The chemistry of precipitation and its relation to aerosol in Beijing

Aohan Tang\textsuperscript{a}, Guoshun Zhuang\textsuperscript{a,b,c,*}, Ying Wang\textsuperscript{a,b}, Hui Yuan\textsuperscript{a,b}, Yele Sun\textsuperscript{a}

\textsuperscript{a}Center for Atmospheric Environmental Study, Department of Chemistry, Beijing Normal University, Beijing 100875, China
\textsuperscript{b}Center for Atmospheric Chemistry Study, Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, China
\textsuperscript{c}The Institute of Atmospheric Physics, CAS, NZC/LAPC, Beijing 100029, China

Abstract

Fifty-three rain events throughout the entire year of 2003 were collected in Beijing and the concentration of 15 major ions with the pH of the rainwater were analyzed. The close correlations of the acidity in rainwater with the concentrations of aerosol and gases in the air were observed and elaborated. The scavenging of the pollutants from the air directly affects the pH and composition of the rainwater. The major ions in rainwater in Beijing were SO$_4^{2-}$, NO$_3^-$, Cl$^-$, NH$_4^+$, Ca$^{2+}$, Mg$^{2+}$, K$^+$, and F$^-$. The alkaline cations, NH$_4^+$ and Ca$^{2+}$, acted as acid neutralizers and buffered the acidity of rain. The temporal variation of those major pollution ions in rainwater was similar to that of the air pollution. The concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ have increased for the last two decades and likely indicated that the air pollution has become more and more serious in Beijing since the 1980s. The ratio of the concentration of SO$_4^{2-}$ to NO$_3^-$ observed in 2003 was much lower than that in 1981, indicating that the air pollution resulting from the traffic emission, NO$_x$, has been more significant. A remarkably positive correlation between pH and Ca$^{2+}$ concentration illustrates that Ca$^{2+}$ generally from mineral aerosols plays an important role in buffering rainwater acidity in Beijing and in northern China at all times. The concentrations of SO$_4^{2-}$ and NO$_3^-$, the predominant acid anions in rain, was much higher in Beijing than other cities, suggesting that the anthropogenic air pollution in Beijing has been a much more serious problem than other places.

$^*$ Corresponding author. Center for Atmospheric Environmental Study, Department of Chemistry, Beijing Normal University, Beijing 100875, China. Tel.: +86 21 5566 4579; fax: +86 10 8290 2844.
E-mail addresses: gzhuang@bnu.edu.cn, gzhuang@fudan.edu.cn (G. Zhuang).

Keyword: Rainwater; Precipitation; pH; Acid rain; Aerosol; Buffer; Scavenging

1. Introduction

Precipitation is a quick and effective scavenging process to the aerosols and their components in the air. Nature keeps its stability and balance because of such a sink mechanism. The composition of precipitation, which is determined by “in-cloud” and “below-cloud” scavenging processes and incorporates both the gases and aerosol particles in the air, is very important to the environment and those organisms on the surface of the earth. The composition of rainwater varies from site to site, region to region due to the difference of the local sources. In the big cities there are more complicated components in the aerosols because of the industrial and traffic pollution, resulting in more
complicated composition of rainwater. To understand the air pollution comprehensively in such a big city, it is indispensable to study the precipitation deeply.

Rainwater chemistry has been the subject of intense research for the last two decades because of the increased awareness towards the environmental problems caused by acid rain. Especially, in developing countries concerns about air pollution and acid rain have emerged to be both the social and scientific issues due to the rapid economic development and the consequent increase in energy consumption. Following Northeast America and Central Europe, the East Asian region has become one of the seriously afflicted acid-rain areas in the world. In China, acid precipitation often occurs in its south part though the emissions of the precursors of acid rain are stronger in the North China. For example, although the air pollution in Beijing and Sichuan are all in the region mainly controlled by SO₂ emission, the acidity of rainwater in Sichuan, southwest of China, is mainly higher than that in Beijing. There must be other factors that influence the acidity of rainwater in Beijing, which should be taken into consideration thoroughly. To date, there has been fewer studies on the precipitation in Beijing, while there were many reports on the aerosol of Beijing. Zhao and Xiong (1988) measured the chemical compositions of rainwater in 1981 and reported that Beijing was in a non-acid rain area. Wang and Ding (1997) monitored the pH value and analyzed the relationship between pH value and airflows in Beijing by back trajectories for the typical precipitation events from August to September in 1994. However, these studies did not investigate deeply the composition and the sources of those components in rain, nor the causes of the acidity in rainwater and its relation to the aerosols in the air. With the rapid economic development, the local environment and the climate have changed greatly in Beijing since the 1980s. To have a systematic investigation in finding how the air and precipitation respond to the rapid economic development in Beijing, we collected and analyzed the rain samples throughout the year of 2003 in Beijing. In this study, we report the detailed observation in the 1-year monitoring campaign of the precipitation and elaborate the close correlations of the acidity in rainwater with the concentrations of aerosol and gases in the air in Beijing.

