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

F. Yang[1], J. Tan[1], Z. B. Shi[2], Y. Cai[1], K. He[3], Y. Ma[3], F. Duan[3], T. Okuda[4], S. Tanaka[4], G. Chen[5], and L. Bai[6]

[1] College of Earth Science, Key Laboratory of Computational Geodynamics, Graduate University of Chinese Academy of Sciences, Beijing 100049, China
[2] School of Geography, Earth and Environmental Science, University of Birmingham, Edgbaston Birmingham B15 2TT, UK
[3] School of Environment, Tsinghua University, Beijing100084, China
[4] Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan
[5] Chongqing Environmental Protection Bureau, Chongqing 401147, China
[6] Tianjin Key Laboratory of Water Resources and Environment, Tianjin Normal University, Tianjin 300387, China

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Correspondence to: F. Yang (fmyang@gucas.ac.cn)

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Abstract

Precipitation samples on an event basis were collected from March 2001 through August 2005 at an urban location in Beijing. Ionic species in the samples were measured with ion chromatography to understand the long-term changes in the precipitation chemistry and their causes. Most precipitation samples had an intermediate pH (6.1–7.3) and 16 % were acidic. As the major ions, SO_4^{2-} plus NO_3^-, and NH_4^+ plus Ca^{2+} comprised more than 80 % of anionic and cationic mass, respectively. 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 enhanced conversion of gaseous precursors to acid compounds, and increased regional transport. The average ratio of neutralizing to acidifying potential (i.e. NP/AP) was as high as 1.2 but it exhibited a significant decline pattern, indicative of a long-term increasing trend in the acidifying potential of the wet depositions. This is mainly ascribed to reduced input of two major alkaline agents – NH_4^+ and Ca^{2+} – over increased input of a minor alkaline agent – Mg^{2+} – according to the magnitudes of their neutralization factors. The equivalent mass ratio of NO_3^- to nss-SO_4^{2-} presented an evident increasing trend with a still low mean value of 0.37±0.11. This indicates that the relative contribution of NO_3^- to the wet deposition acidity was strengthened in recent years while the precipitation acidity in Beijing was still overwhelmingly from sulfur but not nitrogen.

1 Introduction

The chemical composition of atmospheric depositions is the signature of numerous physical and chemical mechanisms of aerosol and precursor emissions, transport, chemical reactions, and removal processes. Therefore, the chemistry of wet depositions can provide insights into temporal evolution of atmospheric pollution, and be used as a pertinent indicator to evaluate natural process versus anthropogenic influences

(Grodzińska-Jurczak and Godzik, 1999; Tang et al., 2004; Özsoy et al., 2008). Acid deposition has been one of the most significant environmental issues in China 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), 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 the south of 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, and the trend in precipitation chemistry and its influence under the background of fast economic development are of great concern.

As the capital and one of the most populated mega cities in China, Beijing has experienced rapid urbanization and motorization since the 1980s. Along with soaring demand in energy to fuel its economic development, the vehicular exhaust pollution becomes more and more outstanding in Beijing while the traditional pollution caused by coal burning has not been effectively controlled. In addition, a great deal of construction activities inevitably cause fugitive dust and exacerbate particulate loadings. Meanwhile, the precipitation pH in Beijing exhibited an evident decreasing trend (Ding et al., 1997; Wang and Zhang, 1997; Feng et al., 2001). To improve the air quality in the capital area, the municipal government has initiated a series of clean air programs starting in 1998 (www.bjepb.gov.cn). As a result, air quality compliance days, which are defined when the maximum air pollution index of SO_2, NO_2, and PM_{10} is no more than 100, have kept increasing thereafter (www.bjepb.gov.cn), but less than what was expected in terms of particulate pollution (Yang et al., 2011a). Some recent studies showed that pH and chemistry of precipitation in Beijing were noticeably different before and after the year of 2000 (Tang et al., 2004; Hu et al., 2005; Xu and Han, 2009). To our knowledge, there are none 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 NO_2) and neutralizing substances in Beijing and nationwide 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. This paper will summarize the major findings with a focus on temporal variations in the precipitation chemistry. Possible mechanisms influencing these variations will also be discussed.

