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Yuesi Wang \(^a\), Wenpeng Yu \(^a\), Yuepeng Pan \(^a\) & Dan Wu \(^b\)

\(^a\) State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, People's Republic of China

\(^b\) Department of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, People's Republic of China

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Acid neutralization of precipitation in Northern China

Yuesi Wang,1 Wenpeng Yu,1 Yuepeng Pan,1,* and Dan Wu2

1State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, People’s Republic of China
2Department of Environmental Science and Engineering, Nanjing University of Information Science and Technology, Nanjing, People’s Republic of China

*Please address correspondence to: Yuepeng Pan, State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (LAPC), Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, People’s Republic of China; e-mail: pyp@dq.cern.ac.cn

There is an increasing concern over the impact of human-related emissions on the acid precipitation in China. However, few measurements have been conducted so far to clarify the acid-neutralization of precipitation on a regional scale. Under a network of 10 sites across Northern China operated during a 3-year period from December 2007 to November 2010, a total of 1118 rain and snow samples were collected. Of this total, 28% was acid precipitation with pH < 5.6. Out of these acid samples, 53% were found highly acidic with pH value below 5.0, indicating significantly high levels of acidification of precipitation. Most of the acidity of precipitation was caused by H2SO4 and HNO3, their relative contribution being 72% and 28%, respectively. However, the contribution of HNO3 to precipitation acidity will be enhanced due to the increasing NOx and stable SO2 emissions in future. Neutralization factors for K+, NH4+, Ca2+, Na+, and Mg2+ were estimated as 0.06, 0.71, 0.72, 0.15, and 0.13, respectively. The application of multiple regression analysis further quantified higher NH4+ and Ca2+ contribution to the neutralization process, but the dominant neutralizing agent varied from site to site. The neutralization was less pronounced in the rural than urban areas, probably due to different levels of alkaline species, which strongly buffered the acidity. Presence of high concentrations of basic ions was mainly responsible for high pH of precipitation with annual volume-weighted mean (VWM) values larger than 5.6 at several sites. It was estimated that in the absence of buffering ions, for the given concentration of SO42− and NO3−, the annual VWM pH of precipitation would have been recorded around 3.5 across Northern China. This feature suggested that emissions of particles and gaseous NH3 played very important role in controlling the spatial variations of pH of precipitation in the target areas.

Implications: Acid precipitation has long been recognized as a serious environmental problem in East Asia, especially in China. The present study identifies that acidity of precipitation in Northern China generated by H2SO4 and HNO3 was primarily neutralized by Ca2+ and NH4+. However, in the future, acidity due to HNO3 may increase as a result of the increasing trends of NOx and stable trends of SO2 emissions in megacities. The reducing primary emissions of particles and gaseous ammonia may offer more clear-sky days in urban areas, but might also lead to enhanced acid precipitation in Northern China in the near future.

Introduction

Acid precipitation has become a common concern of scientists, policy makers, and governments as a result of its potential for environmental stress in terrestrial ecosystem and aquatic systems, and also because of its indirect effects on human health. Acid precipitation is primarily caused by the presence of strong acids such as H2SO4 and HNO3, which are contributed by SO2 and NOx, respectively. The major sources of SO2 include coal combustion and diesel burning in thermal power plants and industries, whereas that of NOx includes transport sector. Acid precipitation has been reported as common phenomenon in North America and Central Europe (Balasubramanian et al., 2001; Galloway et al., 1982; Rodhe et al., 2002; Willey et al., 2006).