2. Experimental

2.1. Sample collection

Beijing, the capital of China, lies in north China at 39.9°N and 116.4°E with an area of 16 427.2 km² and a population of ~11 million. The climate of this metropolitan region is cold and dry in winter and hot and wet in summer. The precipitation is ~380 mm yearly. The rain samples were collected on the roof of the Science and Technology Building, ~40 m above the ground, at Beijing Normal University (BNU) that was located in a traffic area between the second and third Ring roads of Beijing (the detail was given elsewhere, Sun et al., 2004). A polypropylene bag fixed on a rack ~1 m above the roof, which was freed from any obstacles in sight, was used to collect the rain sample manually. Before each sampling the bag was rinsed thoroughly with deionized water (Barnstead, EasyPure LF compact ultrapure water system, the resistivity of the water is 18.1–18.3 MΩ cm⁻¹) several times till the conductivity of the water became less than 2 μS cm⁻¹. To prevent any contamination from dry deposition, the collector surface was covered with a plastic lid that was removed while sampling just prior to the onset of rain. Each sampling started at the onset of each rainfall event. In addition, a plastic pail (inner diameter 18.2 cm) was also used to collect rainwater synchronously, which was used only for measuring the rainfall amount of each event. For the intensive rainfall events, rainwater was collected sequentially and we separated the samples of the first 10 min collecting from the rest. The volume weighted mean concentration of those sequential samples of the intensive rainfalls was calculated and used in this study. As the rainfall intensity was mostly weak in Beijing and the rainfall amount of the first 10 min in those week rain events was not enough for the normal analysis, we collected these rainwater samples for the entire event. The collected rainwater was gathered in a 50 ml polypropylene bottle that was washed twice or three times with ultra-pure water till the conductivity was lower than 2 μS cm⁻¹ and full of the pure water for at least 24 h before using it. In case the overall rainfall amount was lower than 0.8 mm, the sample was not enough for the chemical analysis and such a rain event was neglected. The pH value was measured immediately after the collection of the samples, and the rain samples were filtered through 0.45 μm Millipore membrane filter and stored in a refrigerator at 4 °C prior to chemical analysis.

Fifty-three rain samples were collected effectively in 2003 in Beijing and the concentrations of the related components and the rainfall of each event was measured simultaneously. There were totally 75 rain events in 2003 in Beijing according to the annual weather report from CDC online (www.cdc.cma.gov.cn), and those rainfalls in winter were too small to be measured. As summer is the rainy season of Beijing and the rainfall increases rapidly with the arrival of the southeast monsoon (Wang and Ding, 1997), the rain samples collected in this study covered all of those rain events in the entire summer and all of those notable rain events in other seasons and it could be seen as a good representative of the rain of the entire year in Beijing.
In addition, a total of 55 TSP samples were collected before or after the rain events from the same sampling site. An aerosol middle-flow impact sampler (Beijing Geological Instrument—Dickel Co., Ltd., model: (TSP/PM$_{10}$/PM$_{2.5}$)-2, flow rate: 77.59 L min$^{-1}$) was employed for TSP sampling. The aerosols were collected on the Whatman 41 filter membrane (Whatman Company, UK) and the membranes after sampling were weighed using an analytical balance (model: Sartorius 2004MP) with a reading precision 10$^{-1}$ mg after stabilizing under constant temperature (20$\pm$5°C) and humidity (40$\pm$2%). All the procedures were strictly quality-controlled to avoid any possible contamination to the samples. The detailed procedures were given elsewhere (Sun et al., 2004; Dan et al., 2004). The monthly average values of mass concentration of PM$_{10}$, SO$_2$, and NO$_2$ in Beijing were obtained from Air Pollution Index (API, API = 100 corresponds to Chinese air quality standard II) in the annual report of China EPA at www.bjepb.gov.cn, which were converted to concentrations. The formulas used for converting API to concentration is 

\[ C = C_{low} + \left[ \frac{(I-I_{low})}{(I_{high}-I_{low})} \times (C_{high}-C_{low}) \right], \]

where $C$ is the concentration and $I$ is the API value. $I_{high}$ and $I_{low}$, the two values most approaching value $I$ in the API grading limited value table, stand for the value larger and lower than $I$, respectively; $C_{high}$ and $C_{low}$ represent the concentrations corresponding to $I_{high}$ and $I_{low}$, respectively.

