Response to referees' comments on "Five-year record of atmospheric precipitation chemistry in urban Beijing, China"

The authors are grateful to all the reviewers and the editor very much for their general and specific comments on our manuscript. Their detailed comments are very valuable for the improvement of the paper. We have addressed all the comments point-by-point as below. All the relevant corrections and changes are highlighted in the following revised manuscript.

Referee #2 (specific comments)

1. In abstract, "Most precipitation samples had an intermediate pH (6.1-7.3) and 16% were acidic". Please give the pH ranges of the left 16% rainfall samples. Most precipitation samples should be replaced by nearly 84% precipitation samples.

Response: *The suggestion has been taken. The sentence was reworded as* "Intermediate pH (6.1-7.3) was recorded in approximately two-thirds of the precipitation samples and acidic pH (4.2-5.6) in only 16% of the samples".

2. In Introduction part, the author should give a brief introduction of air pollution levels in Beijing in recent studies, and possible influence on acidity of precipitation.

Response: *Thanks for the comment. The suggestion has been taken. We add some words about Beijing's air pollution levels in introduction section accordingly.*

3. If possible, please give a repeatability experiments result table.

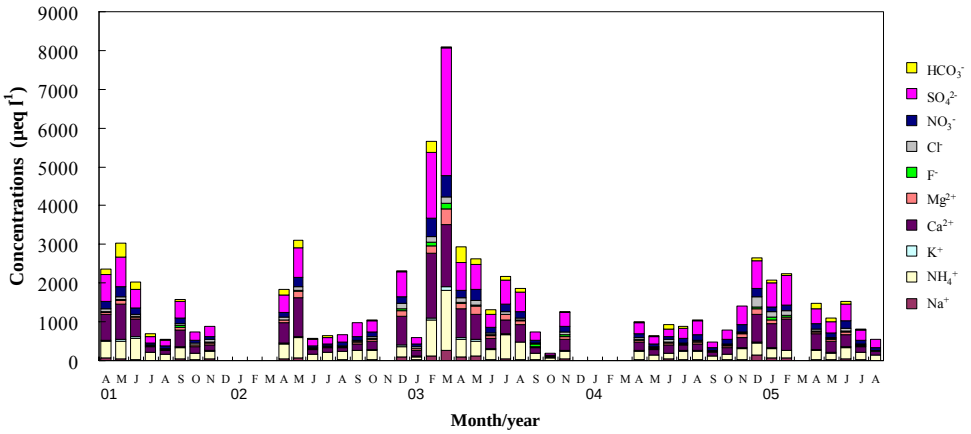
Response: *Thanks for the comment. The precision of ionic measurements in this study has been already addressed very clearly, including the variations in replicate measurements for each ion (see P28101 L25-27). Thus we think it is not necessary to give a table on the replicate measurements.*

4. The ions concentration in Figure 5 is the annual volume-weighted or not? If yes, please describe it in MS.

Response: *Thanks for the comment. The ionic concentrations in Fig. 5 are the concentration percentiles and the single volume-weighted mean of each ion. To make it clear, we specify this in the sentence on P28103 L19* "Statistics of ionic concentrations for all the precipitation samples are shown in Fig. 5" *by changing it into* "Fig. 5 illustrates the statistics of concentrations of ions in the precipitations, including the 10th, 25th, 75th, and 90th percentiles and VWM of each ion.".

5. Please give the meaning of x-axis of Figure 6.

Response: *The suggestion has been taken. We have modified the Fig. 6 as below.*



6. If possible, please describe the seasonable variation of acidity and chemical composition of rainfall samples.

Response: *Thanks for the comment. The seasonal variations in acidity and chemical composition of rainfall samples have been discussed separately in section 3.1 and 3.3.*

7. The paper could have been better-written. Revising the entire MS by a native English speaker is highly required prior to publishing.

Response: *Thanks for the nice suggestion. The general use of English language has been polished by a native speaker and many corrections have been made accordingly (see the highlighting revisions and changes implemented in the manuscript behind this point-to-point response).*

Referee #3 (specific comments)

1. P28098 L2: it is better to change "from March 2001 through August 2005" into "from March 2001 to August 2005".

Response: *The suggestion has been taken.*

2. P28102 L13-14: If possible, it is better to compare the authors' annual precipitation volume with those reported by the local Beijing Meteorological Bureau or EPB, which can be a well reference of spatial difference of precipitation within Beijing.

Response: *The suggestion has been taken. We reword the sentence* "These volumes were largely lower than long-term average in Beijing (www.bjmb.gov.cn)" *as* "These volumes were similar to the reported range of 339-483 mm for the whole city through the years (www.bjstats.gov.cn) but largely lower than long-term average in Beijing Metropolis (www.bjmb.gov.cn)".

3. P28102 L17-L18: the original expression should be given firstly before the simplified name of "VWM EC ".

Response: *The suggestion has been taken. We change "VWM EC" into "The volume-weighted mean (VWM) of EC". The words for the simplified form "EC" has been given when it first appears on P28101 L13.*

4. P28102 L13: it is better to change "Total precipitation amount" into "Annual total precipitation amount".

Response: *The suggestion has been taken. We change "*Total precipitation amount*" into "*The annual total precipitation amount*".*

5. P28102 L17: the words for the simplified form "VWM" should be given when it first appears.

Response: *The suggestion has been taken. See the response to point 3.*

6. P28103 L13: it is better to change "and averaged at" into "with an average of".

Response: *The suggestion has been taken.*

7. P28104 L7-9: a reference or the method about how to calculate non-sea salt Ca^{2+} and non-sea salt SO_4^{2-} should be given?

Response: *The suggestion has been taken. We add "*calculated from the ion ratio Ca^{2+}/Na^{+} in seawater equal to 0.0379*" and "*calculated from the ion ratio SO_4^{2-}/Na^{+} in seawater equal to 0.252" *at the ends of* "The non-sea calcium (nss-Ca^{2+})*" and "*The non-sea salt sulfate (nss-SO_4^{2-})*", respectively.*

8. P28104 L8: the definite article is better to be added before "total calcium".

Response: *The suggestion has been taken. We add (i.e., non-sea-salt plus sea-salt calcium) behind "total calcium".*

9. P28104 L13-14: it is better to change "Compared to the long-term observation at 9 sampling sites in the Tokyo Metropolitan with precipitation pH of 4.5 during June 1990–May 2002" into "Compared to the long-term observation during June 1990–May 2002 at 9 sampling sites in the Tokyo Metropolitan with severe acid precipitation".

Response: *The suggestion has been taken. We change "*Compared to the long-term observation at 9 sampling sites in the Tokyo Metropolitan with precipitation pH of 4.5 during June 1990–May 2002*" into "*Compared to the long-term observation from 1990 to 2002 in the Tokyo Metropolitan area with severe acid rain*".*

10. P28107 L17-18: it is better to give out the details and the source reference of SO2 and NO2 concentration decrease.

Response: *Thanks for the suggestion. We double check the NO_2 data (it is not NO2 but NOx data was reported in 1998 by Beijing Municipal Environmental Protection Bureau) and make revision and add the source reference accordingly. The sentence "*However, the decrease in SO_4^{2-} and increase in NO_3^- did not scale to or even opposed to the 58% and 11% decrease in annual mean concentrations of SO_2 and NO_2 in Beijing from 1998 to 2005*" has been changed into "*However, the decrease in SO_4^{2-} level did not scale to the 58% decrease in the annual mean SO_2 concentration from 1998 to 2005 (50 μg m^{-3} in 2005). What seems more surprising is that the NO_3^- growth was opposite to the 5% reduction in the annual mean NO_2 concentration from 1998 to 2005 (66 μg m^{-3} in 2005)*".*

11. P28107 L20-21 and P28110 L22: maybe it is not appropriate to conclude a "substantial" decrease on NO2 concentration during the past decade, please check it.