2 Experimental

2.1 Sampling location and sample collection

Beijing is located on the northern border of the Great North China Plain with a landmass of 16 410 km^2 (Fig. 1). As one of the most populated cities in China, its 15.8 million population is concentrated in the urbanized area accounting for only 6 % of the city's landmass, i.e. within the fifth ring road – an express highway that encircles the city at an about 14 km radius from the city centre (Beijing Municipal Bureau of Statistics, 2008). The main terrain of Beijing is plain, with surrounding mountains on three sides, i.e. the Mongolian to the north, the Yanshan Mountain to the northeast, and the Bohai Sea is 160 km to the southeast. Thus the air pollutants can not be easily dispersed. Lying in the 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 and Beijing is apt to be impacted by regional and/or local soil dust, while at other times the local winds are moderate and mostly from the south and southeast (Yang et al., 2011a).

Sampling of atmospheric precipitation 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 15 March 2001 through 18 August 2005 (Fig. 1). About 12 km northwest of the city centre, the THU site lies within the western part between the northern forth and fifth ring roads, which are two of the artery roads with busy traffic circling urban area. Our previous studies showed that it is representative of an urban area because of the

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strong impact by a mixture of emission sources due to rapid urbanization in and around this area (He et al., 2001; Yang et al., 2011a). Precipitations were collected with a dry-wet 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 sample was collected once every continuous rainfall. Totally 137 precipitation samples were collected over the study period.

2.2 Sample analyses and quality control

Precipitation sample was weighed in the laboratory and calculated for the volume. The precipitation was 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 °C), and the electrical conductivity (EC) was measured with an electrical conductivity meter (AOL-40, Denki Kagaku Keiki). H^+ concentration was determined by calculation from the pH of the filtrate. 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/1 mM 2,6-Pyridinedicarboxylic acid/24 mM Boric acid 1.0 (ml min^{-1}) for cations. For anions except HCO_3^- they were AS12A (Dionex) and 2 mM Na_2CO_3/4 mM $NaHCO_3$ 1.0 (ml min^{-1}), while for HCO_3^- they were ICE-AS1 (Dionex) and Milli-Q (Millipore), respectively. If not all the above anions (except HCO_3^- for some samples) and cations were measured due to insufficient rainfall volume, the precipitation sample was not considered in this study. 6 out of the 137 rain samples were thus discarded.

For ionic analyses, repeatability was determined by analysis of precipitation samples 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 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 of set by USEPA is 15–30 % for samples having ion sum $>100\,\mu\text{eq}\,\text{l}^{-1}$ (Ayers, 1995). The concentration ratio of sum anions to sum cations was systematically <1 (Fig. 2b), suggesting an anion deficit. This predominance is very frequent 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

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 largely lower than long-term average in Beijing (www.bjmb.gov.cn). As shown in Fig. 3, monthly mean precipitation amount varied markedly with a peak in summer. About 78 % of the rain was deposited during the four months from June to September (rainy months). VWM EC in the precipitation was $66.5\,\mu\text{S}\,\text{cm}^{-1}$, which was greater by a factor 4.6 than that ($14.6\,\mu\text{S}\,\text{cm}^{-1}$) measured at a remote site in Mt. Waliguan (marked in Fig. 1), i.e. the Global Atmosphere Watch Baseline Observatory of World Meteorological Organization (WMO) located in the east edge of Qinghai-Tibetan Plateau in Northwest China (Tang et al., 2000). This indicates a substantial impact of the anthropogenic pollution on the urban atmospheric environment in Beijing.

Figure 4 illustrated the frequency distribution of precipitation pH. This pH distribution pattern was similar to a unimodal distribution, but was 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 VWM of 6.0 for the total 131 precipitations. Approximately two-thirds of precipitation samples had pH values between 6.1 and 7.5, whereas only 16 % of the rain events were acidic with pH < 5.6 – the pH value of pure water in equilibrium with atmospheric CO_2. This distribution reflected the alkaline nature of rainwater in urban Beijing. It should be also noted, however, that nine of thirteen low pH (< 5.0) rains were collected in the latter two years. This trend is consistent with the noticeable decreasing trend in rainfall pH during 1980–2000 as noted earlier (Ding et al., 1997; Wang and Zhang, 1997), indictive of 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 Sect. 3.4. The monthly VWM pH values varied from 5.3 to 6.8 and averaged at 6.2. Only August had VWM pH less than 5.6. There were eleven low pH rains occurring during July–September and their majority came in August. Since summertime precipitations shared two-third annual volume and usually presented low pH values (Fig. 3), yearly wet deposition acidity was mainly determined by the rains falling in this season.