2.2. Sample analysis

The filtered sample stored in refrigerator was divided into two aliquots. The first was used for measuring the concentrations of anions and cations, and the second was preserved and used for measuring the trace metals. In this study, only the ions in the soluble parts of the rainwater samples were discussed. The filtrates were analyzed by Ion Chromatography (IC, Dionex 600, USA), which consists of a separation column (Dionex Ionpac AS11), a guard column (Dionex Ionpac AG 11), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), and a gradient pump (Dionex Ionpac GP50). Ten anions (F$^-$, CH$_3$COO$^-$, HCOO$^-$, MSA, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, C$_2$O$_4^{2-}$, PO$_4^{3-}$) and five cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) were quantitatively measured. The gradient weak base eluent (76.2 mM NaOH + H$_2$O) was used for anion ion detection, while the weak acid eluent (20 mM MSA) for cation ion detection. The recovery of each ion was in the range of 80–120%. The relative standard deviation of each ion was less than 5% for reproducibility test. The quality assurance was routinely carried out by using Standard Reference Materials produced by National Research Center for Certified Reference Materials, China. A pH meter (model: Orion 828) with a combination glass electrode was used for pH measurement. The pH meter was calibrated before every measurement using standard pH 4.00 and 6.86 buffer solutions. The details were given elsewhere (Yuan et al., 2003).

3. Results and discussion

3.1. The acidity of rain in Beijing

Fig. 1(a) and (b) shows the frequency distribution and the event variation of pH of the rainwater in Beijing in 2003. As the pH of the unpolluted natural water in equilibrium with atmospheric CO$_2$ is 5.6, the rainwater, in which the pH is less than 5.6, is considered to be acid rain. It could be seen clearly that there were five acidic events out of the 53 events in 2003, 9% of the total rain events measured, in which the pH values were less than 5.6, and two events, in which the pH values were approaching 4.5. Perhaps using pH$<5$ to be the critical line of the acid rain would be more reflective of the effects of human-induced pollution in the absence of a substantial amount of base cations (Seinfeld and Pandis,
samples, anions HCO$_3^-$ samples with lower ratio, which indicated that in those measured practically. However, there were a few that the majority of the ions in rain samples were study fell within this acceptable range, which indicated 2000). The observed ratio of cations to anions in this samples is within the range of 1

2. Ionic composition of rainwaters in Beijing

Ten anions (F$^-$, CH$_3$COO$^-$, HCOO$^-$, MSA, Cl$^-$, NO$_2^-$, NO$_3^-$, SO$_4^{2-}$, C$_2$O$_4^{2-}$, PO$_4^{3-}$) and five major cations (Na$^+$, NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$) were quantitatively measured with IC. As IC is unable to measure HCO$_3^-$ and CO$_3^{2-}$ we did not report the concentrations of these two ions in this study although the carbonate/bicarbonate ions in rainwaters would generally be in equilibrium with CO$_2$ in the air. To ensure the reliability of these ion data and to find the possibility of any other ions that exist in rain with notable concentrations and should not be ignored, the balance of anions with cations must be checked carefully at first. Fig. 2 shows the ion balance for all the rain samples measured in this study. It seems generally acceptable if the concentration ratio of measured anions (Σ$-$) to cations (Σ$+$) in rainwater samples is within the range of 1±0.25 (Zhang et al., 2000). The observed ratio of cations to anions in this study fell within this acceptable range, which indicated that the majority of the ions in rain samples were measured practically. However, there were a few samples with lower ratio, which indicated that in those samples, anions HCO$_3^-$ and some organic acids were probably present in notable concentrations. The volume-weighted average concentrations (VWM) of the major ions in a period (in the entire year or in a month) were calculated with the formula $C = \sum_{i=1}^{n} C_i Q_i / \sum_{i=1}^{n} Q_i$, where $Q_i$ is the rainfall amount in mm and $C_i$ is the measured concentration in μeq L$^{-1}$. Accordingly, the average pH in a period could be calculated from the volume-weighted average concentration of H$^+$, i.e. $pH = -\log[H^+]$.

