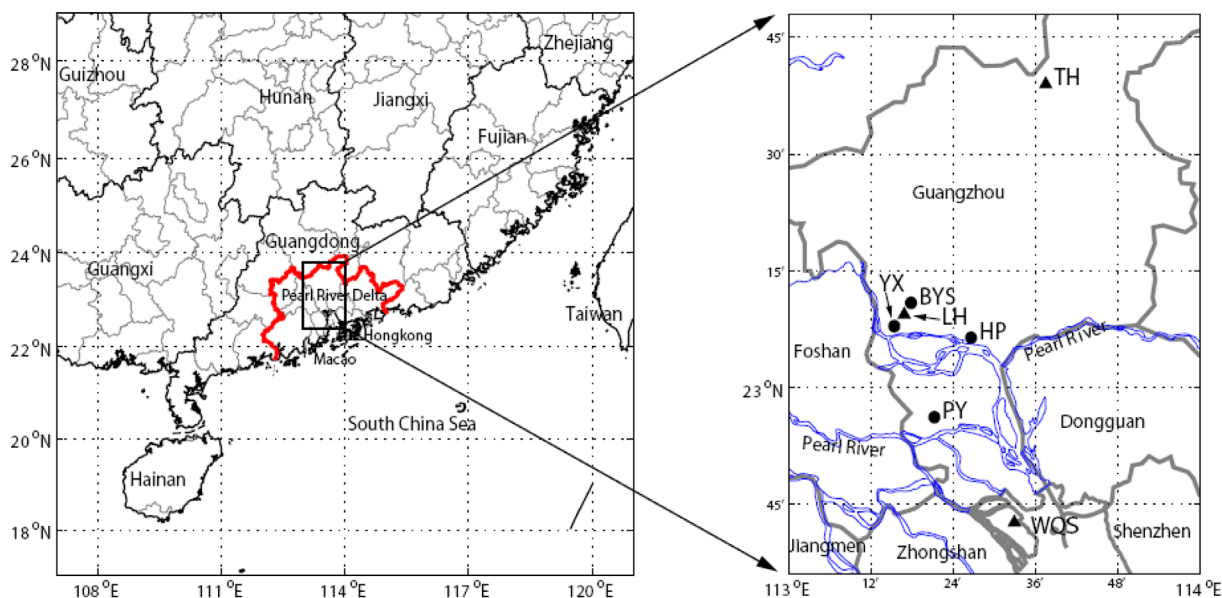


Fig. 1. Locations of four precipitation chemistry monitoring sites since 1994 (close circle symbols, YX, BYS, HP and PY) and three air quality monitoring sites since 1986 (triangle symbols) in Guangzhou, Southern China. The boundary for the Pear River Delta (left panel) and for the rivers (right panel) is coloured in red and blue, respectively.

and urbanisation during the past three decades, and is now one of China's main industrial centres as well as a megacity cluster. Guangzhou covers an area of 7434 km², with a population of more than 10 million as of 2010. The downtown area of Guangzhou city is about 60 km north of the Pearl River Estuary (Fig. 1). The anthropogenic emissions of SO₂ and NO_x in the PRD region for the year 2006 were estimated to be 711 and 892 kilotons, respectively, of which 21% and 26% were emitted from Guangzhou (Zheng et al., 2009). Power plant, transportation and industry were the three largest contributors, together making up about 90% of the total emissions (Wang et al., 2005; Zheng et al., 2009). The concentrations for some air pollutants have apparently changed during rapid urbanisation since 1980 (Wang et al., 2009a, b).

2.2. Precipitation collection and chemical analysis since 2001

Four sites were established to monitor chemical composition of precipitation in this city since 1992 (Fig. 1), i.e., Guangzhou Environmental Monitoring Centre in Yuexiu District (YX in short hereafter), Baiyun Mountain in Baiyun District (BYS), Huangpu Environmental Monitoring Station in Huangpu District (HP) and Panyu Environmental Monitoring Station in Panyu District (PY). Site YX is surrounded by commercial complexes and city main roads with heavy traffic. This site thus represents typical urban conditions. Site YYS is located at a building (Guanyunge) on the top of Baiyun Mountain with an altitude of 300 m above sea level. This site is about 7 km north of the Guangzhou urban centre and represents a suburban forest site. Site HP is located on the rooftop of the building of Huangpu Environmental Monitoring Station, in close proximity to an industrial centre in the east of Guangzhou with many large power plants and petrochemical factories situated. Site PY is located on the rooftop of the building of Panyu Environmental Monitoring Station. Panyu District is a satellite city of Guangzhou with a relatively smaller population and less industrial activities. This site lies about 27 km south of the Guangzhou urban centre and about 34 km northwest of the Pearl River Estuary, representing a suburban site (Fig. 1). Sites YX, HP and PY are state-controlled sites of the acid rain monitoring network in China, and site YYS is a city-controlled site.

From 2001 to 2010, rain samples were automatically collected on the basis of rain events using automatic precipitation samplers. In total, 2499 samples were collected from the four monitoring sites. Acidity (pH) was measured immediately after collection, and the precipitation samples were then sent to the laboratory in Guangzhou

Environmental Monitoring Centre for later analysis of ions by ion chromatography. Of these precipitation samples, 2481 samples had been determined for concentrations of major cations and ions. We checked the quality of analytical data by a cation–anion balance (R_1) and by comparison of measured conductivity with the conductivity calculated from the concentration of all measured ions (R_2), similar to quality assurance/quality control program for wet deposition monitoring in East Asia adopted by Acid Deposition Monitoring Network in East Asia (EANET, <http://www.eanet.cc/product/qaqc/qaqcwet.pdf>). R_1 and R_2 were calculated using the following equations.

$$R_1 = 100 \times (C - A)/(C + A)(\%) \quad (1)$$

where C and A are total cation (C) equivalent concentration (sum cations, $\mu\text{eq L}^{-1}$) and total anion (A) equivalent concentration (sum anion, $\mu\text{eq L}^{-1}$), respectively.

$$R_2 = 100 \times (\Lambda_{\text{calc}} - \Lambda_{\text{meas}})/(\Lambda_{\text{calc}} + \Lambda_{\text{meas}})(\%) \quad (2)$$

where Λ_{calc} and Λ_{meas} are calculated EC (Λ_{calc} , mS m^{-1}) and measured EC (Λ_{meas} , mS m^{-1}), respectively.