3.2 Chemical composition and sources of major ions

Statistics of ionic concentrations for all the precipitation samples are shown in Fig. 5. SO_4^{2-}, NO_3^-, NH_4^+, and Ca^{2+} were the most abundant ions and their single VWM concentrations were 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^- explained 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^+.

Major anthropogenic ions – SO_4^{2-}, NO_3^- and NH_4^+ – accounted for 63 % of 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+} – together contributed 28 % to the total ionic mass, indicating crustal material was an important contributor to precipitation neutralization. The non-sea calcium (nss-Ca^{2+}) accounted for 99.6 % of total calcium for all the wet samples, indicating that sea salt did not have strong impact on wet deposition in Beijing. The non-sea salt sulfate (nss-SO_4^{2-}) accounted for 97.8 % of the total sulfate.

Table 1 lists the VWM pH and 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 at 9 sampling sites in the Tokyo Metropolitan with precipitation pH of 4.5 during June 1990–May 2002, VWM concentrations of the two major anions – SO_4^{2-} and NO_3^- – in Beijing were higher by a factor of 3.8 and 7.6, and those of the two major cations – NH_4^+ and Ca^{2+} – were higher 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 that measured in Guangzhou (marked in Fig. 1) in 2005 (Table 1) (Huang et al., 2009). In comparison with those monitored at the Mt. Waliguan site, 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 greater 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 results suggest that a large fraction of the F^- in Beijing precipitations was likely from anthropogenic source. Based on a study conducted 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 inorganic ions 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. 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 (Tang et al., 2005; 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) is much higher than their 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., 2011a). 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, NO_x, and NH_3. While SO_2 and NO_x are believed to be mainly emitted from fossil fuel combustion, the major anthropogenic sources of ammonia in East Asia were estimated to be mainly from chemical fertilizer, livestock, and energy consumption (Zhao and Wang, 1994). Factor 3 is dominated by Ca^{2+}, F^-, NO_3^-, and K^+, likely pointing to soil dust as a major source. It is noted that there are plentiful 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 significant part of NO_3^- exists in coarse particles since it is apt to react with soil dust after its conversion from NO_x (Seinfeld and Pandis, 1998).

3.3 Temporal variations in concentrations of major ions

Time series of monthly average concentrations of ions in the precipitation experienced dramatic variations (Fig. 6). Both high loadings of crustal-related and anthropogenic ions usually appeared during the months from November to April while their low levels usually occurred in rainy months. This seasonal pattern was most likely due to the combination 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, coal combustion activities were considerably enhanced (about 5 million tons additional coal consumed) for heating in Beijing during official four-month heating period lasting from the mid-November to mid-March, resulting in extra anthropogenic emissions of gaseous pollutants (e.g. SO_2 and NO_2) 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 VWM concentrations 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 ($r = -0.18$ 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 were collected in March 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 20 March when daily PM_{10} concentration was as high as 179 $\mu g\,m^{-3}$. In addition, the average ionic concentrations in July and August of 2003 were higher than those in other years by a factor of 2.6–3.4. Along with the above differences was that the seasonal distribution of precipitation volume in 2003 differed enormously from other years. The precipitation volumes in the winter, spring, and fall in that year increased by 50–160 % whereas the summer volume substantially decreased. 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 ions in Beijing precipitations in 2003 were also reported by Hu et al. (2005).

In regression over the study period, it is found that SO_4^{2-} maintained a steady level and NO_3^- exhibited a clear growing level, whereas NH_4^+ and Ca^{2+} showed an evident decline in their levels. This indicates that the enhancement of precipitation acidity was mainly due to reduced input of alkaline agents. In comparison with the study conducted in Beijing during 1995–1998 (Table 1), VWM concentrations of most ions 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-} 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.