Fig. 3 shows the concentrations of the major ions in rain samples collected in Beijing in 2003. The concentrations of the major ionic species were in the following order: SO$_4^{2-}$ > NH$_4^+$ > Ca$^{2+}$ > NO$_3^-$ > Cl$^-$ > Mg$^{2+}$ > Na$^+$ > F$^-$ > K$. The most abundant ions in the rainwater in Beijing were SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and Ca$^{2+}$, and the VWM concentrations of these ions were in the order of magnitude of several hundred micro-equivalents per liter. There was the second group of ions, i.e. Cl$^-$, F$^-$, K$^+$, Na$^+$ and Mg$^{2+}$, which was in an order of magnitude of several tens of micro-equivalents per liter. As the composition of rainwater is determined by the scavenging processes of both gases and particles in the air, the magnitude of the concentration of ions in rainwater samples could reflect how serious the air pollution was. Table 1 lists the concentrations of the major ions in the rainwater samples collected from three cities: Beijing, Shanghai, and Lhasa. These three cities lie in different places. Lhasa, the capital city of Tibet, China, is on a high elevation, and Shanghai is a metropolis near the East Sea. It could be seen that the alkaline rain occurred in Lhasa, where the concentrations of SO$_4^{2-}$ and NO$_3^-$ were only in the order of magnitude of several micro-equivalents per liter, two orders of magnitude less than that in Beijing, indicating that the anthropogenic pollutants in Beijing were much heavier than those clean background sites, such as Lhasa. However, the concentration of Ca$^{2+}$, the dominant cation in the rainwater of both cities, in Beijing was in the same order of magnitude as that in Lhasa. Ca$^{2+}$ was from the air-borne continental dust,
one of the major sources in the aerosols in Beijing and Lhasa. The concentrations of the anions and cations in the rainwater in Shanghai were one order of magnitude higher than that in Lhasa and were lower than that in Beijing. These results revealed that both Beijing and Shanghai were faced with heavy anthropogenic pollution compared with Lhasa, and the situation in Beijing was even more serious than that in Shanghai. The pH value in Beijing was mostly not in the range of acid rain, which was because of the fact that Ca\(^{2+}\) and NH\(_4^+\) in the rainwaters of Beijing were the predominant alkaline cations that restrained acidity. The equivalent ratio of \((\text{Ca}^{2+} + \text{NH}_4^+)/\left(\frac{\text{SO}_4^{2-} + \text{NO}_3^-}{\text{Ca}^{2+} + \text{NH}_4^+}\right)\) could be used as an index for evaluating the degree of the anthropogenic activity. In the rainwater of Lhasa, the ratio of \((\text{Ca}^{2+} + \text{NH}_4^+)/\left(\frac{\text{SO}_4^{2-} + \text{NO}_3^-}{\text{Ca}^{2+} + \text{NH}_4^+}\right)\) was 15.5, the highest among the three cities, and Lhasa had one of the lowest acidification, as the pH of the rainwater was in the alkaline range, which was only because of the neutralization of the basic cations. In contrast, the ratio of \((\text{Ca}^{2+} + \text{NH}_4^+)/\left(\frac{\text{SO}_4^{2-} + \text{NO}_3^-}{\text{Ca}^{2+} + \text{NH}_4^+}\right)\) in the rainwater of Beijing was lower than that in Shanghai, the pH in the rainwaters in Beijing is higher than that in Shanghai, and the rainwaters in Beijing were mostly non-acidic. This was likely due to the much higher concentrations of \((\text{Ca}^{2+} + \text{NH}_4^+)\) plus the higher concentration of Mg\(^{2+}\) in the rainwaters in Beijing compared to that in Shanghai. The high concentrations of SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), NH\(_4^+\), Ca\(^{2+}\), and H\(^+\), in the rainwaters would have a great impact on the hydrobiological system on the surface of the earth on both local and regional scales and have attracted extensive concern, as the wet deposition participates actively in the balance of the air–water–soil system.