In the present study, almost all samples (99.9%) had C+A of greater than 100 $\mu\text{eq L}^{-1}$. Usually, data with $\pm 8\%$ of R_1 were accepted when $C+A > 100 \mu\text{eq L}^{-1}$ in data quality control, for example, at EANET. However, the adoption of such criteria would exclude 60% of the data (not shown). The adoption of the required criteria for R_2 of $\pm 9\%$ and $\pm 13\%$ when Λ_{meas} is $> 3 \text{ mS m}^{-1}$ and between 0.5 and 3 mS m^{-1} , respectively, would exclude about one third of the data (not shown), suggesting that these criteria are not suitable for our study city with strong air pollution. Instead, to be consistent with the data quality control conducted for the period before 2001, we removed three samples from further statistical analysis for our dataset (2001–2010), since the concentrations for those three samples were extremely high (sum ion concentrations $> 20\,000 \mu\text{eq L}^{-1}$) and R_1 were obviously deviated from the 1:1 lines (not shown). This was supported by the fact that the regression linear lines (sum anions = $1.004 \times$ sum cations, $R^2 = 0.89$, $P < 0.0001$ for sum ion; measured EC = $1.108 \times$ calculated EC, $R^2 = 0.89$, $P < 0.0001$) were quite close to the 1:1 lines (not shown).

2.3. Previous data sources for 1983–2000

In the study city, monitoring of acid rain started at the end of 1982 (Huang et al., 1999) with 13 monitoring sites. In 1984, this was adjusted to nine sites. Since 1992, four representative monitoring sites described above have been remained active (Huang et al., 1999). From 1983 to 1985, only the pH value was measured for precipitation. Starting from 1986, pH, major cations (NH_4^+ , Ca^{2+} , Mg^{2+} ,

Na^+ and K^+) and anions (SO_4^{2-} , NO_3^- , F^- and Cl^-) were determined for all precipitation samples. In this study, data for precipitation chemistry before 2001 were derived from published papers (1986–1990 from Quan et al., 1992; 1991–2000 from Ye et al., 2008).

In previous publications, only volume–weight mean (VWM) concentrations and pH values over all sites were presented. Thus, for the period 1986–2000, annual deposition was calculated by reported VWM concentrations (Quan et al., 1992; Ye et al., 2008) multiplying mean annual precipitation in Guangzhou. To constrain the uncertainty on calculating the annual N and S deposition in this period, we calculated the N and S deposition for the period 2001–2010 by two methods. One method was the same as used for the period 1986–2000, the other method was to calculate annual flux for each site and to average them (see below). We found that the two calculations yielded very similar results. For example, when averaged for all four sites, the results by the former method were lower by 1%–5% than those by the latter method for S and N deposition. This suggests that the method seems to be a reasonable approach for the period before 2001.

2.4. Statistical analysis

Correlation analysis with the two-tail significance test was used to examine the relationships between variables. The trend analysis was performed by using a least-squares linear and quadratic regression approach to the non-normalised raw data (for pH, acid rain frequency, and both mean annual weighted concentrations and depositions). All analyses were conducted using PASW Statistics 18.0 for Windows. Statistically significant differences were set at P values < 0.05 unless otherwise stated.

3. Results and discussion

3.1. Temporal changes since 2001

Although several policies have been implemented to reduce SO_2 emissions since 2001, the national SO_2 emissions during the first five years (10th Five-Year Plan) actually increased by 28%, from 19.9 Tg in 2001 to 25.5 Tg in 2005 (Fig. 2a), due in part to a lag of installing flue gas desulphurisation (FGD) and phasing out small inefficient units in the power sector. In 2006, China's Ministry of Environmental Protection (MEP) reaffirmed its commitment and resolved to cut the national SO_2 emissions in its 11th Five-Year Plan (2006–2010) by 10% (i.e., to 22.9 Tg in 2010), relative to the 2005 level. As a result, in 2010 the SO_2 emissions (21.8 Tg) decreased by 14% against the 2005 level (Fig. 2a). SO_2 emissions in Guangdong province exhibited a pattern similar to that in the nation;

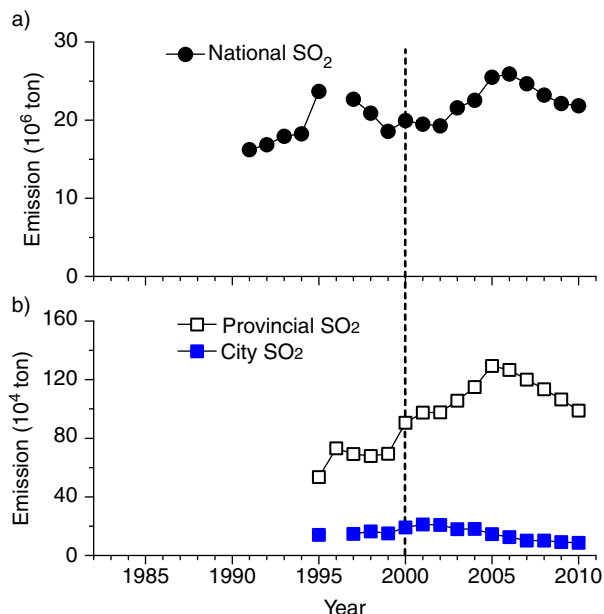


Fig. 2. Annual emissions of SO_2 in (a) China and (b) Guangdong Province and Guangzhou city. Data are from Report on the State of the Environment in China (<http://jcs.mep.gov.cn/hjzl/zkgb/>) for SO_2 emissions in China, from Guangzhou Statistical Yearbook (<http://data.gzstats.gov.cn/gzStat1/chaxun/njsj.jsp>) for SO_2 and from Guangdong Environmental Quality Report (http://www.gdepb.gov.cn/hjzlyxx/hbzkgb/200906/t20090615_62862.html) for SO_2 emissions in Guangdong province. The dash line indicates when the policy of SO_2 emission abatement started. In Guangzhou, SO_2 emissions were reduced since 2001.

SO_2 emissions increased by 33% in 2005 relative to that in 2001 and were reduced to the 2001 level in 2010 (Fig. 2b). In Guangzhou city, however, SO_2 emission decreased more substantially, with a rate of 7% per year since 2001; annual emissions in 2010 were reduced by 60% compared to the maximum recorded in 2001 and by 40% compared to the level in 2005 (Fig. 2b).

Annual mean pH values in the study city, however, showed a decrease from 4.65 in 2001 to 4.34 in 2005, and thereafter a marked increase to 5.08 in 2010 (Fig. 3a). Monthly mean pH values also displayed the same trend over this time period (Fig. 4a). Correspondingly, acid rain frequency showed an opposite trend, i.e., increased to 83% in 2005 from 68% in 2001 and decreased to 48% in 2010 (Fig. 3b). Acid rain frequency was reversely correlated with annual mean precipitation pH, as evidenced by high and negative correlation between these two variables ($R^2 = 0.82$, $P < 0.001$, $n = 10$). These results clearly indicate that a recovery from acid deposition occurred only since 2005 (Fig. 3).