Response: *The suggestion has been taken. We double check it as mentioned in the last response and change "*the substantially decrease in atmospheric SO_2 and NO_2*" into "*more or less decline of ambient SO_2 and NO_2 levels*".*

12. P28109 L18: it is better to change "and averaged at" into "with an average of".

Response: *The suggestion has been taken.*

13. P28110 L2: it is better to change "from March 2001 through August 2005" into "from March 2001 to August 2005".

Response: *The suggestion has been taken.*

Five-year record of atmospheric precipitation chemistry in urban Beijing, China

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Abstract

To investigate the chemical characteristics of precipitation in the polluted urban atmosphere in Beijing and possible mechanisms influencing their variations, a total of 131 event-based precipitation samples were collected from March 2001 to August 2005. Ionic species in the samples were measured by using ion chromatography. Intermediate pH (6.1-7.3) was recorded in approximately two-thirds of the precipitation samples and acidic pH (4.2-5.6) in only 16% of the samples. The precipitation acidity was on the growth track and the process was likely being accelerated. SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} were the most abundant ions in the precipitations, with their single volume-weighted mean (VWM) concentration all above 100 μeq L^{-1}. The two major anions and two major cations accounted for more than 80% of total anionic and cationic mass, respectively. The VWM SO_4^{2-} concentration decreased by only 13% compared to that during 1995-1998, much less than the 58% reduction in the annual average SO_2 concentration from 1998 to 2005 in Beijing. What seems more counterintuitive is that the VWM NO_3^- concentration nearly doubled over the period although the annual average NO_2 concentration decreased by 5% from 1998 to 2005. These results imply that the conversion of gaseous precursors to acid compounds and/or the regional transport were reinforced over the decade. The average ratio of neutralizing potential to acidifying potential (i.e. NP/AP) was as high as 1.2 but experienced an evident decline trend. This was mainly ascribed to reduced input of NH_4^+ and Ca^{2+} and increased input of NO_3^-. Furthermore, the equivalent mass ratio of NO_3^- to non-sea-salt SO_4^{2-} presented an increasing trend over the study period, suggesting that the contribution of NO_3^- to the precipitation acidity increased in recent years. However, the mean ratio was only 0.37±0.11 in the study period, which is significantly lower than those reported in some metropolitan areas in developed countries. This shows that the precipitation acidity in Beijing was still dominantly from excessive emissions of sulfur while its contribution was being progressively taken by nitrogen.

1 Introduction

Long-term variation in the chemical characteristics of dry and wet depositions provides important information on the temporal evolution of atmospheric pollution, and can be used as a pertinent indicator to evaluate natural process versus anthropogenic influences (Grodzińska-Jurczak and Godzik, 1999; Tang et al., 2005). Because wet deposition often plays a more important role in flux compared to dry deposition, chemical analyses of precipitation enables a partial assessment of local air quality (Özsoy et al., 2008). In China, acid deposition has been one of the most significant environmental issues since the late 1970s. Widespread acid rain was observed in southern and southwestern China before the 1990s (Zhao et al., 1988; Wang and Wang, 1995; Ding et al., 1997),

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and more recently it has extended to eastern and central China (Larssen et al., 2006; Huang et al., 2008; Wang and Xu, 2009; Xie et al., 2009; Tang et al. 2010; Ge et al., 2011). Beijing is located out of the traditional regions of acid rain in China. However, high concentrations of air pollutants in and around Beijing most likely lead to high loadings of various chemical species to the ecosystem through atmospheric depositions. For example, the average concentrations of sulfate and nitrate in fine particles – two dominant acidic species – could be much higher than those in some cities with severe acid deposition in southern China, such as Chongqing and Guangzhou (Yang et al., 2011a). Thus the trend in precipitation chemistry and its influence on the ecosystem are of great concern, particularly when considering the fast economic and population growth in Beijing.

As the capital and one of the most populated mega cities in China, Beijing has experienced rapid urbanization and motorization in the past three decades, which leads to soaring demand for energy. During the process, the motor vehicle pollution emerges and becomes increasingly prominent, while the traditional pollution caused by coal burning has not yet been effectively controlled, a common phenomenon in Chinese megacities (He et al., 2011). In addition, a great deal of construction activities inevitably cause fugitive dust and exacerbate particulate pollution. To improve the capital's air quality, the municipal government has initiated a series of clean air programs starting in 1998 (www.bjepb.gov.cn), and Beijing has been leading the country in progressive introduction of increasingly stringent emission standards for motor vehicles and coal-fired boilers compared to state criteria. As a result, the air quality compliance days have kept increasing thereafter (www.bjepb.gov.cn), but less than what was expected in terms of particulate pollution as compared to SO_2 and NO_2 (Yang et al., 2011b).

Meanwhile, the precipitation acidification in Beijing is undergoing an evident increasing trend, especially under the background of complex air pollution mentioned above (Ding et al., 1997; Wang and Zhang, 1997; Feng et al., 2001; Hu et al., 2005). Some recent studies showed that pH and precipitation chemistry in Beijing were noticeably different before and after the year of 2000, which was likely related to the variations in atmospheric pollution type (Tang et al., 2005; Hu et al., 2005; Xu and Han, 2009). To our knowledge, there are no studies that are based on long-term surface measurements to track the changing precipitation chemistry along with the changing emissions of acidic precursors (i.e. SO_2 and NOx) and neutralizing substances in Beijing after 2000. In 2001, we initiated a precipitation monitoring program in urban Beijing to evaluate the magnitude as well as temporal trends and sources of acids and toxics substances in atmospheric depositions. This paper will summarize the major findings with a focus on the temporal variations in the precipitation chemistry. Possible mechanisms influencing these variations will also be discussed.

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2 Experimental

2.1 Sampling location and sample collection

Beijing is located at the northern tip of the Great North China Plain with a landmass of 16410 km^2 (Fig. 1). As one of the most populated cities in China, its 20 million inhabitants are concentrated in the urbanized area, which is only 6% of the city's landmass (Beijing Municipal Bureau of Statistics, 2011). The main terrain of Beijing is plain, with surrounding mountains on three sides, i.e. the Mongolia to the north, the Yanshan Mountain to the northeast. The Bohai Sea is about 160 km to the southeast. This topography does not favor the dispersion of the air pollutants. Lying in the north warm temperate zone, Beijing has typical continental monsoon climate with four distinct seasons. From November-April, the prevailing airflow from the northwest is dry and cold, while at other times the local winds are moderate and mostly from the south and southeast (Yang et al., 2011b).

Sampling of atmospheric precipitations was conducted in the semi-residential area inside the campus of TsingHua University (here referred to as THU, 40°19'N, 116°19'E) from March 15, 2001 to August 18, 2005 (Fig. 1). About 12 km northwest of the city centre, the THU site lies within the western part between the northern fourth and fifth ring roads, which are two of the artery roads with busy traffic encircling urban area at about 9 and 14 km radii from the city centre, respectively. Precipitations were collected with a dry-wet deposition auto-sampler (DRS-154W, Koshin Denki Kogyo, Japan), which was deployed on the rooftop of a 5 m tall building. The sampler has a removable lid activated by a wetness sensor, which opens the funnel above a 5 L polyethylene bucket under a funnel of 155 mm in diameter when precipitation happens. The wet deposition sample was collected for every continuous rainfall. In total, 137 precipitation samples were collected over the study period.