### Table 1

<table>
<thead>
<tr>
<th>Area</th>
<th>Period</th>
<th>pH</th>
<th>SO(_4^{2-})</th>
<th>NO(_3^-)</th>
<th>Ca(^{2+})</th>
<th>NH(_4^+)</th>
<th>((\text{Ca}^{2+} + \text{NH}_4^+)/\left(\frac{\text{SO}_4^{2-} + \text{NO}_3^-}{\text{Ca}^{2+} + \text{NH}_4^+}\right))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lhasa(^a)</td>
<td>1998–2000</td>
<td>7.95–6.97</td>
<td>6.11</td>
<td>7.28</td>
<td>198.77</td>
<td>8.70</td>
<td>15.5</td>
</tr>
<tr>
<td>Beijing</td>
<td>2003</td>
<td>6.48</td>
<td>380.14</td>
<td>117.87</td>
<td>159.04</td>
<td>210.70</td>
<td>0.73</td>
</tr>
<tr>
<td>Shanghai</td>
<td>1999</td>
<td>5.92</td>
<td>95.04</td>
<td>40.39</td>
<td>95.00</td>
<td>80.55</td>
<td>1.3</td>
</tr>
</tbody>
</table>

\(^a\)Zhang et al. (2002).  
\(^b\)Xu et al. (2000).

### Table 2

Rotated factor matrix of rainwater samples at Beijing

<table>
<thead>
<tr>
<th>Variable</th>
<th>PC1</th>
<th>PC2</th>
<th>PC3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>F(^-)</td>
<td>0.21</td>
<td>0.95</td>
<td>0.02</td>
<td>0.94</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.58</td>
<td>0.78</td>
<td>0.01</td>
<td>0.95</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>0.82</td>
<td>0.30</td>
<td>0.29</td>
<td>0.85</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.93</td>
<td>0.30</td>
<td>0.12</td>
<td>0.97</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>0.26</td>
<td>0.92</td>
<td>0.16</td>
<td>0.94</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>0.91</td>
<td>0.26</td>
<td>0.00</td>
<td>0.90</td>
</tr>
<tr>
<td>K(^+)</td>
<td>0.66</td>
<td>0.71</td>
<td>0.05</td>
<td>0.94</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.62</td>
<td>0.64</td>
<td>0.36</td>
<td>0.93</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.61</td>
<td>0.49</td>
<td>0.47</td>
<td>0.83</td>
</tr>
<tr>
<td>pH</td>
<td>0.10</td>
<td>0.04</td>
<td>0.04</td>
<td>0.89</td>
</tr>
</tbody>
</table>

| Eigen value | 4.02 | 3.77 | 1.36 |
| %Variance   | 40%  | 38%  | 14%  |
| Category    | Secondary Pollution | Soil |

To analyze the relation of the acidity with the components in rainwater and further identify their sources, the principal component analysis (PCA) (STATISTICA\(^\text{®}\) software) was used to identify the sources of those components in rainwater and analyze their relationship with the acidity in rain samples. As shown in Table 2, three principal components (PCs) were extracted from the Beijing rainwater samples, which explained 91% of variance. The communalities for all species were higher than 0.82, indicating that the three factors identified were reasonable. PC1 has high loadings for NO\(_3^-\), SO\(_4^{2-}\), and NH\(_4^+\), which was associated with the secondary aerosol source, such as the chemical transformation of SO\(_2\), NO\(_x\) on the surface of the aerosols. PC2 has high loadings for F\(^-\), Cl\(^-\), Na\(^+\), and K\(^+\), which was likely associated with the anthropogenic pollution sources, such as factory emissions, biomass burning, garbage incineration, and so on. The association of Na and Cl with the influence of sea breeze could be a minor source (Yuan et al., 2004). In PC3 there was a high loading for pH, moderate loadings for Ca\(^{2+}\) and Mg\(^{2+}\), and weak loadings for other ions. PC3 was likely associated with the soil as a source. Moreover, it may indicate the relationship between acidity and ions of rainwater. Acidity could be seen as the ultimate reflection of the chemical characteristics of the rainwater, which is the result of interactions/reactions...
among various components. The moderate loading for Ca\(^{2+}\) perhaps indicated that Ca\(^{2+}\), in turn, the soil source, played an important role in buffering the acidity of rainwater in Beijing.