Due to the rapid increase in SO2 and NOx emissions during past two decades, acid rain has become an increasing serious issue in China (Larssen et al., 2006; Tang et al., 2010). Although the concentrations of acidic species SO42− and NO3− in northern part of China are reported to be much higher than that in the southern acid rain areas, the precipitation pH in the former was not lower than the latter (Huang et al., 2008; Sun et al., 2011; Tang et al., 2005). This might be due to the abundance of alkaline particles and NH3 in the atmosphere, which largely neutralizes the acidity of precipitation in Northern China (Wang and Ding, 1997; Wang, 1985). However, implementation of particulate matter reduction policy has not only resulted in decreasing trend of air particulate levels, but also enhanced the frequency of acid precipitation at some sites in Northern China (Tang et al., 2010). This has led to an ambiguity about the impact of declining alkaline species on acid precipitation in various areas of Northern China. It is to be mentioned that under national monitoring programs of China, general urban air quality parameters and pH of precipitation are measured while little has been done involving chemistry measurements. Also, in such a vast
geographical area of China, very limited studies have been reported on the acid neutralization of precipitation that has extended beyond a period of 3 years.

Hence, the present study was carried out to strengthen our knowledge about current status of acid precipitation and its spatiotemporal distribution in Northern China. We have also attempted to identify the causes of acidification of precipitation and its neutralization by alkaline species at different sites. Additionally, we have evaluated the possible trends of acid precipitation in the target areas.

**Experimental**

**Site description**

The present study was carried out from December 2007 to November 2010 at 10 sites representing urban, industrial, agricultural, and rural characteristics across Northern China. These sites include two urban sites (Beijing [BJ] and Tianjin [TJ]), two suburban sites (Cangzhou [CZ] and Yangfang [YF]), three industrial sites (Baoding [BD], Tanggu [TG], and Tangshan [TS]), two agricultural sites (Luancheng [LC] and Yucheng [YC]), and one rural site (Xinglong [XL]). The general location of each site is shown in Figure 1. The mean annual precipitation ranged from 400 to 800 mm, and mean annual air temperature was 8–14 °C; more detailed information of the 10 selected sites in the study have been presented elsewhere (Pan et al., 2010a).

**Precipitation measurement**

Rainwater samples were collected on 24-hr basis using an automatic wet–dry collector (APS-2B; Xianglan Scientific Instruments Co., Changsha, China). The collector can be equipped with an area of 707 cm² aperture sampling rainfall. The rainfall sensor controls the cover device to open up the collection funnel only at the start of rain, and then rainwater flows from the funnel down into a plastic 15-L bottle. The funnel lid closes automatically when rainfall ceases and rainwater has evaporated from the sensor surface. This feature of collector is very useful to collect desired rain event with minimal contamination from dry deposition. After sampling, the collection system is systematically cleaned with distilled water. Snow samples were collected with a clean plastic bucket having an inner diameter of 22 cm as soon as possible after a snowfall event. Precipitation samples in the study, including both rainwater and melted snow, were filtered, stored, and transported following the procedure described in detail previously (Pan et al., 2010a).

After collection, an aliquot was taken into a beaker immediately for measurement of pH by a digital pH meter with a glass electrode. The pH meter was calibrated with pH 4.0 and 6.86 buffer solutions, corrected to ambient temperature. An additional aliquot was prepared and refrigerated for later analysis of F⁻, Cl⁻, SO₄²⁻, NO₂⁻, NO₃⁻, and NH₄⁺ by ion chromatography (model ICS-90; Dionex Corporation, Sunnyvale, USA) and K⁺, Na⁺, Ca²⁺, and Mg²⁺ by inductively coupled plasma mass spectrometry (ICP-MS) (model 7500a; Agilent Technologies, Tokyo, Japan, USA), according to standard laboratory procedure (Pan et al., 2010b, Sun et al., 2011), in the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry (Beijing, China). The detection limits are better than 5 µg/L for all ions determined through analyses of blank samples.