These counterintuitive features of less than expected decrease in SO_4^{2-} and unexpected increase in NO_3^- concentrations (as compared to the substantial decrease in atmospheric SO_2 and NO_2) in the precipitations are likely due to the increased regional transport and enhanced conversion of gaseous precursors to acid compounds and/or secondary particles. Opposite to the decline of mean concentrations of SO_2 and NO_2 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 greater 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 NO_2) 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 covers densely populated and coal-fired cities (such as Tianjin Municipality, Shijiazhuang, and Jinan marked in Fig. 1) and the SO_2 and NO_2 emission per land area are 3.3 and 4.4 times of their corresponding national averages (Yang et al., 2011b). In addition, the decrease in SO_4^{2-} in the particulate matter which frees up ammonia to react with nitric acid, forming more NO_3^- (Seinfeld and Pandis, 1998), was at least partly responsible for the nearly doubled NO_3^- concentrations in precipitation. 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 $[NO_3^- + \text{nss-}SO_4^{2-}]$ as acidifying potential (AP) and $[NH_4^+ + \text{nss-}Ca^{2+}]$ 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 considerable decreasing trend over the study period with a reduction of the regression intercepts from 1.5 to less than 1.0. 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 pattern for Beijing precipitations. Given low pH rains concentrated 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:

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

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, indicative of 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+}, while 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 annual mean concentrations ranging 141–165 $\mu g\,m^{-3}$ while gaseous pollutants were effectively reduced as noted earlier (www.bjepb.gov.cn). Also noted is that the activity level of construction was increased year by year in the past decade due to rapid urbanization and it was enhanced dramatically after Beijing won the bid in 2001 to host the 2008 Olympic Games. According to a statistics there were more than 1200 construction and demolition sites, covering a total area of about 32 km^2 in June 2001 (Yang et al., 2004).

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 $[NO_3^-]/[\text{nss-}SO_4^{2-}]$ 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 and averaged 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), reflecting that the enhancement of relative 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., 2011b). This $[NO_3^-]/[\text{nss-}SO_4^{2-}]$ value is much greater than that in Chongqing during the same period (0.18 ± 0.35) – a typical acid rain area with abundant high-sulfur coal consumption in Southwest China (marked in Fig. 1) – but is only half of that in Tokyo Metropolitan (calculated from Table 1), indicating that the precipitation acidity in Beijing was still overwhelmingly from sulfur (i.e. sulfur type) but not nitrogen.

4 Conclusions

Event-based precipitation samples were collected from March 2001 through August 2005 at an urban location in Beijing to investigate chemical compositions and temporal variations in the precipitation chemistry and to explore the possible mechanisms influencing the trends. The pH of single rain event 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 mainly determined by the precipitations in summer and early fall, as they shared about 80 % of the annual volume and usually presented low pH values. The enhancement of precipitation acidity over the study period was mainly due to reduced input of alkaline agents. SO_4^{2-} was the most abundant single ion in precipitation with the VWM concentration of as high as 314 µeq l^{-1} and accounted for 30 % of total ionic mass. 84 % of anion 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 measured cation mass.

Concentrations of both crustal-related and anthropogenic ions in the precipitation were much higher 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, NP/AP ratio exhibited a significant decreasing trend over the study period and particularly compared to that (1.45) determined pre-1998. In contrary to substantial decline of SO_2 and NO_2 in ambient air of Beijing over the past decade, mean concentrations of SO_4^{2-} and NO_3^- in the precipitations showed less than expected decline and unexpected growth, respectively. The enhancement of relative contribution of NO_3^- to precipitation acidity was also a long-term trend, although the precipitation acidity was still overwhelmingly from sulfur but not nitrogen.

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Table 1. VWM pH and VWM concentrations (µeq l^{-1}) of major ions in precipitations in this study and some selected location in East Asia. The selected locations in China are marked in Fig. 1.

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	–[a]	15.5	30.2	132[b]	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)

[a] Not determined.
[b] Nss-SO_4^{2-}.

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Table 2. Factor analysis of major ions in precipitation.