Kulshrestha et al. (1995) suggested neutralization factor (NF) to describe the interaction between cations and anions. The roles of NH\(_4^+\), Ca\(^{2+}\) and Mg\(^{2+}\) have been validated by calculating NFs in rainwaters as below:

\[
NF_{\text{Ca}^{2+}} = \frac{\text{Ca}^{2+}}{\text{NO}_3^- + \text{SO}_4^{2-}}, \quad NF_{\text{NH}_4^+} = \frac{\text{NH}_4^+}{\text{NO}_3^- + \text{SO}_4^{2-}}, \quad NF_{\text{Mg}^{2+}} = \frac{\text{Mg}^{2+}}{\text{NO}_3^- + \text{SO}_4^{2-}}.
\]

The equivalent concentrations of the ions in the 53 rain samples were used in this calculation. To verify which cation (NH\(_4^+\), Ca\(^{2+}\), and Mg\(^{2+}\)) more frequently neutralized the acidic components in the rainwater, a triangular diagram (Fig. 4) was drawn, showing the relative proportion of these three NFs. The examination of the NF (NF\(_{\text{NH}_4^+}\), NF\(_{\text{Ca}^{2+}}\), NF\(_{\text{Mg}^{2+}}\)) triangle revealed that both Ca\(^{2+}\) and NH\(_4^+\) were the predominant neutralizers in rainwater samples, and only \(\sim 10\%\) of the neutralization was by Mg\(^{2+}\). It has been well known that the high concentration of calcium in the rainwater of Beijing was closely related to the surface soil and/or the coal fly ash, which were from the re-suspension in the city itself and/or from the long-range transport from outside Beijing (Sun et al., 2004). The high concentration of calcium in the aerosols in Beijing due to the dry and rainless condition resulted in high concentration of Ca\(^{2+}\) and, in turn, the strong buffer capacity in rainwater, which greatly reduced the acidity of the rain.

The high concentration of NH\(_4^+\), another major neutralizer, in rainwater was certainly related to the introduction of gaseous ammonia (NH\(_3\)) into the air, which was mainly from plants, fertilizer use, cattle breeding, and industrial processes. The concentrations of Ca\(^{2+}\) and NH\(_4^+\) could be related to variation of meteorological conditions and the activity of human beings, such as land use (Lee et al., 2000). Fig. 5 shows the seasonal variation of the equivalent concentration ratio of NH\(_4^+\) to Ca\(^{2+}\) in rainwater samples. As NH\(_3\) emission favors warm weather conditions (Yamulki and Harrison, 1996) and Ca\(^{2+}\) was in the highest concentration in the dry season of winter, which was mainly introduced from wind-blown soil, there was a peak value of [NH\(_4^+\)]/Ca\(^{2+}\) in summer. Thus, the buffering of the acidity and the lower acidity in summer was more due to the NH\(_4^+\) and the dilution of higher rainfall amount in this season, whereas in winter it could be more related to Ca\(^{2+}\), although both NH\(_4^+\) and Ca\(^{2+}\) were the major buffers in either season.

### 3.4. The correlation of the acidity in rainwater with the components in the air

#### 3.4.1. The correlation of the acidity in rainwater with gaseous components in the air

Cloud and precipitation could incorporate both aerosol particles and gases, as precipitation originates from the condensation of water vapor that subsequently becomes a raindrop. Rainwater would wash out the components in the air while it falls to the ground. Figs. 6(a) and (b) shows the monthly variation of pH value in rainwater and the concentrations of SO\(_2\) and NO\(_2\) in 2003. It could be seen that pH value in the rainwater varied regularly with the variation of the monthly concentrations of SO\(_2\) and NO\(_2\) in the air. The concentrations of NO\(_2\) and SO\(_2\) peaked in November.
and the pH was lowest in November. A pattern of a clear negative correlation of the pH value with the concentration of NO\textsubscript{2} and SO\textsubscript{2}, i.e. an evident positive correlation of the acidity in rainwater with the concentration of NO\textsubscript{2} and SO\textsubscript{2} in the air was observed. Zhao et al. (2001) found a similar result in Zhengzhou, where the climate and geographical environment is similar to Beijing. The acidity of rainwater was affected by the physico-chemical processes of washing and absorption of SO\textsubscript{2} and NO\textsubscript{2} during the course of rain (Zhao et al., 2001; Shi et al., 2000; Liu et al., 2000). During the course of rainfall there was a dissolution process, including hydration, of SO\textsubscript{2} and NO\textsubscript{2}. The hydrates donated another proton to the solution and directly affected the acidity of rainwater. The three acidic samples of 53 rain events occurred in spring and winter when the emission of SO\textsubscript{2} and NO\textsubscript{2} is the highest in the entire year 2003, which resulted in such acidic rainwater. The positive correlation of the acidity in rainwater with the concentration of NO\textsubscript{2} and SO\textsubscript{2} in the air illustrated that SO\textsubscript{2} and NO\textsubscript{2} were the important precursors of the acidic compositions and the major contributors of the acidity in rainwater.