**Results and Discussion**

**Variation of pH of precipitation**

Figure 2 shows the frequency distribution of pH of the precipitation during the years 2008–2010 across Northern China (the definition of year 2008 was from December 2007 to November 2008; 2009 was from December 2008 to November 2009; and 2010 was from December 2009 to November 2010). As the pH of the unpolluted cloud in equilibrium with atmospheric CO₂ is 5.6, the rainwater in which the pH is less than 5.6 is considered to be acid rain (Tang et al., 2005). The frequency of acid precipitation in Northern China ranged from 7.8% to 50.0%, averaging 27.9% at the 10 selected sites. The highest frequency of acid precipitation was noticed at the XL site (50.0%), followed by the CZ (44.2%), LC (33.6%),
Origin of acidity of precipitation

The variation of pH at the 10 sites, derived from annual volume-weighted mean (VWM) concentrations of H\(^+\), is presented in Figure 3, which showed relatively higher value at some urban centre sites (e.g., BJ and TJ) than at suburban rural sites (e.g., CZ and XL). The measured pH ranged from 4.01 (XL in 2010) to 6.78 (BJ in 2008) with the 3-year arithmetic mean of 6.1, across Northern China, which showed a very large fluctuation than other studies (Balasubramanian et al., 2001; Kulshrestha et al., 2003; Kulshrestha et al., 2009; Lee et al., 2000). Out of 1118 precipitation samples, 164 (15%) represented severe acid precipitation (pH < 5.0), 144 (13%) were gentle acid precipitation (5.0 ≤ pH ≤ 5.6) and 811 samples (72%) exhibited nonacid precipitation (pH > 5.6). Worthy of mention is the fact that there were 176 cases—16% of the total precipitation samples—that appeared pH ≥ 7.0, especially at the TG, TJ, and LC sites. This high percentage of precipitation samples with pH values larger than 7.0 was observed to be alkaline, indicating strong inputs of alkaline species to precipitation in this region (Lee et al., 2000).

Y.C (32.4%), TS (31.4%), BD (26.4%), TG (19.4%), YF (11.3%), BJ (9.7%), and TJ (7.8%) sites.

As shown in Figure 2, it was clear that at the rural site XL and the suburban site CZ, almost half of the precipitation events were acidic. In contrast, the lowest frequency of acidic precipitation was seen at the two megacity sites BJ and TJ. More frequent occurrence of acid precipitation at rural and suburban sites might be due to the low concentrations of alkaline ions (such as NH\(_4^+\) and Ca\(^{2+}\)), which resulted in insufficient neutralization of acidity, whereas the lowest frequency of acid precipitation at the BJ and TJ sites was probably due to high loadings of particulate matter in the atmosphere. It is not surprising, considering that various construction-related activities at urban sites generate suspended particulate matter. Mostly, the particulate matter is rich in Ca\(^{2+}\) and gives rise to high pH of precipitation on scavenging in the target areas (Sun et al., 2011; Wang et al., 2009). This finding is similar to that observed at Hyderabad, an urban city located in south-central India (Kulshrestha et al., 2003; Kulshrestha et al., 2009). The relatively lower frequency of acidic precipitation at the industrial sites TS and BD, the agricultural sites YC and LC, and the coastal site TG can also be explained by higher interference of alkaline matter as compared to rural site XL.