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
NH_4^+	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	–

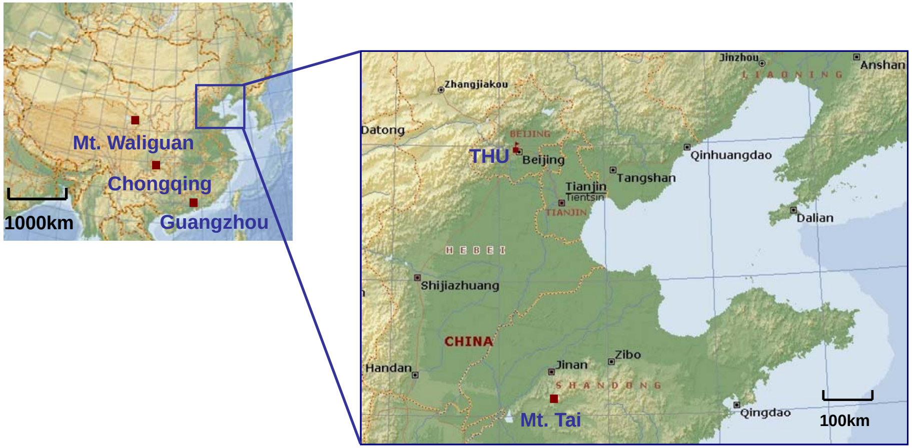

Fig. 1. Sampling site (THU) in Beijing. The locations of some major cities with more than one million population related in this study (such as Tianjin, Shijiazhuang, Jinan, Handan, and Zibo) are marked with square symbol. The locations of remote Mt. Waliguan (36°17′ N, 100°54′ E; elevation 3816 m) with 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.

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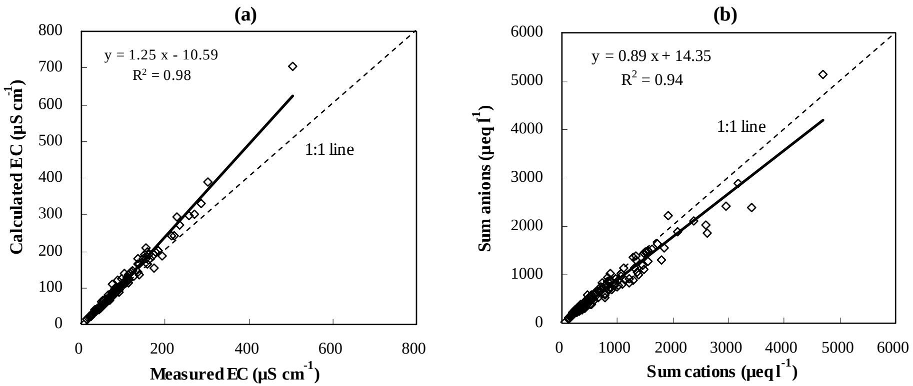

Fig. 2. Quality control of chemical analysis for **(a)** the calculated EC versus the measured EC and **(b)** the ionic balance, $n = 131$.

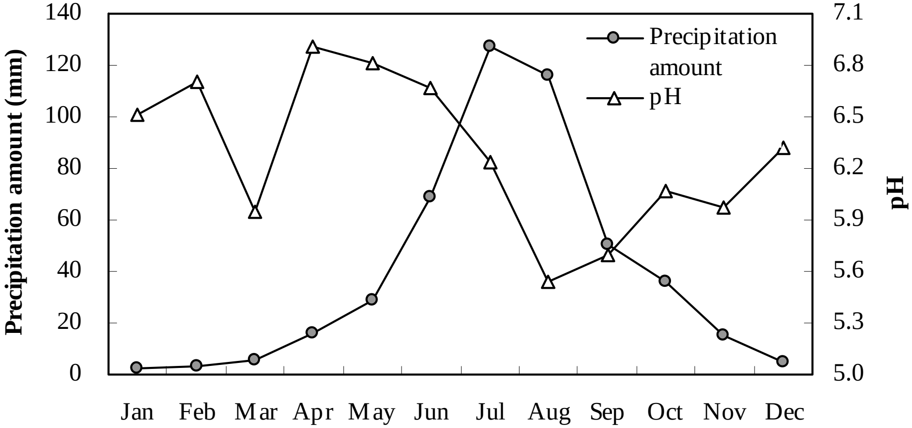

Fig. 3. Monthly mean of precipitation amount and VWM pH values of the precipitations.