Why did not precipitation pH increase constantly following constant reduction in SO_2 emission in the study city?

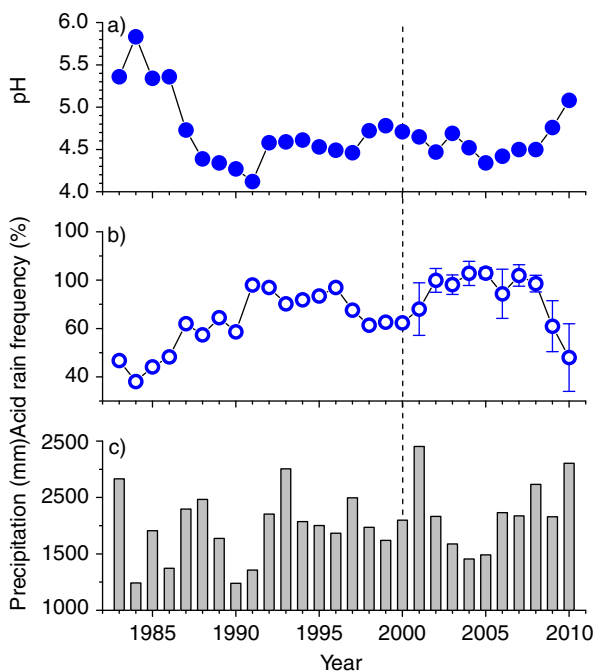


Fig. 3. Annual precipitation (a) pH value, (b) acid rain frequency and (c) precipitation in Guangzhou city since 1983. Mean of four monitoring sites and standard error of mean are presented for the period of 2001–2010. The dash line indicates when the policy of SO_2 emission abatement started. In Guangzhou, SO_2 emissions were reduced since 2001.

Was the change in precipitation pH over time caused by the change in precipitation amount (Fig. 3b)? In general, precipitation has a strong dilution effect on ion concentrations, as demonstrated by Huang et al. (2009) for the study city. In the present study, we also see such a dilution effect when analysed across all samples (not shown). However, this dilution effect exists for both acidifying ions and neutralising ions in precipitation. Therefore, if annual precipitation is high, we may not expect an increase in precipitation pH due to the dilution effect, because pH reflects the balance of total anions and total cations. This can be supported by our results. First, we find no correlation between precipitation pH and precipitation amount across all samples over the study period (not shown). Second, within a year, precipitation pH was low in rainy season (April–September) while high in dry season (October–March, Fig. 4), suggesting that low pH in rainy seasons was caused by more acidifying pollutants than neutralising pollutants in precipitation. Thus, the dilution effect cannot explain the precipitation pH change over time.

We examine if precipitation acidity reflected the change patterns of air pollutants over the period since 2001, because precipitation can scavenge air pollutants. The concentrations of all pollutant species exhibited a similar temporal pattern, increased and then decreased, with the exception of NO_x concentration, which significantly decreased with time (Fig. 5 and Table 1). However, the concentrations of

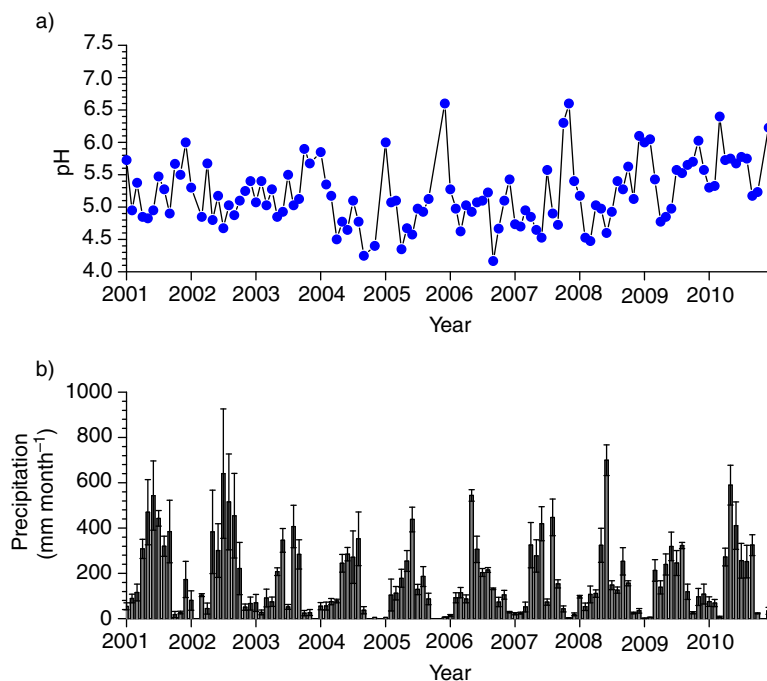


Fig. 4. Monthly mean (a) pH values and (b) precipitation amount in Guangzhou city since 2001.

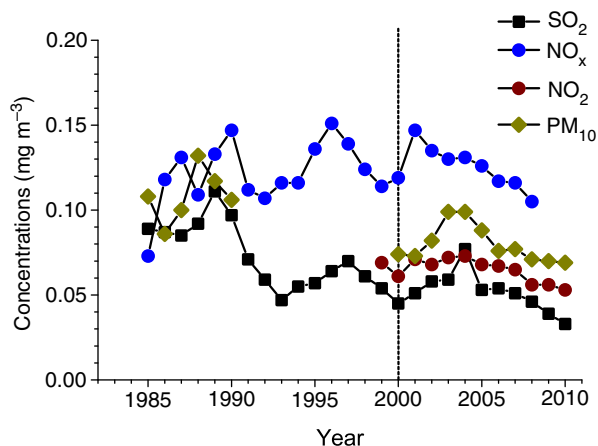


Fig. 5. Long-term trends of annual mean concentrations of major air pollutants in Guangzhou city (three sites in Fig. 1) since 1986. The dash line indicates when the policy of SO₂ emission abatement started. In Guangzhou, SO₂ emissions were reduced since 2001. Data were supplied by Guangdong Environmental Monitoring Center.

these species started to decline more early than SO₂ emissions in Guangdong. Also, we find no relationship between annual mean precipitation pH and annual mean air concentrations of any pollutants in Guangzhou. This result suggests that precipitation acidity in the study city was not controlled by local emissions of air pollutants. Therefore, we speculate that precipitation acidity was more controlled by the emissions of pollutants from surrounding areas of the study city than by local emissions.