Because the naturally existing CO\(_2\), NO\(_x\), and SO\(_2\) will dissolve into the clouds and droplets and result in pH values of the precipitation in the clean atmosphere that are between 5.0 and 5.6 (Charlson and Rodhe, 1982; Galloway et al., 1993), perhaps using pH < 5.0 as the critical baseline of the heavily acidic precipitation would be more reflective of the effects of human-induced emissions in the absence of base materials (Charlson and Rodhe, 1982). If so, there were no events that would be considered highly acidic at the TJ site, indicating that the acid precipitation was not serious. However, heavily acid precipitation did exist at some sites, such as XL, CZ, LC, and YC. The frequency of severe acid precipitation with pH < 5.0 ranged from 0% to 31%, averaging 14% at the 10 sites; the highest values were found at the XL site (31%), followed by the CZ (24%), BD (19%), LC (21%), YC (17%), TS (10%), TG (7%), YF (4%), and BJ (2%) sites. It should be noted that the frequency of acid precipitation with pH < 5.6 at the TS site was higher than it was at the BD site; however, the frequency of acid precipitation with pH < 5.0 at the BD site was higher than it was at the TS and other agricultural sites. This is an indication of the more serious acidification of precipitation in BD than in another industrial site TS. Overall, pH of individual precipitation events ranged from 3.1 to 9.4, with a 3-year arithmetic mean of 6.1, across Northern China, which showed a very large fluctuation than other studies (Balasubramanian et al., 2001; Kulshrestha et al., 2003; Kulshrestha et al., 2009; Lee et al., 2000). Out of 1118 precipitation samples, 164 (15%) represented severe acid precipitation (pH < 5.0), 144 (13%) were gentle acid precipitation (5.0 ≤ pH ≤ 5.6) and 811 samples (72%) exhibited nonacid precipitation (pH > 5.6). Worthy of mention is the fact that there were 176 cases—16% of the total precipitation samples—that appeared pH ≥ 7.0, especially at the TG, TJ, and LC sites. This high percentage of precipitation samples with pH values larger than 7.0 was observed to be alkaline, indicating strong inputs of alkaline species to precipitation in this region (Lee et al., 2000).
Acidity could be estimated using the sum of nss-SO$_4^{2-}$ and NO$_3^-$ in precipitation (Rodhe et al., 2002).

In this study, the sum of annual VWM concentration of nss-SO$_4^{2-}$ and NO$_3^-$ fell within the range of 189.4–613.6 μeq/L with the 10-site average values of 312.0 μeq/L during the 3-year period. Based on the above assumption, these values correspond to precipitation pH in the range of 3.21–3.72, with a mean value of pH 3.52. The measured and estimated pH by the above assumption is given in Figure 3. In general, pH estimated in this manner was found to be very low at the 10 sites. Interestingly, the estimated pH value was not significantly different either at the 10 sites or in different years, indicating the characteristics of acidity of precipitation caused by H$_2$SO$_4$ and HNO$_3$ across Northern China are regional on an annual basis. In other words, in the absence of neutralization of acidity, precipitation with a lower pH value (around 3.5) would widely affect Northern China.

To examine the relative contribution of nss-SO$_4^{2-}$ and NO$_3^-$ to the total acidity of precipitation for the 10 sites on an annual basis, the equivalent ratios of nss-SO$_4^{2-}$ to the sum of nss-SO$_4^{2-}$ and NO$_3^-$ were obtained (Safai et al., 2004). These ratios ranged from 0.63 to 0.83, with an average value of 0.72, suggesting that about 72% of precipitation acidity was caused by nss-SO$_4^{2-}$, whereas the remaining (28%) was due to NO$_3^-$. Although sulfuric acid is still a primary contributor to the acidity of precipitation in Northern China, the contribution of nitric acid was found to be relatively higher at the BJ site (32%) and its suburban YF site (33%) than at some agricultural sites (e.g., YC, 23%; LC, 22%). This difference reflected the impacts of traffic emissions in urban areas. It is to be noted that due to the adjustment of energy structure and multipollutant control strategy, the trend of SO$_2$ emissions would be stable or would decreased insignificantly but NOx emissions from the transport sector, especially in megacities, will keep on rising in the near future (Zhao et al., 2009). This will enhance HNO$_3$ contribution to precipitation acidity in future. In Beijing, for example, the ratio of equivalent concentrations of SO$_4^{2-}$ to NO$_3^-$ decreased rapidly from 1981 to the present, declining from 5.4 to 1.7 (Figure 4). If this trend continues, it can be expected that NO$_3^-$ will play a more important role than SO$_4^{2-}$ in determining precipitation acidity in the coming decades.