2.2 Sample analysis and quality control

The precipitation samples were weighed in the laboratory and calculated for the volume. The precipitations were then filtered through a Millipore filter with a pore size of 0.45 μm. The pH of the filtrate was measured with a pH meter (pH/Ion meter F-24, Horiba) under controlled room temperature (25 ºC), and the electrical conductivity (EC) was measured with an electrical conductivity meter (AOL-40, Denki Kagaku Keiki). H^+ concentration was calculated from the pH of the filtrate. The concentrations of ten major ions (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^-) were determined with Ion Chromatography (IC7000-1, Yokokawa Analytical Systems) in Keio University (Okuda et al., 2005). The separator column was ICS-C25 (YAN) and the eluent was 5 mM Tartaric acid/1mM 2,6-Pyridinedicarboxylic acid/24mM Boric acid 1.0 [ml/min] for cations. For anions except HCO_3^- the separator column was AS12A (Dionex) and the eluent was

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2mM Na_2CO_3/4mM $NaHCO_3$ 1.0 [ml/min], while for HCO_3^- they were ICE-AS1 (Dionex) and Milli-Q (Millipore), respectively. Note that we excluded 6 out of the 137 precipitation samples, whose volume is too small to reliably determine the concentrations of all the above mentioned ions except HCO_3^-.

Precision of ionic analysis was determined from at least 4 replicate measurements. The result showed that the variation for Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, and HCO_3^- was ≤ 2%, while for K^+ it was 7%. The quality of analytical data was also checked by a cation-anion balance and by comparison of measured conductivity with the conductivity calculated from the concentration of all measured ions and their specific conductivity. As shown in Fig. 2a, the conductivity ratio of that calculated to measured was >1, indicative of an ionic deficiency in these cases. The ion balance check proved to be reliable according to the acceptable range (15-30%) set for samples having ion sum > 100 μeq L^{-1} by USEPA (Ayers, 1995). The ratio of total anions to cations was systematically <1 (Fig. 2 b), suggesting an anion deficit. This predominance is frequently reported in the literature, and usually ascribed to some unmeasured anions such as bicarbonate (if not included) and short-chain organic acids (Zhang et al., 1996; Hontoria et al., 2003).

3 Results and discussion

3.1 Precipitation amount and pH distributions

The annual total precipitation amount was 345, 461, 411, and 546 mm from 2001 to 2004 with an average of 441 mm for the four years. These volumes were similar to the reported range of 339-483 mm for the whole city through the years (www.bjstats.gov.cn) but largely lower than long-term average in Beijing Metropolis (www.bjmb.gov.cn). As shown in Fig. 3, monthly mean precipitation amount varied markedly with a peak in the summer. About 78% of the rain was deposited from June to September (rainy months). The volume-weighted mean (VWM) EC in the precipitation was 66.5 μS cm^{-1}, which was larger by a factor 4.6 than that (14.6 μS cm^{-1}) measured at a remote site in Mt. Waliguan (Fig. 1), which is the Global Atmosphere Watch Baseline Observatory of World Meteorological Organization (WMO) located at the eastern tip of Qinghai-Tibetan plateau in Northwest China (Tang et al., 2000). This indicates a substantial impact of anthropogenic pollution on the urban atmospheric environment in Beijing.

As illustrated in Fig. 4a, the frequency distribution of precipitation pH is similar to a unimodal distribution. This is very different from the bimodal pH distribution found in the Mediterranean precipitation (Aiuppa et al., 2003). The pH value of single precipitation varied from 4.2 to 7.5 with an arithmetic mean of 6.3 and the VWM of 6.0 for the total 131 precipitation samples. Intermediate pH (6.1-7.5) was recorded in approximately two-thirds of precipitation samples, whereas acidic pH

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(pH <5.6) was observed in only 16% of the samples. This distribution reflected the alkaline nature of rainwater in urban Beijing. It should be noted, however, that nine of thirteen low pH (<5.0) rain samples and the three lowest pH (<4.5) rain samples were collected in the latter two years (Fig. 4b). Besides, there existed a decreasing trend in the rainfall pH based on linear regression (Fig. 4b), which is consistent with the trend during 1980-2000 as noted earlier (Ding et al., 1997; Wang and Zhang, 1997). This points to a decreasing buffering capacity due to a prevalent input of acid compounds and/or reduced input of neutralization of base agents. Therefore, the alkalinity of precipitation in Beijing was decreasing and the process was likely being accelerated. This will be further discussed in section 3.4. The monthly VWM pH values varied from 5.3 to 6.8 with an average of 6.2. Only August had a VWM pH less than 5.6. There were eleven low pH rains collected during July – September and the majority of them were in August. Since summertime rainfall volume shared two-thirds of annual volumes and usually presented low pH values (Fig. 3), the yearly wet deposition acidity was mainly determined by the rains falling in this season.

3.2 Chemical composition and sources of major ions

Fig. 5 illustrates the statistics of concentrations of ions in the precipitations, including the 10th, 25th, 75th, and 90th percentiles and VWM of each ion. SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} were the most abundant ions and their single VWM concentration was all above 100 μeq L^{-1}. NH_4^+ plus Ca^{2+} summed to 502 μeq L^{-1} and comprised 83% of total cationic mass while SO_4^{2-} plus NO_3^- accounted for 84% total anionic mass. SO_4^{2-} was the most abundant single ionic component in the precipitations, accounting for 30% of total ionic mass. NO_3^- was the second most abundant anion, followed in decreasing order by HCO_3^-, Cl^- and F^-. For the cations, NH_4^+ and Ca^{2+} were followed in decreasing concentration by Mg^+, Na^+, and K^+.

The major anthropogenic ions – SO_4^{2-}, NO_3^- and NH_4^+ – accounted for 63% of the total ionic mass, indicating that anthropogenic sources predominated in rainfall ions. Despite high contribution of anthropogenic anions such as SO_4^{2-} and NO_3^-, H^+ accounted for only 0.2% of total inorganic ionic mass due to the extensive neutralization by alkaline substances. Two major crustal-related ions – Ca^{2+} and Mg^{2+} – contributed 28% to the total ionic mass, indicating crustal material was an important contributor to precipitation neutralization. The non-sea-salt calcium (nss-Ca^{2+}, calculated from the ion ratio Ca^{2+}/Na^+ in seawater equal to 0.0379) accounted for 99.6% of the total calcium (i.e., non-sea-salt plus sea-salt calcium) for all the precipitation samples, indicating that sea salt did not have strong impact on wet deposition in Beijing. The non-sea-salt sulfate (nss-SO_4^{2-}, calculated from the ion ratio SO_4^{2-}/Na^+ in seawater equal to 0.252) accounted for 97.8% of the total sulfate.