To confirm the above speculation, we link the changed precipitation pH over time in our study city to the changes in SO₂ emissions both in the study city and in Guangdong Province. The results support our speculation. We find that the changes in precipitation acidity and acid rain frequency in Guangzhou since 2001 appear to better mimic the pattern of SO₂ emissions in Guangdong Province rather

than the pattern in Guangzhou (Fig. 2). During the period 2001–2010, annual mean pH values were negatively correlated with SO₂ emission rates in Guangdong Province ($R^2=0.44$, $P=0.04$, $n=10$), but not with the emission rates in the study city ($R^2=0.10$, $P=0.38$, $n=10$). This result supports our speculation that precipitation chemistry seems be largely controlled not by local SO₂ emissions in the study city, but by the SO₂ emission patterns on a larger, provincial scale (e.g. the SO₂ emissions imported from neighbouring big cities in the south to Guangzhou, such as Shenzhen, Dongguan, Zhongshan and Jiangmen, Fig. 1). This is consistent with back trajectory analysis of NOAA HYSPLIT model, which showed that 62% and 69% of precipitation in 2008 and 2009 were of marine origin, respectively, most of which were transported from the south to Guangzhou city and passed over those former mentioned cities (Fang et al., 2011b).

To further confirm our speculation, we link precipitation acidity to each ion species to examine if the change in precipitation SO₄²⁻ concentration associated with SO₂ emissions was the main controlling ion. Correlation analysis showed that among all ion species, annual mean precipitation pH values were significantly related to SO₄²⁻ concentration only ($R^2=0.43$, $P=0.038$, $n=10$, Figs. 3 and 6), suggesting that SO₄²⁻ was the strongest controller in precipitation acidity in the study city. As observed in many cities in China (Yang et al., 2004; EANET, 2010), our results showed that SO₄²⁻ was predominant in anions and explained 53%–64% of total anion equivalents (Fig. 6b). Similar to the acidity in precipitation, we find that SO₄²⁻ concentration in precipitation did not decrease immediately following the reduction of SO₂ emission since 2001 in the study city (Fig. 6b). Rather, we found that SO₄²⁻ concentration increased since 2001 until 2005 and then decreased when examining both annual mean concentrations (Fig. 6b and Table 2) and monthly mean concentrations over time (Fig. 7d, $R^2=0.10$, $P<0.001$, $n=113$),

Table 1. Temporal patterns of annual SO₂ emissions and annual mean concentrations of major air pollutants

	Trends	R^2	P	Trends	R^2	P
	Since 1986			Since 2001		
SO ₂ emissions in China ^a	increase	0.45	<0.001	Quadratic	0.76	<0.001
SO ₂ emissions in GD ^b	quadratic	0.83	<0.001	Quadratic	0.79	<0.001
SO ₂ emissions in GZ ^b	quadratic	0.76	<0.001	Decrease	0.95	<0.001
SO ₂ concentration in GZ ^c	decrease	0.54	<0.001	Quadratic	0.66	0.009
NO _x concentration in GZ ^c	ns ^d	0.04	0.26	Decrease	0.93	<0.001
NO ₂ concentration in GZ ^c	quadratic	0.75	<0.001	Quadratic	0.88	<0.001
PM ₁₀ concentration in GZ ^c	decrease	0.49	<0.001	Quadratic	0.42	0.06

^aSince 1991.

^bSince 1995.

^cSince 1986.

^dns, not significant; Bold values indicate significant temporal trends over time.

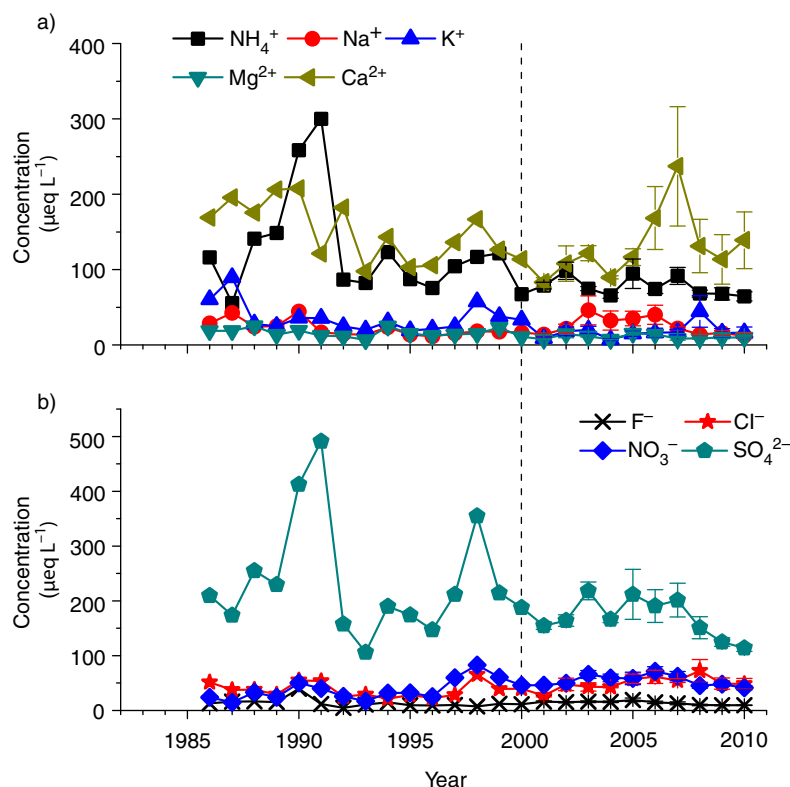


Fig. 6. Long-term trends of annual mean concentrations of major (a) cations and (b) anions in precipitation in Guangzhou city since 1986. Mean of four monitoring sites and standard error of mean are presented for the period of 2001–2010. The dash line indicates when the policy of SO_2 emission abatement started. In Guangzhou, the rate of SO_2 emissions has reduced since 2001.

consistent with the changes in the SO_2 emissions at the provincial (Guangdong) and national scales (Fig. 2). Further analysis indicated that the correlation of annual mean SO_4^{2-} concentration and SO_2 emissions in Guangdong

across the period of 2001–2010 was marginally significant ($R^2=0.36$, $P=0.07$, $n=10$), while the correlation of annual mean SO_4^{2-} concentration and SO_2 emissions in Guangzhou was not ($R^2=0.43$, $P=0.04$, $n=10$).