**Acid neutralization of bases**

In comparison to the estimated pH (without including alkaline matter), measured pH values showed larger spatial and interannual variation (Figure 3), indicating that locally incorporated alkaline matter plays an important role in determining the pH of precipitation at various sites of the network in Northern China. Since the interference of alkaline matter is local in nature, spatial and interannual variation of measured pH is reflected
been reported from Greece (Anatolaki and Tsitouridou, 2009) and India (Kulshrestha et al., 2003; Kulshrestha et al., 2005; Shukla and Sharma, 2010), highlighting the role and mechanism of buffering of precipitation acidity by alkaline compounds such as CaCO₃ particles originated from construction sources and gas NH₃ released due to the agricultural activities (Anatolaki and Tsitouridou, 2009).

In order to evaluate the effect of alkaline species (e.g., NH₄⁺, Ca²⁺, and Mg²⁺) on the neutralization process, the neutralization factor (NF) was calculated according to eq 1, proposed by previous studies (Kulshrestha et al., 2003; Possanzini et al., 1988).

\[
NF(X) = \frac{X}{\text{NO}_3^- + \text{SO}_4^{2-}}
\]

The annual variations of NF for K⁺, NH₄⁺, Ca²⁺, Na⁺, and Mg²⁺ at the 10 sites are shown in Figure 5. At most sites, NH₄⁺ had the highest neutralization effect, whereas at TS, TJ, and YF sites, Ca²⁺ was the primary neutralizing agent during the 3-year period. In addition, the neutralization by Ca²⁺ was higher than NH₄⁺ at the BD, YC, and XL sites in 2008 and the BJ site in 2009. Of note, the NF of K⁺ was higher at the XL site in 2010, probably due to its contribution from biomass burning (Chow, 1995; Radojevic and Tan, 2000; Wang et al., 2007), considering the very high concentrations of K⁺ (127.6 μEq/L) at XL in 2010 (about 10 times higher than 2008 and 2009). Overall, the 10-site averages of NF values for K⁺, NH₄⁺, Ca²⁺, Na⁺, and Mg²⁺ during the 3-year period were 0.06, 0.71, 0.72, 0.15, and 0.13, respectively, suggesting that major neutralization, possibly resulting from NH₄⁺ and Ca²⁺, has occurred. Generally, the contribution of K⁺, Na⁺, and Mg²⁺ to the overall neutralization process was very low in Northern China.

It should be stressed here that using the NF to examine the neutralization effect of these cations on acids might be to some extent overestimated (Huang et al., 2008), because the alkaline species were not always fully contributed to the neutralization process in the precipitation (Draaijers et al., 1997). This finding clearly. In other words, alkaline matters are responsible for the variation of annual pH observed in Northern China.

It is worth noting that the estimated pH was lower than the measured pH by 1.82 (0.38–3.25). This discrepancy indicates that the precipitation had experienced some neutralization (Lee et al., 2000). In order to investigate whether the acidity is neutralized or not, and to determine to what extent the acidity is neutralized, fractional acidity (FA) was computed as the equivalent ratio of H⁺ to the sum of nss-SO₄²⁻ and NO₃⁻ (Balasubramanian et al., 2001; Kaya and Tuncel, 1997; Rodhe et al., 2002). Assuming this hypothesis, the ratio of FA would be unity if the precipitation acidity generated by strong acids (i.e., H₂SO₄ and HNO₃) is not neutralized at all, whereas deviations from unity represent the magnitude of neutralization (Tuncer et al., 2001). In this study, average of FA at the 10 sites during the 3-year period was observed to be 0.04, indicating that approximately 96% of the acidity in precipitation is neutralized by counter cations, which might be primarily represented by Ca²⁺ and NH₄⁺. Of note is the fact that annual FA was lower than 0.08 at most sites except for the XL site, which had a value of 0.41 in 2010. The relatively higher FA at the XL site might be partly due to the lower concentration of alkaline species.