3.4.2. The correlation of the acidity in rainwater with aerosols in the air

The scavenging process of aerosols from the air could greatly affect the acidity of rainwater as mentioned above. Aerosol particles could either contribute to or buffer/restrain the acidity in rainwater. Figs. 7(a) and (b) illustrates the monthly variation of pH against the variation of the concentrations of PM\textsubscript{10} and TSP in 2003, respectively. There was a negative correlation of pH value with PM\textsubscript{10} (Fig. 7(a)), whereas there was a roughly positive correlation with TSP (Fig. 7(b)). PM\textsubscript{10} refers to those particles that are less than 10\textmu m in aerodynamic diameter, and TSP are those particles with size less than 100\textmu m in the air. It is clear that PM\textsubscript{10} are finer particles than TSP. As pollution aerosols, such as sulfate and nitrate that mostly exist in finer particles are the major contributors to acidity while they are scavenged into rainwaters (Zeng et al., 2001; Wang et al., 2000, 2001), the acidity of the rainwaters could increase with the increase of PM\textsubscript{10} roughly as shown in Fig. 7(a). However, the soil particles, i.e. the mineral aerosols, that contain more basic oxides, such as Fe/Al/Si/Ca oxides, which could adsorb and neutralize acidic gases, such as NO\textsubscript{x}, SO\textsubscript{2}, etc., could neutralize and

![Fig. 6](image-url)  
(a) Monthly variation of rainwater pH and concentration of SO\textsubscript{2} in atmosphere; (b) monthly variation of rainwater pH and concentration of NO\textsubscript{2} in atmosphere.

![Fig. 7](image-url)  
(a) Monthly variation of rainwater pH and concentration of PM\textsubscript{10} in the air; (b) monthly variation of rainwater pH and concentration of TSP in the air.
decrease the acidity in rainwater, as Ca\textsuperscript{2+} does (see Section 3.3). These mineral particles exist more in coarse particles compared with pollution aerosols although a considerable part of them is also in the finer mode. For example, mineral aerosols accounted for 27–60% of the TSP collected on non-dust storm days in Beijing (Sun et al., 2004). The scavenging of coarse particles played an important role in buffering and neutralizing acidity of rainwater. Wang (1992) reported that the critical buffering capacity of Beijing aerosol was 375.4 neq m\textsuperscript{−3}, three times higher than that in South China. This was one of the dominant reasons why Beijing was mostly a non-acid region even though the air pollution has been very serious there. Chai et al. (2001) compared the pH value in rainwater and these major air pollutants in Zhengzhou, China, and found that the mass concentration of TSP could be an index representing rainwater acidity. Although this index might not be applicable to wet precipitation anywhere, the correlation of the pH of rainwater with TSP should be taken into account seriously in Beijing.