Table 2. Temporal patterns of precipitation chemistry since 2001^a

	Trends	R^2	P		Trends	R^2	P
pH	quadratic	0.68	0.007				
ARF (%) ^b	quadratic	0.82	0.001				
	Annual concentration ($\mu\text{eq L}^{-1}$)				Annual deposition ($\text{kg ha}^{-1} \text{yr}^{-1}$)		
NH_4^+	ns ^c	0.12	0.177	$\text{NH}_4^+\text{-N}$	ns	0.10	0.196
Na^+	quadratic	0.50	0.040	Na	ns	0.19	0.183
K^+	ns	0.03	0.294	K	ns	0.06	0.238
Mg^{2+}	ns	0.10	0.699	Mg	ns	0.11	0.790
Ca^{2+}	ns	0.16	0.221	Ca	ns	0.06	0.243
F^-	quadratic	0.71	0.006	F	ns	0.11	0.188
Cl^-	increase	0.26	0.076	Cl	ns	0.12	0.171
NO_3^-	quadratic	0.60	0.016	$\text{NO}_3^-\text{-N}$	ns	0.16	0.137
SO_4^{2-}	quadratic	0.67	0.008	$\text{SO}_4^{2-}\text{-S}$	decrease	0.40	0.003
				DIN	ns	0.13	0.161

^aFor pH and acid rain frequency since 1983, $n=28$, and for concentration and deposition of ions since 1986, $n=25$.

^bAcid rain frequency.

^cns, not significant; Bold values indicate significant temporal trends over time.

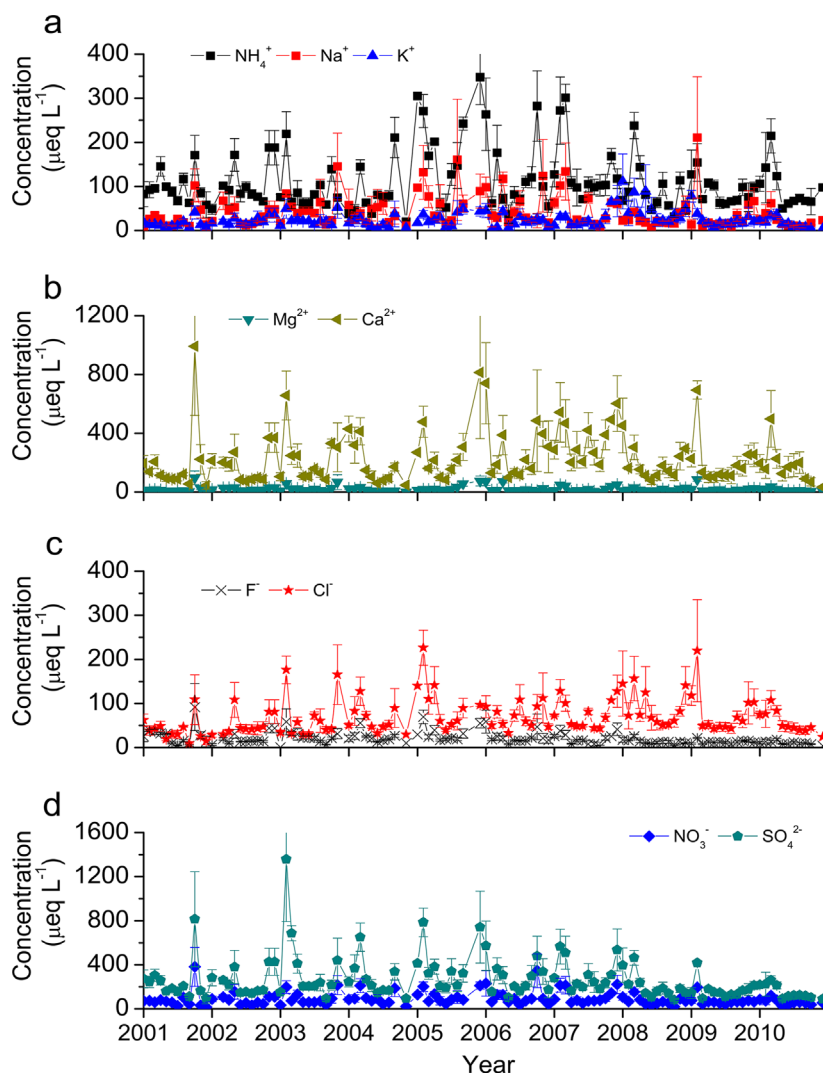


Fig. 7. Monthly mean concentrations of (a) NH_4^+ , Na^+ , K^+ , (b) Mg^{2+} , Ca^{2+} , (c) F^- , Cl^- , and (d) NO_3^- , SO_4^{2-} in precipitation in Guangzhou city since 2001.

During the period 2001–2010, unlike SO_4^{2-} concentration (Figs. 6b and 7d), annual SO_4^{2-} deposition (shown as SO_4^{2-} –S deposition), as we expected, decreased with time during this period, albeit with a large inter-annual variability ranging from 37 to 73 $\text{kg S ha}^{-1} \text{ yr}^{-1}$ (Fig. 8b and Table 2). S deposition in precipitation did not reflect the patterns of SO_2 emission rates in Guangdong and in China, but more reflected the pattern of SO_2 emission in Guangzhou city (Fig. 2). The relationship of SO_4^{2-} –S deposition and SO_2 emission in Guangzhou city was marginally significant ($R^2=0.33$, $P=0.08$, $n=10$), indicating that decreased SO_4^{2-} –S deposition should be partially attributed to the reduced SO_2 emissions in the study city (Fig. 2b).

Collectively, our results showed that in the study city, SO_2 emissions have been decreasing steadily since 2001, but

a marked recovery of precipitation acidity occurred only since 2005. The change in precipitation acidity over the period 2001–2010 was mainly controlled by total SO_2 emissions from the surrounding areas of the study city, not by local emissions within the study city or by the changes in annual precipitation amounts. The reduction in local SO_2 emissions might have, to a certain degree, facilitated to reduce the S deposition in precipitation.

The temporal patterns of annual deposition rates during the period 2001–2010 were not clear for all ion species other than SO_4^{2-} (Fig. 8 and Table 2), although annual mean concentrations of Na^+ , NO_3^- and F^- (Fig. 6 and Table 2) and monthly concentrations of all other ions increased then decreased over the same time period, with the exception of Mg^{2+} concentration ($R^2=0.03$ – 0.14 ,

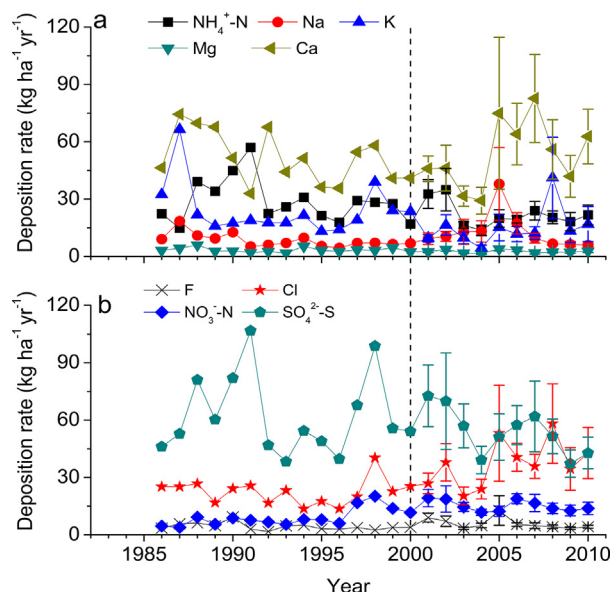


Fig. 8. Long-term trends of annual deposition rates of major (a) cations and (b) anions in precipitation in Guangzhou city since 1986. Mean of four monitoring sites and standard error of mean are presented for the period of 2001–2010. The dash line indicates when the policy of SO_2 emission abatement started. In Guangzhou, the rate of SO_2 emissions has reduced since 2001.