On the other hand, the estimated pH could be equivalent to the measured one when no neutralization occurs and to determine to what extent the acidity is neutralized or not, and to determine to what extent the acidity is neutralized, fractional acidity (FA) was computed as the equivalent ratio of H⁺ to the sum of nss-SO₄²⁻ and NO₃⁻ (Balasubramanian et al., 2001; Kaya and Tuncel, 1997; Rodhe et al., 2002). Assuming this hypothesis, the ratio of FA would be unity if the precipitation acidity generated by strong acids (i.e., H₂SO₄ and HNO₃) is not neutralized at all, whereas deviations from unity represent the magnitude of neutralization (Tuncer et al., 2001). In this study, average of FA at the 10 sites during the 3-year period was observed to be 0.04, indicating that approximately 96% of the acidity in precipitation is neutralized by counter cations, which might be primarily represented by Ca²⁺ and NH₄⁺. Of note is the fact that annual FA was lower than 0.08 at most sites except for the XL site, which had a value of 0.41 in 2010. The relatively higher FA at the XL site might be partly due to the lower concentration of alkaline species.
is not surprising, considering that alkaline compound in aerosols (e.g., calcium) can be transformed to nitrate and sulfate salts by the reactions with acidic species (e.g., H$_2$SO$_4$ and HNO$_3$) in the atmosphere during transport (Winchester and Wang, 1989), although most calcium compounds exist in the form of alkaline calcium carbonates in the source region (Lee et al., 2000).

To determine which sources are important in neutralization of precipitation in Northern China, a correlation study was carried out examining the association with or affinity of [SO$_4^{2-}$ + NO$_3^-$] towards specific cation(s). In the study, NH$_4^+$ was more highly correlated with the sum of SO$_4^{2-}$ and NO$_3^-$ ($r = 0.60$, $P < 0.001$) than that of others cations including Ca$^{2+}$ ($r = 0.51$, $P < 0.01$), Mg$^{2+}$ ($r = 0.45$, $P < 0.05$), and Na$^+$ ($r = 0.37$, $P < 0.05$). This result demonstrated the major role that ammonia can play if it is present in excess of stoichiometric requirements (Shukla and Sharma, 2010). However, the quantity of NH$_4^+$ in precipitation was insufficient to neutralize the SO$_4^{2-}$ and NO$_3^-$ for most sites during the study period. Therefore, other cations should additionally neutralize remaining SO$_4^{2-}$ and NO$_3^-$ and Ca$^{2+}$ could play that role in this case.

If H$_2$SO$_4$, HNO$_3$, NH$_3$, and CaCO$_3$ are the only constituents involved in the acidification and neutralization of precipitation, a linear relation between the sum of H$^+$ + NH$_4^+$ + Ca$^{2+}$ and nss-SO$_4^{2-}$ + NO$_3^-$ can be expected (Kaya and Tuncel, 1997; Rodhe et al., 2002). Indeed, the hypothesis is confirmed by the regression coefficient ($r = 0.62$, $P < 0.001$) between variables (Figure 6). When the data of TJ in 2010 (Figure 6, in the dashed cycle) was excluded from the database, the coefficient increased to 0.78. In other words, it can be concluded that the acidity in precipitation is mainly caused by H$_2$SO$_4$ and HNO$_3$ and neutralized by CaCO$_3$ and NH$_3$.

Further to scale down and to quantify the relative contributions of NH$_3$ and CaCO$_3$ to the neutralization of acidity in precipitation at each site, a multiple linear regression analysis (MLR) was applied to SO$_4^{2-}$ and NO$_3^-$ separately using H$^+$, Ca$^{2+}$, and NH$_4^+$ as independent variables in eq 2 (Kaya and Tuncel, 1997):

\[
\begin{align*}
\text{SO}_4^{2-} &= z_0 + z_1 \, \text{NH}_4^+ + z_2 \, \text{Ca}^{2+} + z_3 \, \text{H}^+ \\
\text{NO}_3^- &= \beta_0 + \beta_1 \, \text{NH}_4^+ + \beta_2 \, \text{Ca}^{2+} + \beta_3 \, \text{H}^+
\end{align*}
\]