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Table 1 lists the VWM pH and VWM concentrations of each ion, in addition to those from other earlier studies conducted in Beijing and other selected locations in East Asia. Compared to the long-term observation from 1990 to 2002 in the Tokyo Metropolitan area with severe acid rain, the VWM concentrations of SO_4^{2-} and NO_3^- in Beijing were higher by a factor of 3.8 and 7.6, and those of NH_4^+ and Ca^{2+} by a factor of 6.5 and 9.6, respectively. The SO_4^{2-} level was also considerably higher than those measured in some typical acid rain regions in China, such as Guangzhou (Fig. 1, Table 1) (Huang et al., 2009). In comparison with those monitored at the remote Mt. Waliguan site, the VWM concentrations of SO_4^{2-} and Ca^{2+} in Beijing precipitations were a factor of 7.7 and 7.0 higher, respectively. These comparisons reveal that both crustal-related and anthropogenic sources (such as fossil fuel combustion) had significant impact on the ambient environment in urban Beijing.

The concentration of F^- was comparable to that measured in Beijing during 1995-1998 (Table 1), and was one to two orders of magnitude higher than those observed in Tokyo (1.7-1.9 μeq L^{-1}) in Japan (Feng et al., 2003), Virginia (0.6 μeq L^{-1}) and Delaware (0.3 μeq L^{-1}) in USA (Barnard and Nordstrom, 1982), Mid-Wales (0.3 μeq L^{-1}) in the UK (Neal, 1989), and much higher than the World average (5.3 μeq L^{-1}) (Zheng, 1996). Tang et al. (2000) reported that F^- in nearly half of the total 57 rain samples collected at Mt. Waliguan was below detection limit. These comparisons suggest that a large fraction of the F^- in Beijing precipitations was likely from anthropogenic sources. Based on a field study during 1995-1998, Feng et al. (2003) ascribed the soil dust and coal combustion as the two major sources of F^- in Beijing precipitation.

Factor analysis was performed to further investigate the major sources of chemical species in the precipitations. Three factors were identified with the cumulative variance more than 90% (Table 2). The communalities of all the ions are no less than 0.80, indicating that these extracted factors are reasonable. The first factor, which explains 40% of variance, is strongly correlated with Cl^-, Na^+, and Mg^{2+}, and moderately correlated with K^+, F^-, and NO_3^-. This factor was likely associated with certain anthropogenic sources, such as industrial emissions, municipal waste incineration, biomass burning, coal combustion, and fugitive dust as well. Although a strong correlation exists between Na^+ and Cl^- (r = 0.89), the association of Na and Cl with the influence of sea breeze could be only a minor source, consistent with the findings by Tang et al. (2005) and Xu and Han (2009). This is supported by the fact that the average Na^+ and Cl^- ratio of 2.1 (ranging from 0.7 to 13) was much higher than the reported ratio of 1.16 from seawater (Moller, 1990). This is understandable since Beijing is about 160 km away from the Bohai Sea in the southeast and the wind from that direction in summer is usually mild (Yang et al., 2011b). Factor 2 has high loading for SO_4^{2-}, NO_3^-, and NH_4^+, suggestive of the secondary pollution formed in the atmosphere from their precursors – SO_2, NOx,

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and NH_3. While SO_2 and NOx are believed to be mainly emitted from fossil fuel combustion such as coal combustion and vehicle tailpipe emission, the major anthropogenic sources of ammonia in East Asia were estimated to be mainly from chemical fertilizer used in agriculture, livestock breeding, and energy consumption (Zhao and Wang, 1994). Vehicular emission, chemical engineering, biologic process and biomass burning could play a role as well in the high levels of NH_4^+ in Beijing precipitation (Tang et al., 2000; Hu et al., 2005). Factor 3 is dominated by Ca^{2+}, F^-, NO_3^-, and K^+, likely indicative of soil dust as a major source. It is noted that there are plenty of calcareous soil and high aerosol loadings in Beijing and surrounding region, of which a large portion was expected from soil dust (Yang et al., 2002; Guinot et al., 2007). Also noted is that a significant part of NO_3^- is usually associated with soil particles in coarse mode (Seinfeld and Pandis, 2006).

3.3 Temporal variations in concentrations of major ions

Monthly average concentrations of each ion in the precipitation were subject to dramatic variations (Fig. 6). Both higher loadings of crustal-related and anthropogenic ions usually appeared during the months from November to April while lower loadings in rainy months. This seasonal pattern was most likely due to the combined effect of seasonal variations in emission and rain intensity. During those months, the northwesterly Asian monsoon was dominant, leading to frequent uplift of wind-blown mineral particles from both local areas and remote deserts or arid regions. In addition, the coal combustion activities were highly enhanced (about 5 million tons additional coal consumed) for heating in Beijing during the official four-month heating period lasting from mid-November to mid-March, resulting in extra anthropogenic emissions of gaseous pollutants and particles (He et al., 2001). Meanwhile, usually there are sparse rains (about 19% of the annual rainwater volume in this study) during this period. For the effect of rain intensity on ionic mass, many previous studies demonstrated in different areas that ionic concentrations decreased with increasing precipitation amount due to processes such as diffusion aerosol, initial rain evaporation and dilution (Tuncer et al., 2001; Feng et al., 2001; Xie et al., 2009). The monthly variations in the VWM concentrations of precipitation ions in the present study were largely controlled by rainwater amount as well since all the ions were more or less negatively correlated with precipitation volume (correlation coefficient r = –0.18 to –0.34).

All ionic species reached the maximum monthly average concentrations in March 2003, followed by the preceding month. It is noted that there were only two precipitation samples collected in March over the study period and both in 2003. Of the two samples the one with much higher volume (17.4 mm vs. 5.1 mm for the other event) was collected on March 20th when daily PM_{10} concentration was as high as 179 μg m^{-3}. In addition, the average ionic concentrations in July

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and August of 2003 were higher than those in other years by a factor of 2.6-3.4. It is worth noting that the seasonal distribution of precipitation volume in 2003 differed enormously from those in the other years. The precipitation volumes in the winter, spring, and fall in 2003 increased by 50-160% whereas the summer rain volume substantially declined. The low annual volume and abnormal seasonal distribution of precipitation in 2003 likely played a role in the monthly variations in precipitation chemistry. High concentrations of precipitation ions in Beijing in the year 2003 were also reported by Hu et al. (2005).

Based on linear regression throughout the study period, SO_4^{2-} maintained a steady concentration level, whereas NO_3^- exhibited an increasing trend and NH_4^+ and Ca^{2+} a decreasing trend in their concentrations. In comparison with the study conducted in Beijing during 1995-1998 (Table 1), the VWM concentrations of most ions in this study decreased by 13% (SO_4^{2-}) to 64% (Cl^-), whereas those of NO_3^- and NH_4^+ increased by 94% and 75%. This is in agreement with the finding by Okuda et al. (2011) that opposite to the decreasing trend in other water-soluble ions of particulate matter in Beijing was an evident increasing trend in nitrogen-containing species in recent years. However, the decrease in SO_4^{2-} level did not scale to the 58% decrease in the annual mean SO_2 concentration from 1998 to 2005 (50 μg m^{-3} in 2005). What seems more surprising is that the NO_3^- growth was opposite to the 5% reduction in the annual mean NO_2 concentration from 1998 to 2005 (66 μg m^{-3} in 2005).