$P < 0.001$ to $= 0.05$ except Mg^{2+} for which $R^2 = 0.008$, $P = 0.24$, $n = 113$, Fig. 7).

3.2. Long-term changes since 1983

To assess the effectiveness of reducing SO_2 emissions on precipitation chemistry, we combined the results from last five years and compared the observations with historic records (Fig. 9). Moreover, we performed regression analysis to see the long-term trends over time since 1986 (for pH and acid rain frequency since 1983, Table 3). In general, we found that the five-year means in 2005–2010 were not significantly different from the previous periods, except Cl^- and NO_3^- -N deposition, which were significantly higher than those in 1986–1990 and 1991–1995 (Fig. 9d).

Across the whole study period since 1986, annual mean precipitation pH values showed a decrease then an increase while acid rain frequency showed the reverse trends (Fig. 3 and Table 3). The annual mean concentrations of NH_4^+ , K^+ , Mg^{2+} and SO_4^{2-} decreased while those of Cl^- and NO_3^- increased (Fig. 6 and Table 3). The long-term trends were not significant for deposition rates except NO_3^- -N and F^- , which showed an increase and later a decrease (Fig. 8 and Table 3). Annual mean SO_4^{2-} concentration was significantly correlated with annual

mean pH, with annual mean concentrations of NH_4^+ and F^- (Figs. 3 and 6).

3.3. Current status in comparisons with other regions

Precipitation pH values in Guangzhou city (in 2010) are slightly higher than that in many other cities in southern China such as Xiamen, Shanghai, Chongqing and Zhuhai but are obviously lower than the cities in northern China such as Beijing, Xi'an and Zhengzhou (Table 4). Compared with cities in neighbouring countries, the pH values are slightly higher than the averages for Southern Korean (4.70, Lee et al., 2000) and Japan (4.52, Okuda et al., 2005), but are much lower than that of Northern India (6.80, Mouli et al., 2005).

Current annual SO_4^{2-} -S deposition in precipitation observed here is among the highest in Chinese cities ($43 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in 2010, Table 4). S deposition in Guangzhou is approximately three times that in Xiamen (Table 4). A range of $14\text{--}30 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in precipitation was reported for four forest sites of IMPACT (Tieshanping in Chongqing, Caijiatang in Hunan, Leigongshan in Guizhou, Liuxihe in Guangdong) in southern China (Larssen et al., 2011).

The DIN deposition rate in our study city ($35.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in 2010, Table 4) is also higher than those in many other cities; for example, DIN deposition is $7\text{--}30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in Beijing, Xi'an, Zhengzhou, Shanghai, Xiamen and Zhuhai (Table 4), and higher than those in agriculture areas, for example, in Jiangsu province (27 and $24 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Yang et al., 2010) and Taihu Lake ($28 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Xie et al., 2008), higher than those in rural areas in Guangdong Province ($< 18 \text{ kg N}$, Chen and Mulder, 2007; Fang et al., 2011c). However, similar rates or even higher rates of DIN deposition than in Guangzhou have also been reported in many other cities or in agriculture areas in China. DIN deposition of higher than $30 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ has been found at four (two in Beijing, one in Huiming of Shandong province and one in Fenghua of Zhejiang, $30\text{--}39 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) of 15 sites across China (Zhang et al., 2008), at Dinghushan in Guangdong ($32 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Fang et al., 2008), and at a site in an urban area of Zhangzhou city in Fujian province ($37 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Xiao et al., 2005).

The DIN deposition rates have been monitored to be $2\text{--}3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in some remote areas in China (Liu et al., 1993) and $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in Hawaiian islands (Carrillo et al., 2002). Across the four sites in Guangzhou city, DIN deposition of approximately $37 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ was 10–30 times the background levels mentioned above. The DIN deposition in the study city is three times the mean DIN

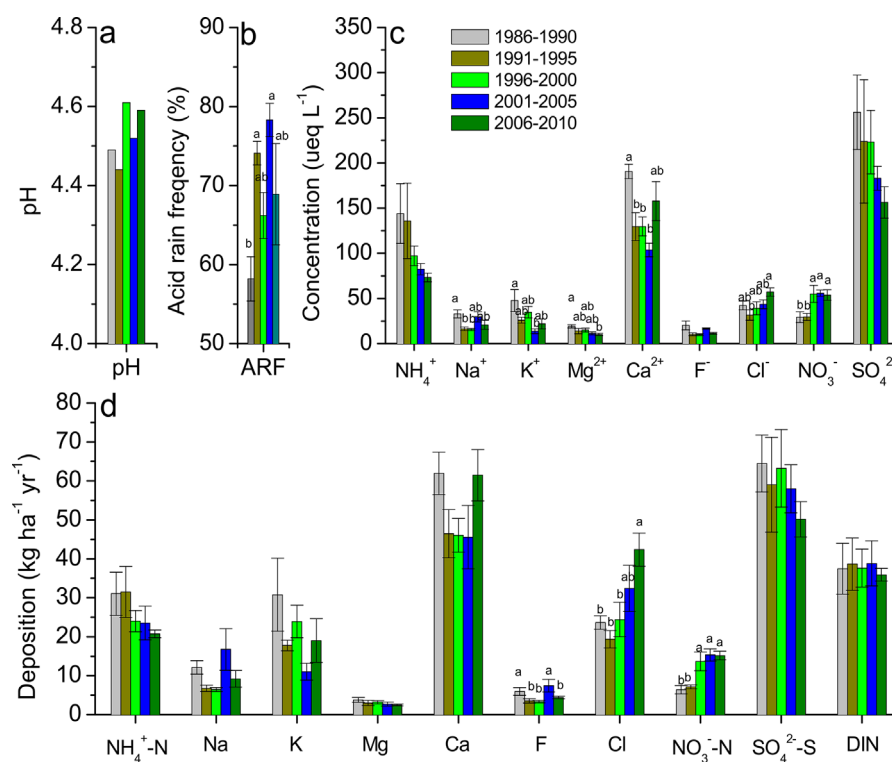


Fig. 9. Five-year means of (a) pH, (b) acid rain frequency, (c) concentrations and (d) annual deposition rates of major cations and anions in precipitation in Guangzhou city since 1986. $n = 5$. Different letters indicate significant differences between periods obtained by one-way ANOVA.