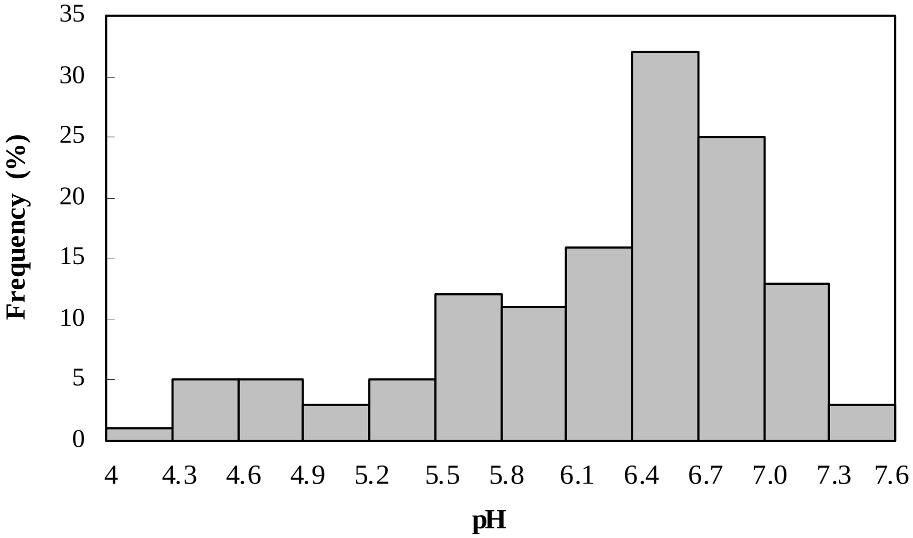

Fig. 4. Frequency distribution of precipitation pH values, $n = 131$.

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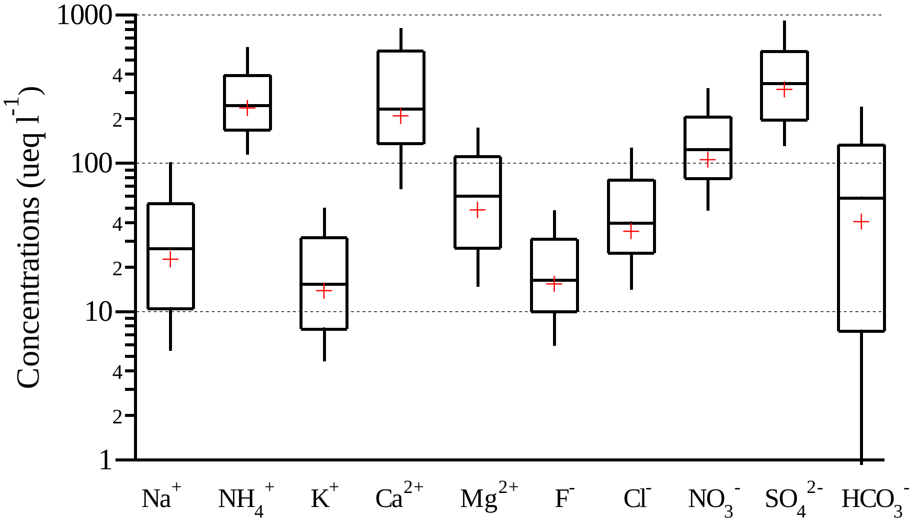

Fig. 5. Statistics of concentrations of ions in the precipitations. The box plots indicate the 10th, 25th, 75th, and 90th percentiles and the VWM concentration (cross symbol) of each ion.