These counterintuitive long-term changes in SO_4^{2-} and NO_3^- concentrations in the precipitations as compared to their precursors were likely due to the increased regional transport and reinforced conversion of precursors to acid compounds and/or secondary particles. While huge progress has been made in eliminating small coal boilers in urban Beijing, it is still popular to burn coal at the household level in sprawling brick-home suburbs and surrounding areas, and to burn agricultural field residue after harvest. Opposite to the more or less decline of ambient SO_2 and NO_2 levels in Beijing from 1998 to 2005, the national SO_2 emissions (2549.3 Mt in 2005) increased by 22% in the span (EQA, 1998, 2005). The national NO_X emission had undergone even much larger growth during the period (18.6 Mt in 2004 vs. 11.7 Mt in 1998) according to Zhang et al. (2007). Therefore, it was anticipated that there were growing contributions of transported gaseous precursors (SO_2 and NOx) and particularly the formed acid compounds (i.e. SO_4^{2-} and NO_3^-) to Beijing, especially from the vast eastern region upwind to the south in rainy months. This region is densely populated, with several large urban centers such as Tianjin Municipality (13 million), Shijiazhuang (10 million), Jinan (6.8 million), and Qingdao (8.7 million), which are typical industrial, coal-burning cities within several hundred kilometers of Beijing (Fig. 1). In these areas, emission controls on stationary

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sources and vehicles are not as stringent as in Beijing, and emissions are high (Streets et al., 2007). The SO_2 and NO_2 emission per land area in the eastern region of China was 3.3 and 4.4 times of their corresponding national averages (Yang et al., 2011a). In addition, the sulfate reduction frees up ammonia to react with nitric acid to form more nitrate (Seinfeld and Pandis, 2006), which was at least partly responsible for the nearly doubled NO_3^- concentrations in the precipitations. More careful study is needed to quantitatively determine all the contributions.

3.4 Trends in acidifying and neutralizing potentials, and the form of acidity

Tsuruta (1989) defined [NO_3^-+nss-SO_4^{2-}] as acidifying potential (AP) and [NH_4^++nss-Ca^{2+}] as neutralizing potential (NP). Time series of the ratios of NP to AP (NP/AP) were plotted in Fig. 7a. The high NP/AP (1.2 on average) indicates that wet deposition in Beijing had strong neutralization potential to offset the acidity caused by high loadings of sulfuric and nitric acids. However, the NP/NA ratio exhibited a significant decreasing trend with the regression intercept down from 1.5 to less than 1.0 over the study period. The average ratio was significantly lower than that (1.45) determined in Beijing during 1995-1998 (Feng et al., 2001), suggesting the decreasing neutralization trend was likely a long-term trend for Beijing precipitations. Given that the low pH rains occurred in the latter two years, this trend was likely being accelerated.

Time series of the neutralization factors (NFs) of NH_4^+, Ca^{2+}, and Mg^{2+} based on the following empirical relation are plotted in Fig. 7b-d:

$(NF)_X = [X]/ [NO_3^-$+nss-$SO_4^{2-}]$

where $X = NH_4^+$, nss-Ca^{2+}, and nss-Mg^{2+}.

The NFs of NH_4^+, Ca^{2+} and Mg^{2+} varied largely from 0.19-1.5, 0.15-2.4 and 0.02-0.40 with their average values of 0.60±0.25, 0.60±0.31 and 0.13±0.17 respectively, reflecting the dominant neutralization of NH_4^+ and Ca^{2+} over Mg^{2+}. There were evident decline trends in the NFs of NH_4^+ and Ca^{2+}, whereas that of Mg^{2+} underwent a clear growth over the study period. Although of small neutralization factor, the trend in NF of Mg^{2+} likely pointed to a growing contribution from construction activities since magnesium has been identified as an indicator element of cement dust (Yang et al., 2005). Along with other measures to control stationary and mobile source emissions in Beijing, construction and demolition areas have been required to control fugitive dust. However, ambient PM_{10} were still at high levels with the annual mean concentrations ranging 141-165μg m^{-3} (www.bjepb.gov.cn). This was attributed partially to the unprecedented high levels of construction activities due to rapid urbanization. For example, Yang et al. (2004) reported that there were more than 1200 construction and demolition sites in urban Beijing, covering a total area of about 32 km^2 in June 2001.

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Nitrate-to-sulfate equivalent ratio (i.e. $[NO_3^-]/[SO_4^{2-}]$) can be used to infer the form of acidity in the precipitation (Tuncer et al., 2001). As illustrated in Fig. 8, a clear increasing trend in $[NO_3^-]/[nss\text{-}SO_4^{2-}]$ with a ~0.05 increment to 0.4 in its regression intercept was found over the study period. The ratios varied from 0.16 to 0.74 with an average of at 0.37±0.11. This average ratio was more than twice that (0.15) calculated from the data measured in Beijing during 1995-1998 (Feng et al., 2001), indicating that the relatively reinforced contribution of nitric acid to precipitation acidity was also a long-term trend. This is in agreement with the trends in $[NO_3^-]/[SO_4^{2-}]$ of fine particles from our recent study in Beijing (Yang et al., 2011a). This $[NO_3^-]/[nss\text{-}SO_4^{2-}]$ value was twice as much as that during the same period in Chongqing (0.18±0.35) – a typical acid rain area with abundant high-sulfur coal consumption in Southwest China (marked in Fig. 1) – but was significantly lower than that in Tokyo Metropolis (Okuda et al., 2005) and a metropolis (Newark) in the US East Coast (Song and Gao, 2009). These comparisons showed that the precipitation acidity in Beijing was still dominantly from excessive emissions of sulfur (i.e. sulfur type) but not nitrogen.

4 Conclusions

Event-based precipitation samples were collected from March 2001 to August 2005 at an urban location in Beijing to investigate the temporal variations in the precipitation chemistry and to explore the possible mechanisms influencing the variations. The pH of single rain sample varied from 4.2 to 7.5 with an arithmetic mean of 6.3 and VWM of 6.0 for the total 131 rain events. About 16% of rain events were acidic and the yearly wet deposition acidity was dominated by the summertime precipitations, as they shared about two-thirds of the annual volume and usually had low pH values. The precipitation acidity was on the growth track and the process was likely being accelerated. SO_4^{2-} was the most abundant ion with the VWM concentration of as high as 314 $\mu eq\ l^{-1}$. 84% of anionic mass was from SO_4^{2-} and NO_3^-, followed in decreasing order by HCO_3^-, Cl^- and F^-. The precipitation acidity was predominantly neutralized by NH_4^+ and Ca^{2+} with their percentage contribution of 83% to total cationic mass.

The concentrations of both crustal-related and anthropogenic ions in the precipitation were much higher levels in the dry months and were much lower during the rainy months. The high NP/AP ratio (1.2 on average) indicated that the precipitations in Beijing had strong neutralizing potential to offset the acidity caused by high loadings of sulfuric and nitric acids. However, the NP/AP ratio exhibited a significant decreasing trend over the study period and particularly compared to that (1.45) determined pre-1998. This was mainly resulted from reduced input of NH_4^+ and Ca^{2+} and increased input of NO_3^-. In comparison to more or less decline of SO_2 and NO_2 in the ambient air of Beijing, the mean concentrations of SO_4^{2-} and NO_3^- in the precipitations showed much less decline

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and unexpected growth over the past decade, respectively. The growing contribution of NO_3^- to the precipitation acidity was also a long-term trend, although the acidity was still dominantly from excessive emissions of sulfur.

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Acknowledgments

The authors are grateful to Dr. Xuechun Yu, Dr. Yu Lei, Dr. Yingtao Jia, Dr. Qing Zhao, Tamami Iwase, Hideko Ueda, and Yusuke Suda for their contributions to the filed and laboratory work, and Dr. Li Bai, Qingqing Wang and Lianfang Wei for their contributions to the manuscript preparation. This study was funded by Tsinghua-Keio 3E Project and the National Basic Research Program of China (2010CB951803).