deposition throughout China (Lu and Tian, 2007), about twice the average rate ($17 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) across 31 forest sites in the past two decades compiled by Fang et al. (2011a) and 62% higher than the average rate of DIN ($20 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) across 15 monitoring sites throughout

China (Zhang et al., 2008). One important implication is that such high DIN deposition in Guangzhou city ($18\text{--}65 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, Fig. 8b) can be an important N source bio-available to terrestrial and aquatic ecosystems therein and that elevated N deposition is mainly caused by

Table 3. Long-term patterns of precipitation chemistry since 1983^a

Trends				Trends			
		R^2	P		R^2	P	
pH	quadratic	0.45	<0.001				
ARF (%) ^b	quadratic	0.55	<0.001				
Annual concentration ($\mu\text{eq L}^{-1}$)				Annual deposition ($\text{kg ha}^{-1} \text{ yr}^{-1}$)			
NH_4^+	decrease	0.29	0.015	$\text{NH}_4^+\text{-N}$	decrease	0.15	0.034
Na^+	ns ^c	0.02	0.533	Na	ns	0.03	0.569
K^+	decrease	0.24	0.007	K	ns	0.09	0.079
Mg^{2+}	decrease	0.25	0.006	Mg	ns	0.08	0.085
Ca^{2+}	ns	0.07	0.107	Ca	ns	0.04	0.919
F^-	ns	0.01	0.340	F	ns	0.03	0.660
Cl^-	increase	0.27	0.012	Cl	quadratic	0.48	<0.001
NO_3^-	increase	0.35	0.001	$\text{NO}_3^-\text{-N}$	quadratic	0.53	<0.001
SO_4^{2-}	decrease	0.11	0.053	$\text{SO}_4^{2-}\text{-S}$	ns	0.04	0.180
				DIN	ns	0.04	0.739

^aFor pH and acid rain frequency since 1983, $n = 28$, and for concentration and deposition of ions since 1986, $n = 25$.

^bAcid rain frequency.

^cns, not significant; Bold values indicate significant temporal trends over time.

Table 4. Current status of pH, S and N deposition in precipitation in Guangzhou, in comparison with other Chinese cities

Sites	Sampling period	Precipitation (mm)	pH	SO ₄ ²⁻ -S (kg ha ⁻¹ yr ⁻¹)	NH ₄ ⁺ -N (kg ha ⁻¹ yr ⁻¹)	NO ₃ ⁻ -N (kg ha ⁻¹ yr ⁻¹)	DIN (kg ha ⁻¹ yr ⁻¹)	References
North China								
Beijing	2001–2003	454	6.01	18.1	14.9	5.3	20.2	Yang et al., 2004
Xi'an	2010	459	6.68	14.7	12.0	2.6	14.6	EANET 2010
Zhengzhou	1999	528	6.41	11.8	14.0	3.4	17.4	Zhao et al., 2001
South China								
Chongqing	2010	977	4.15	43.5	19.2	10.6	29.8	EANET 2010
Shanghai	2005	1071	4.49	34.2	12.1	7.5	19.6	Huang et al., 2008
Xiamen	2010	1530	4.57	13.1	8.5	6.2	14.7	EANET 2010
Zhuhai	2010	1857	4.85	11.7	6.4	6.2	12.6	EANET 2010
Guangzhou	2010	2303	5.08	42.8	21.7	13.8	35.5	This study

increased human activities associated with industrialisation, urbanisation and intensified agriculture. Currently, the average DIN deposition in Guangzhou city is much higher than 25 kg N ha⁻¹ yr⁻¹, the threshold above which elevated N leaching has always been observed in the temperate and boreal forests in Europe (Gundersen et al., 2006).

In the present study, NH₄⁺ made up on average 61% of DIN deposition in Guangzhou (Table 4). The proportion of NH₄⁺ is lower than the national level of 72% synthesised by Lu and Tian (Lu and Tian, 2007) and the mean level of 68% at 31 forest sites in China (Fang et al., 2011a), and also lower than that in two Chinese remote sites (73% at Linzhi, Jia et al., 2009 and 86% at Waliguan, Tang et al., 2000). However, NH₄⁺ is still the more dominant N form in our study city than national levels in the U.S. (47%, Holland et al., 2005) and mean level at 12 Japanese EANET sites (48%, EANET, 2010). Compared with other large Chinese cities such as Beijing, Xi'an, Zhengzhou, Shanghai, Chongqing and Xiamen, where NH₄⁺ accounted for 62%–80% of DIN (Table 4), the percentage of NH₄⁺ is lower in Guangzhou. This fact points to the increasing importance of NO₃⁻ in N deposition in the study city and to the need for more concern about the changes in N sources to the atmosphere associated with industrial development.

3.4. Implications for acid deposition control

Our results clearly demonstrated a marked recovery of precipitation from acidification since 2005. For example, in 2010 precipitation pH was 0.7 pH units higher than that in 2005, and acid rain frequency dropped to 48% from 81% in 2005. SO₄²⁻ concentration and deposition decreased by 46% and 16%, respectively. However, current precipitation pH values (in 2010) were still low (on average 5.08), although it was at its highest since 1987 (4.12–4.78, Fig. 3a). Precipitation pH values were between 5.34 and 5.83 during

the period from 1983 to 1985 (Fig. 3a), suggesting slight or no pollution in that period (several years after the Chinese economic reform started in December 1978). These values were about one pH unit higher than the pH values during the 1990s and 2000s (Fig. 3a). The frequency of acid rain significantly decreased since 2005, but was still about 50% (Fig. 3b).

Additionally, current S deposition of 43 kg S ha⁻¹ yr⁻¹, despite having decreased by 40% compared to 2001 since the policy of SO₂ emission abatement started, remained among the highest in China (Fig. 7b and Table 4) and approximately three times the target loading (14–16 kg S ha⁻¹ yr⁻¹) suggested as an upper limit for the prevention of biological and chemical damage to aquatic ecosystems (Gorham et al., 1984; Posch, et al., 2012) and the critical load for soil acidification in most areas of the study region (16 kg S ha⁻¹ yr⁻¹), according to the research of Zhao et al. (2009). Combined with increasing coal consumption (Fig. 10), these results point to the requirement for continued and more stringent abatement policies.