### 3.5. Temporal variation of the acidity and the major components in rainwater

Fig. 8 shows the monthly variation of the concentrations of the major ions in rainwater and the monthly precipitation amount in Beijing in 2003. As illustrated in Fig. 8, the total ion concentration peaked when rainfall bottomed out and the concentration of each ion increased with the decrease of rainfall amount. As raindrops in larger rainfalls tend to be larger than in smaller rainfalls, the smaller the raindrops, the longer their resident time. Thus, raindrops with smaller size could incorporate more aerosol particles and gases than larger ones (Lee et al., 2000). In addition, a large amount of rainfall could dilute the ion concentration. It would be easy to understand that the ion concentrations were generally higher in winter when the rainfall was less and lower in summer when the rainfall was greater, as shown in Fig. 8. Moreover, this could be one more reason why the higher ion concentration was in the rainwater samples in winter, that is, the coal combustion in the heating period of winter contributed to the high air pollution. Fig. 9 shows the monthly variation of pH and the concentrations of the major ions in rainwater in Beijing in 2003. The pH value in rainwater fluctuated slightly from May to October and decreased sharply in November. The concentrations of those major ions in rainwater also increased suddenly in November. This could be attributed to the air pollution due to the coal-combustion, which was very serious in the heating season that starts in November each year in Beijing. The anthropogenic pollution in Beijing is the heaviest in winter because of the coal combustion in the heating season, followed by spring and autumn, and then summer. The variation of the major pollution ions in rainwater is similar to that of air pollution. Table 3 shows the concentrations of the major ions in rainwater in Beijing within the last two decades. The concentrations of SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− increased sharply up to 2003 and the same ascending trend was found for NH\textsubscript{4}+, which indicates the air pollution has become more and more serious in Beijing since the 1980s. It must be noted that the ratio of the equivalent concentration of SO\textsubscript{4}\textsuperscript{2−} to NO\textsubscript{3}− observed in 2003 was 3.23, which was much lower than the ratio of 5.44 obtained in 1981, which was an important indication that the anion composition of the wet precipitation in Beijing has changed much since the 1980s and the air pollution resulting from the traffic emission, NO\textsubscript{x}, has become more and more significant. The concentration of NO\textsubscript{3}− that largely was from the vehicle emission increased greatly, although SO\textsubscript{4}\textsuperscript{2−} has still been the major ion in the rainwater of Beijing. The control of air pollution from traffic emissions should be taken seriously. Table 3 lists the limited data of average Ca\textsuperscript{2+} and pH in some years in the last two decades. As
such data from the literature were very limited, it was impossible to show these data yearly. However, it seemed that there was a notable positive correlation between Ca$^{2+}$ and pH. This finding illustrated that Ca$^{2+}$ plays an important role in buffering rainwater acidity. Soil aerosols could change the distribution pattern of acid rain in East Asia, especially over Northern China. If no soil aerosols were lifted from the arid regions of China, the pH value in Northern China and Korea would decrease by a factor of 0.5–2 (Wang et al., 2002). Concentrations of alkaline components of soil in north China are higher than that in the South, such as calcium and magnesium, which is 3% and 1.5%, respectively, in the north soil, whereas 0.1% and 0.5% in the south (Fan, 2002). The mineral aerosol accounted for 27–60% of the TSP collected in those non-dust storm days in Beijing (Sun et al., 2004) and the crust element, including Fe, Ca, Al, accounted for 70% in the coarse particles in winter (Yang et al., 2002). These coarse and alkaline particles from soil are scavenged by raindrops and then buffered by the acidity of rainwater, which is the critical factor in determination of acidity of the rainwater over Northern China. The high concentration of alkaline dust is an important feature of the atmosphere in north China, thus the deposition of those base ions, such as Ca$^{2+}$, must be taken into account when studying the pH value of precipitation.

4. Conclusion

The analysis of almost all of the rain samples collected in the whole of 2003 showed that: (1) the scavenging of the pollutants from the air affected directly and greatly the pH and the composition of the rainwater in Beijing. (2) The major ions and their concentrations in rainwater followed the order of: SO$_4^{2-}$ > NH$_4^+$ > Ca$^{2+}$ > NO$_3^-$ > Cl$^-$ > Mg$^{2+}$ > Na$^+$ > F$^-$ > K$^+$. (3) SO$_4^{2-}$ and NO$_3^-$ were the major acidifying ions in rainwater of Beijing. Ca$^{2+}$ and NH$_4^+$ were the predominant basic ions in buffering and neutralizing the acidity in rainwater. (4) The correlation of the acidity in rainwater with the concentrations of SO$_2$, NO$_2$, PM$_{10}$, and TSP in the atmosphere showed that the acidity and composition in rainwater were mainly determined by the scavenging processes of those gases and particles in the air. (5) The temporal variation of those major pollution ions in rainwater reflected the variation of air pollution in Beijing. The concentrations of SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ have increased over the last decade, indicating that air pollution has become more and more serious in Beijing since the 1980s. (6) The ratio of the concentration of SO$_4^{2-}$ to NO$_3^-$ observed in 2003 was much lower than that obtained in 1981, indicating that the air pollution resulting from the traffic emission, NO$_x$, has been more and more significant. (7) A remarkably positive correlation between pH and Ca$^{2+}$ concentration for the last 20 years illustrated that Ca$^{2+}$ played an important role in buffering rainwater acidity. (8) The concentration of SO$_4^{2-}$, the predominant acid anion, in rain was much higher in Beijing than other cities, suggesting that anthropogenic pollution has been a much more serious problem here than in other places.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 29837190, 30230310, 20077004 and 20477004), Beijing Natural Science Fund (Grant Nos. 8991002 and 8041003), the special found for the doctoral study of the Education Ministry of China, and also in part supported by LAPC, The Institute of Atmospheric Physics, CAS, and the Swedish International Development Cooperation Agency (SIDA) through the Asian Regional Research Program on Environmental Technology (ARRPET) at the Asian Institute of Technology.

References