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删除的内容: 2011a

删除的内容: 2011b

Table 1. The VWM pH and VWM concentrations (μeq L^{-1}) of ions in precipitations in this study and some selected location in East Asia*

Cities	Period	pH	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}	F^-	Cl^-	NO_3^-	SO_4^{2-}	References
Beijing	2001-2005	6.0	22.5	236	13.8	209	48.4	15.4	34.9	106	314	This Study
Beijing	1995-1998	6.9	57.2	135	33.3	464	86.0	26.9	97.2	54.5	359	Feng et al., 2001
Guangzhou	2005-2006	4.5	18.0	66.2	9.0	131	9.0	12.0	21.0	51.8	202	Huang et al., 2009
Mt. Tai	2004-2006	4.7	25.3	82.2	7.7	61.4	6.2	–**	15.5	30.2	132***	Wang et al., 2008
Waliguan	1997	6.4	8.7	45.5	3.8	34.0	12.1	–	6.1	8.3	24.0	Tang et al., 2000
Tokyo Metropolitan	1990-2002	4.5	37.0	40.4	2.9	24.9	11.5	–	55.2	30.5	50.2	Okuda et al., 2005

*The selected locations in China are marked in Fig. 1. ** Not determined. *** Nss-SO_4^{2-}.

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Table 2. Factor analysis of ions in precipitation

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Variable	Factor 1	Factor 2	Factor 3	Communality
Cl^-	0.89	0.17	0.31	0.92
Na^+	0.88	0.31	0.28	0.94
Mg^{2+}	0.82	0.36	0.33	0.91
K^+	0.65	0.36	0.54	0.84
$NH4^+$	0.20	0.93	0.23	0.96
SO_4^{2-}	0.43	0.75	0.43	0.93
NO_3^-	0.50	0.60	0.54	0.90
Ca^{2+}	0.38	0.36	0.82	0.95
F^-	0.56	0.40	0.58	0.80
Variance (%)	39.9	27.3	23.4	

Fig. 1. Sampling site (THU) in Beijing. The locations of some major cities with more than one million population related in this study (such as Tianjin, Shijiazhuang, Jinan, Handan, and Zibo) are marked with square symbol. The locations of remote Mt. Waliguan (36°17'N, 100°54'E; elevation 3816 m) with rare anthropogenic impact, Mt. Tai, and two typical mega cities with severe acid rain – Chongqing and Guangzhou – are also marked. The topographical map was derived from the Microsoft® Encarta® 2009 © 1993-2008.

Fig. 2. Quality control of chemical analysis: (a) the calculated EC versus the measured EC and (b) the ionic balance, n=131.

Fig. 3. Monthly mean of precipitation amount and VWM pH values of the precipitations.

Fig. 4. Frequency distribution (a) and time series (b) of precipitation pH values, n=131.

Fig. 5. Statistics of concentrations of ions in the precipitations. The box plots indicate the 10th, 25th, 75th, and 90th percentiles and VWM (cross symbol) of each ion.

Fig. 6. Monthly variations in the VWM concentrations of ions in precipitation from April 2001 to August 2005.

Fig. 7. Time series of (a) the equivalent mass ratios of NP to AP, (b) the NF of NH_4^+, (c) the NF of Ca^{2+} and (d) the NF of Mg^{2+}.

Fig. 8. Time series of the equivalent mass ratios of NO_3^- to SO_4^{2-}.

删除的内容: for

删除的内容: the

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删除的内容: and

删除的内容: s

删除的内容: (b)

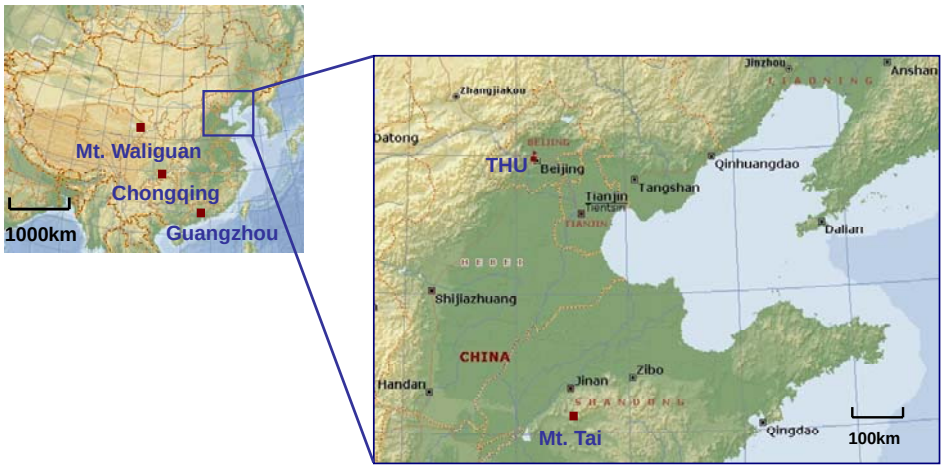

Mt. Waliguan
Chongqing
Guangzhou
1000km
Jinzhou
Anshan
Zhangjiakou
Datong
THU
Beijing
Qinhuangdao
Tangshan
Tianjin
Dalian
Shijiazhuang
CHINA
Handan
Jinan
Zibo
Mt. Tai
Qingdao
100km

Fig. 1.

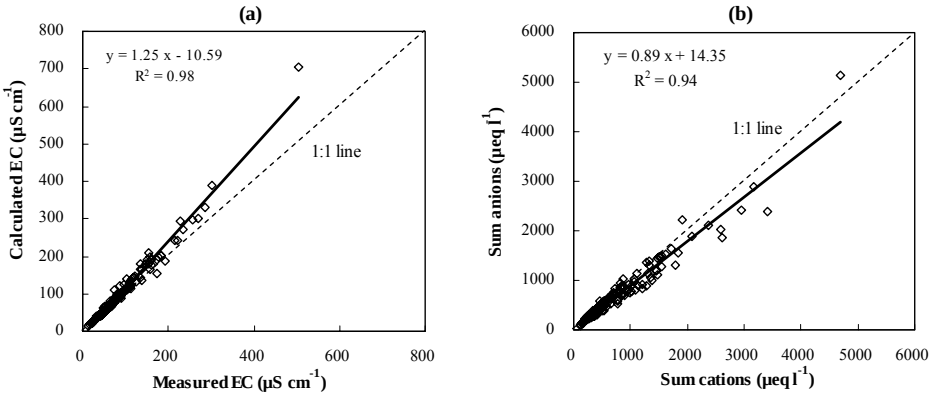

(a)
y = 1.25 x - 10.59
R2 = 0.98
1:1 line
Calculated EC (µS cm-1)
Measured EC (µS cm-1)
0
100
200
300
400
500
600
700
800
0
200
400
600
800
(b)
y = 0.89 x + 14.35
R2 = 0.94
1:1 line
Sum anions (µeq l-1)
Sum cations (µeq l-1)
0
1000
2000
3000
4000
5000
6000
0
1000
2000
3000
4000
5000
6000

Fig. 2.

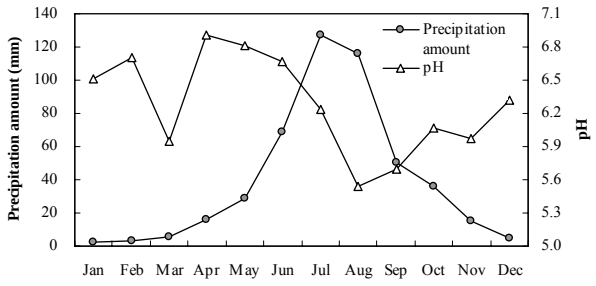

Precipitation amount (mm)
pH
Precipitation amount
pH
140
120
100
80
60
40
20
0
7.1
6.8
6.5
6.2
5.9
5.6
5.3
5.0
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec

Fig. 3.