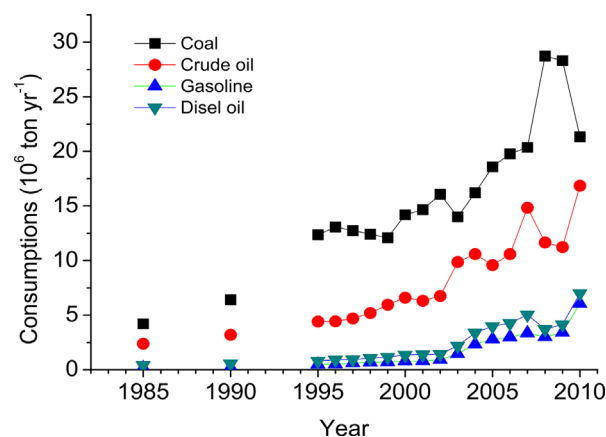


Fig. 10. Fuel consumptions in Guangzhou city from 1985 to 2009. Data are from Guangzhou Statistical Yearbook (<http://data.gzstats.gov.cn/gzStat1/chaxun/njsj.jsp>).

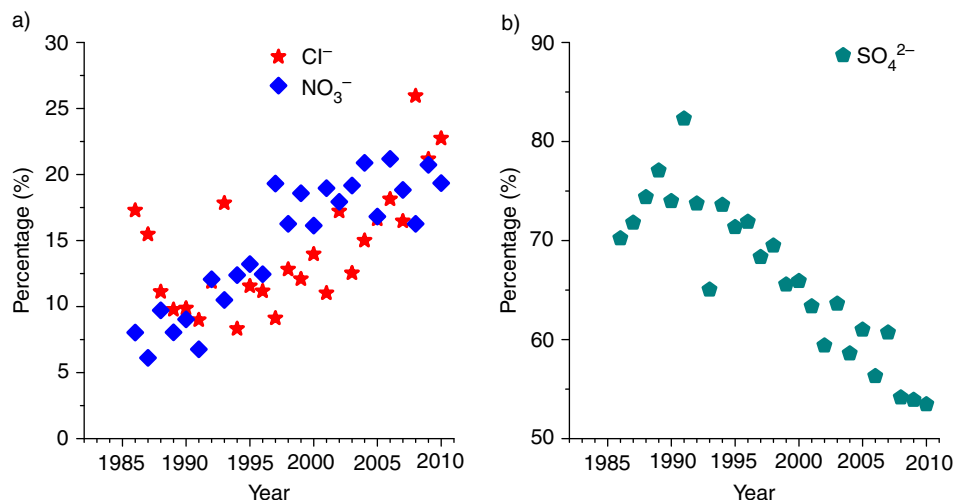


Fig. 11. Long-term trends of proportion of (a) Cl^- and NO_3^- and (b) SO_4^{2-} to sum anions in precipitation in Guangzhou city since 1986.

The results presented in this paper also suggest that a reduction of SO_2 emissions alone was not sufficient for eventual recovery from acid rain. We suggest that controlling the emissions of NH_3 and NO_x is equally important and urgently needed. Atmospheric N deposition poses a threat to natural ecosystems in the study area, causing N saturation and water eutrophication. The DIN deposition (please note N deposition in this study is for bulk precipitation which contains a fraction of dry deposition) was rather large, $38 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ over the last 25 years (Figs. 8 and 9), which is much higher than the threshold of $25 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ over which elevated N leaching occurs in European temperate forests (Gundersen et al., 2006). It means that, together with dissolved organic N (17%–21% of total dissolved N deposition, Li et al., 2002), more than $1000 \text{ kg N ha}^{-1}$ has been deposited into our ecosystems in the past 25 years, which is likely to saturate any given natural ecosystem under warm and humid conditions (Fang et al., 2008).

A significant increase in NO_3^- concentration and deposition has been observed in the study city (Figs. 6 and 8; Table 3). The increased NO_3^- load in precipitation results from the increased vehicle population, but also from increased NO_x production during the coal combustion associated with increased coal consumption (Fig. 10). The NO_x control could be more difficult than SO_2 control, because of an inevitable increase in vehicle population, low penetration rate of denitrogenation technologies (e.g. selective catalytic reduction) in the thermal power sector (less than 10%) and low N removal efficiency of such technologies in China (Zhao et al., 2009). Additionally, more attention should also be paid to the increasing NH_3 emissions, although annual deposition tends to decrease with time. NH_4^+ deposition averaged at $21 \text{ kg N ha}^{-1} \text{ yr}^{-1}$

in 2001–2010, and is still the dominant N form in DIN (Table 4). NH_3 control is also difficult to handle because NH_3 is predominantly released from scattered agricultural activities (Zhao et al., 2009).

We believe that a national SO_2 emission control policy will eventually reduce the emissions of acidifying pollutants, but it will also likely reduce the emissions of the neutralising pollutants (Zhao, et al. 2011). In the study city, PM_{10} concentrations decreased substantially (by 30%) since 2004 (Fig. 5). In China, Ca has been recognised as a very important base cation buffering the acidifying pollutants (Larssen and Carmichael, 2000). In the time period 2001–2010, large depositions of Ca^{2+} might have also played an important role in neutralising the acidity in precipitation, particularly in 2005–2008 (Fig. 8a), since Ca^{2+} was the main component in base cations in precipitation in this study city, accounting for 49% of total cation equivalents, on average (Fig. 6a). 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 (Larssen and Carmichael, 2000). High Ca deposition in 2005–2008 in the study city was most likely caused by intensive construction activities in preparation for the 16th Asian Games (Fang et al., 2011b). We suggest that precipitation may become more acidified in the future because the deposition of alkaline dusts containing Ca is also likely to decrease with stricter SO_2 emission control policy and reduced construction activities.

In addition, we note that Cl^- concentration and deposition significantly increased with time (Figs. 6 and 7; Table 2). In the last five years, Cl^- accounted for up to 11%–26% of total ion equivalents, with an average of 18%, which was similar to the portion of NO_3^- (16%–21%, on average

19%, Fig. 11). Elevated Cl^- concentration in precipitation was likely caused by increased hydrochloric acid (HCl) emissions in the study city due to the increased combustion of coal (Fig. 11, coal contains 0.01%–0.2% Cl by weight in China, Jiang et al., 2001), and to a lesser extent, to increased waste incineration (McCulloch et al., 1999). Due to the high mobility of Cl^- , HCl can readily acidify both soils and surface water (Evans et al., 2011). Thus, HCl emission deserves more attention in order to completely control acid rain and soil and surface water acidification.

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