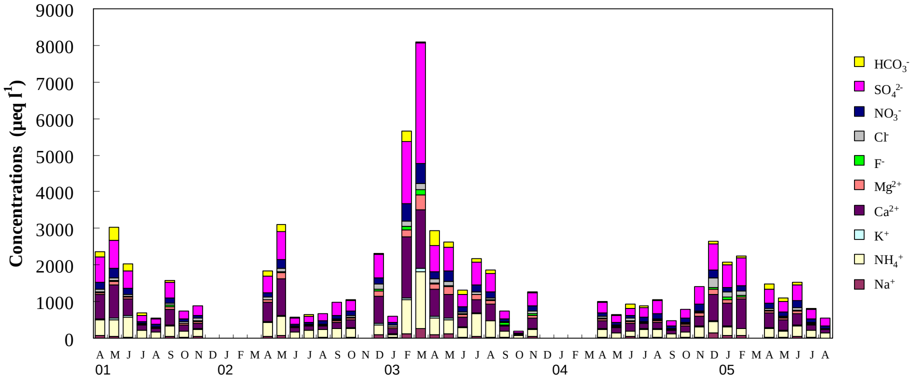

Fig. 6. Monthly variations in VWM concentrations of ions in precipitation from April 2001 to August 2005.

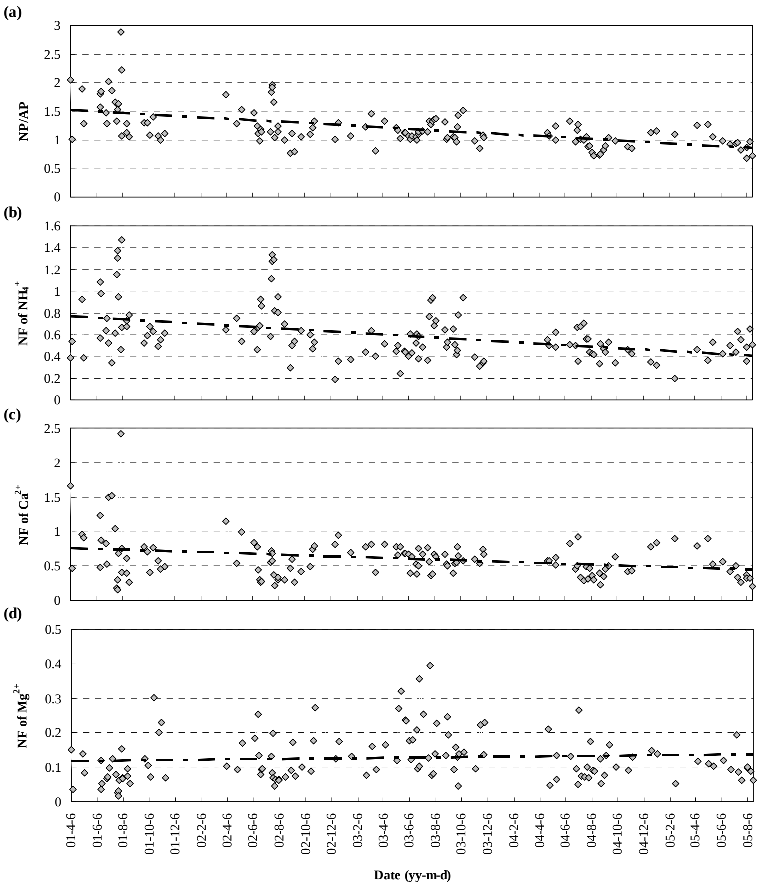

Fig. 7. Time series of **(a)** equivalent mass ratios of NP to AP and NFs of **(b)** NH_4^+, **(c)** Ca^{2+} and **(d)** Mg^{2+}.

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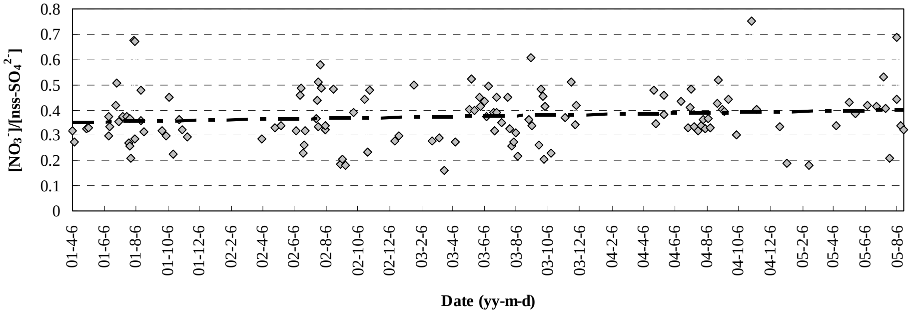

Fig. 8. Time series of equivalent mass ratios of NO_3^- to SO_4^{2-}.