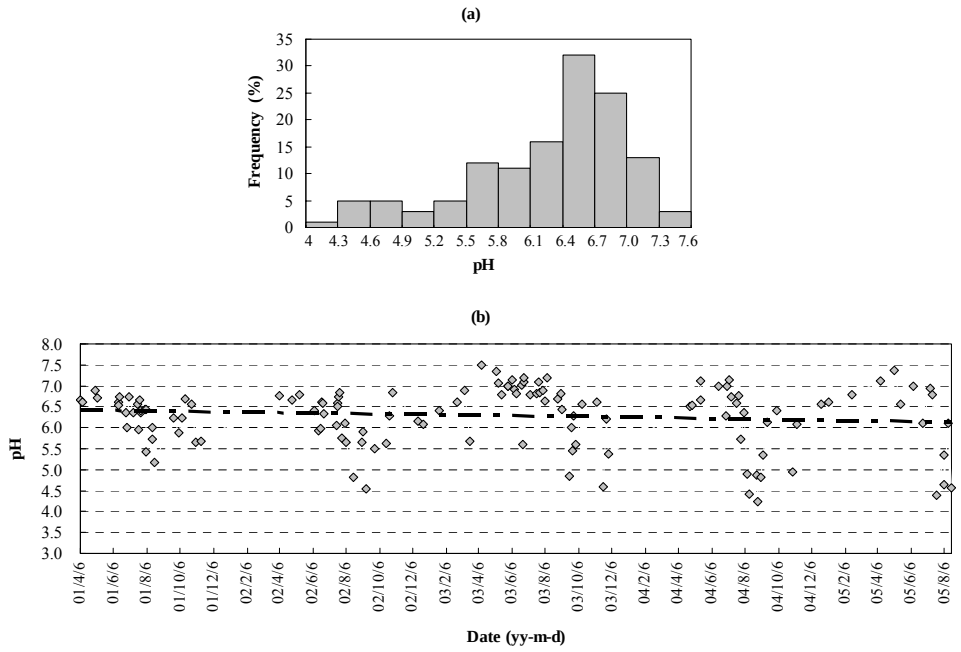
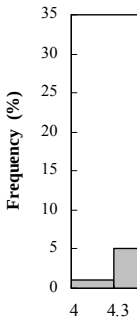

(a)
Frequency (%)
35
30
25
20
15
10
5
0
4 4.3 4.6 4.9 5.2 5.5 5.8 6.1 6.4 6.7 7.0 7.3 7.6
pH
(b)
pH
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
01/4/6 01/6/6 01/8/6 01/10/6 01/12/6 02/2/6 02/4/6 02/6/6 02/8/6 02/10/6 02/12/6 03/2/6 03/4/6 03/6/6 03/8/6 03/10/6 03/12/6 04/2/6 04/4/6 04/6/6 04/8/6 04/10/6 04/12/6 05/2/6 05/4/6 05/6/6 05/8/6
Date (yy-m-d)

Fig. 4.


Frequency (%)
35
30
25
20
15
10
5
0
4 4.3

删除的内容:

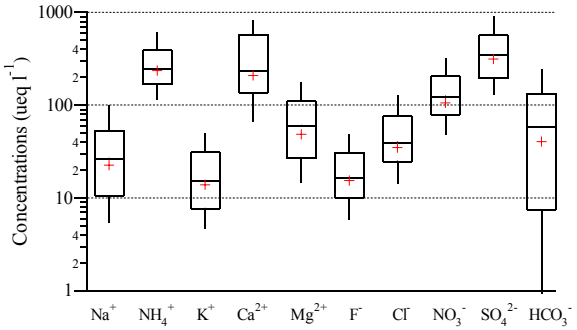

Concentrations (ueq l-1)
1000
4
2
100
4
2
10
4
2
1
Na+
NH4+
K+
Ca2+
Mg2+
F-
Cl-
NO3-
SO4 2-
HCO3-

Fig. 5.

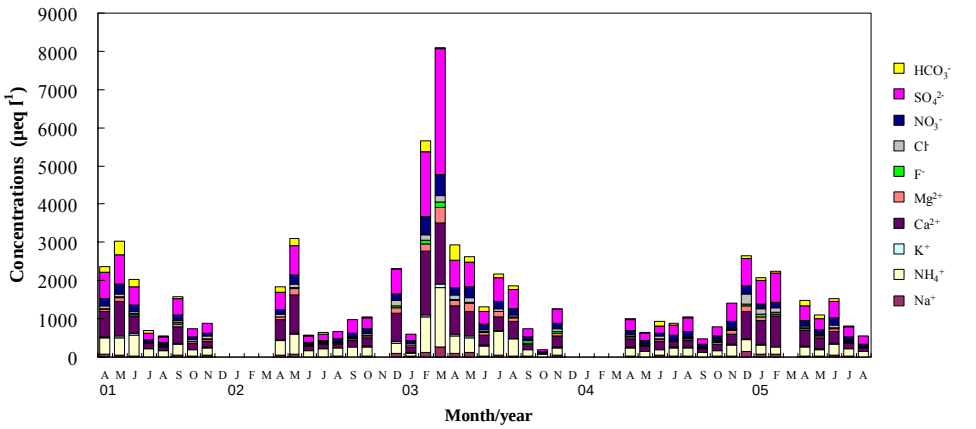
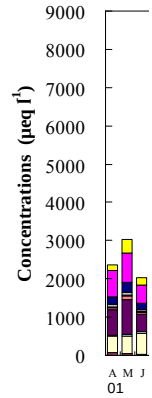

Concentrations (μeq l-1)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A
01
02
03
04
05
Month/year
HCO3-
SO42-
NO3-
Cl-
F-
Mg2+
Ca2+
K+
NH4+
Na+

Fig. 6.

删除的内容:


Concentrations (μeq l-1)
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
A M J
01

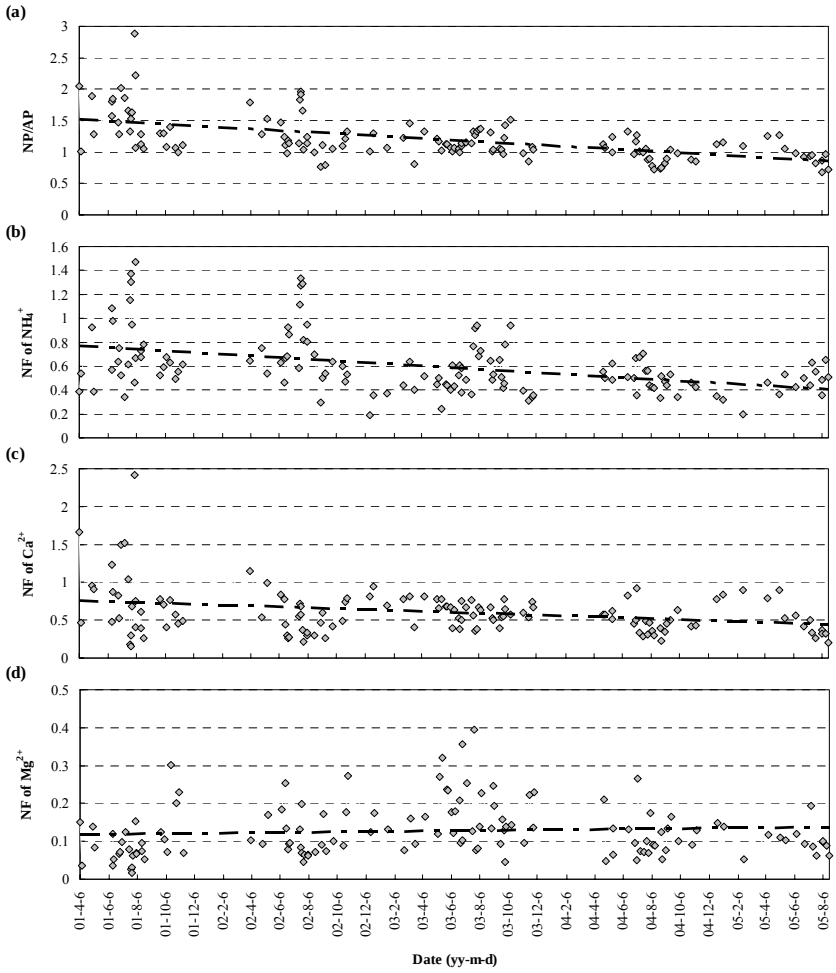


Fig. 7.

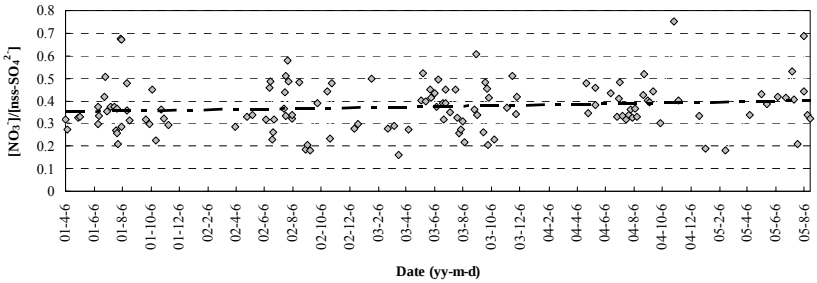

0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
[NO3-]/[nss-SO4 2-]
01-4-6
01-6-6
01-8-6
01-10-6
01-12-6
02-2-6
02-4-6
02-6-6
02-8-6
02-10-6
02-12-6
03-2-6
03-4-6
03-6-6
03-8-6
03-10-6
03-12-6
04-2-6
04-4-6
04-6-6
04-8-6
04-10-6
04-12-6
05-2-6
05-4-6
05-6-6
05-8-6
Date (yy-m-d)

Fig. 8.

页 2: [1] 删除的内容 USER- 2012-1-28 9:38:00
on an

页 2: [1] 删除的内容 USER- 2012-1-28 9:38:00
event basis

页 2: [1] 删除的内容 USER- 2012-1-29 12:00:00
through

页 2: [1] 删除的内容 USER- 2012-1-29 11:40:00
at an urban location in Beijing

页 2: [1] 删除的内容 USER- 2012-1-27 12:15:00
with

页 2: [2] 删除的内容 USER- 2012-1-18 11:06:00
Most

页 2: [2] 删除的内容 USER- 2012-1-27 11:21:00
had an intermediate pH (6.1-7.3)

页 2: [2] 删除的内容 USER- 2012-1-27 11:22:00
were acidic

页 2: [2] 删除的内容 USER- 2012-1-27 11:23:00
As the major ions,

页 2: [2] 删除的内容 USER- 2012-1-29 12:27:00
plus

页 2: [2] 删除的内容 USER- 2012-1-27 11:23:00
, and

页 2: [2] 删除的内容 USER- 2012-1-29 12:29:00

页 2: [2] 删除的内容 USER- 2012-1-28 14:20:00
plus

页 2: [2] 删除的内容 USER- 2012-1-27 11:24:00
comprised

页 2: [2] 删除的内容 USER- 2012-1-28 14:01:00
Different from their more or less reductions of gaseous precursors, the counterintuitive features of much less than expected decrease in SO_4^{2-} levels and unexpected increase in NO_3^- concentrations in the precipitations are likely due to the combination of

页 2: [2] 删除的内容 USER- 2012-1-27 11:30:00

enhanced

页 2: [2] 删除的内容 USER- 2012-1-27 11:30:00

,

页 2: [2] 删除的内容 USER- 2012-1-27 11:30:00

increased

页 2: [2] 删除的内容 USER- 2012-1-30 19:30:00

it exhibited

页 2: [2] 删除的内容 USER- 2012-1-29 11:33:00

significant

页 2: [2] 删除的内容 USER- 2012-1-29 11:33:00

pattern

页 2: [2] 删除的内容 USER- 2012-1-30 19:56:00

indicative of a long-term increasing trend in the acidifying potential of

页 2: [3] 删除的内容 USER- 2012-1-30 19:56:00

wet depositions.

页 2: [3] 删除的内容 USER- 2012-1-30 17:45:00

is

页 2: [3] 删除的内容 USER- 2012-1-28 13:19:00

two major alkaline agents –

页 2: [3] 删除的内容 USER- 2012-1-28 13:22:00

–

页 2: [3] 删除的内容 USER- 2012-1-27 11:36:00

over increased input of a minor alkaline agent – Mg^{2+} – according to

页 2: [3] 删除的内容 USER- 2012-1-30 17:52:00

the magnitudes of their neutralization factors

页 2: [3] 删除的内容 USER- 2012-1-27 11:37:00

T

页 2: [4] 删除的内容 USER- 2012-1-27 11:37:00

evident

页 2: [4] 删除的内容 USER- 2012-1-27 11:40:00

with a still low mean value of 0.37±0.11. This indicates

页 2: [4] 删除的内容 USER- 2012-1-29 11:34:00

relative

页 2: [4] 删除的内容 USER- 2012-1-30 12:03:00

wet deposition

页 2: [4] 删除的内容 USER- 2012-1-18 19:52:00

was strengthened

页 2: [4] 删除的内容 USER- 2012-1-27 11:43:00

while

页 2: [4] 删除的内容 USER- 2012-1-27 11:49:00

overwhelmingly

页 2: [4] 删除的内容 USER- 2012-1-29 11:36:00

but not

页 2: [5] 删除的内容 USER- 2012-1-28 14:22:00

chemistry

页 2: [5] 删除的内容 USER- 2012-1-28 9:55:00

can

页 2: [5] 删除的内容 USER- 2012-1-28 9:55:00

insights into

页 2: [5] 删除的内容 USER- 2012-1-27 15:35:00

4

页 2: [5] 删除的内容 USER- 2012-1-29 13:44:00

;

页 2: [5] 删除的内容 USER- 2012-1-29 13:49:00

页 2: [6] 删除的内容	unknown	2012-1-19 14:30:00

A

页 2: [6] 删除的内容	unknown	2012-1-19 14:30:00

in China

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counterintuitive features of less than expected decrease

页 9: [8] 删除的内容	USER-	2012-1-30 9:46:00

unexpected increase in

页 9: [9] 删除的内容	USER-	2012-1-30 9:46:00

(as compared to the substantial decrease in atmospheric SO_2 and NO_2)

页 9: [10] 删除的内容	USER-	2012-1-30 9:49:00

mean concentrations of

页 11: [11] 删除的内容	USER-	2012-1-30 20:06:00

over the past decade