(2)

MLR results between SO$_4^{2-}$ and NO$_3^-$ or the cations NH$_4^+$, Ca$^{2+}$, and H$^+$ of precipitation samples during the 3-year period at the 10 sites are presented in Table 1. The results at the BD, BJ, and TS sites suggest that NH$_4^+$ and Ca$^{2+}$ were the major neutralizing agents for NO$_3^-$ and SO$_4^{2-}$, respectively. At these sites, out of the total explained variables, more than half of NO$_3^-$ and SO$_4^{2-}$ are in the form of NH$_4$NO$_3$ and CaSO$_4$.

Table 1 also shows that Ca$^{2+}$ was the primary neutralizing agent for both NO$_3^-$ and SO$_4^{2-}$ at the TG, TJ, YC, and YF sites, where out of the total explained variables, 41–88% of NO$_3^-$ and SO$_4^{2-}$ was present as CaSO$_4$ and Ca(NO$_3$)$_2$. On the other hand, NH$_3$ appears to play a more significant role than Ca$^{2+}$ in the neutralizing process at the CZ, LC, and XL sites, where out of the total explained variables, 32–77% of NO$_3^-$ and SO$_4^{2-}$ was present as (NH$_4$)$_2$SO$_4$/NH$_4$HSO$_4$ and NH$_2$NO$_2$. Of note, out of the total explained variables, 14% (or less) of SO$_4^{2-}$ was associated with H$^+$, indicating that H$_2$SO$_4$ was not neutralized by calcium compounds (as CaCO$_3$) and NH$_3$ (Anatolaki and Tsitouridou, 2009). In contrast, a small percentage (~6%) of NO$_3^-$ is in the form of HNO$_3$.

### Table 1. Multiple linear regression data for sulfate and nitrate against ammonium, calcium, and hydrogen

<table>
<thead>
<tr>
<th>Independent Variables</th>
<th>BD</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ % explained by NH$_4^+$</td>
<td>79.0</td>
</tr>
<tr>
<td>% explained by Ca$^{2+}$</td>
<td>14.5</td>
</tr>
<tr>
<td>% explained by H$^+$</td>
<td>2.5</td>
</tr>
<tr>
<td>Total explained (%)</td>
<td>77.3</td>
</tr>
</tbody>
</table>

| SO$_4^{2-}$ % explained by NH$_4^+$ | 12.0 |
| % explained by Ca$^{2+}$ | 87.2 |
| % explained by H$^+$ | 8.1 |
| Total explained (%) | 87.5 |
Conclusions

An investigation of the pH and chemical species responsible for the variations of pH of precipitation was carried out from December 2007 to November 2010 at the 10 selected sites over Northern China. Three major conclusions can be made:

1. pH of individual events revealed that precipitation was mostly alkaline across Northern China, ranging from 3.1 to 9.4 with an overall arithmetic mean of 6.1. However, approximately one-third of precipitation samples were acidic (pH < 5.6), indicating that the acidification of precipitation is a serious problem. H2SO4 was still the major contributor to the acidity of precipitation, but HNO3 may play a more important role than H2SO4 in determining precipitation acidity in the target areas in the future.

2. The observed alkalinity of precipitation was due to the high loadings of alkaline compounds commonly abundant in the atmosphere in Northern China. Alkaline constituents neutralized most of the acidity caused by H2SO4 and HNO3. The calculation of NF indicated that the acidity of the precipitation was largely neutralized by\( \text{Ca}^{2+} \) and \( \text{NH}_4^+ \), whereas \( \text{Mg}^{2+} \), \( \text{Na}^+ \), and \( \text{K}^+ \) played a minor or insignificant role. The application of MLR analysis further revealed that both \( \text{NH}_4^+ \) and \( \text{Ca}^{2+} \) contributed to the neutralization process, but their relative dominance in neutralization varied form site to site.

3. There were insignificant site-to-site and year-to-year variations of pH derived from sum of nss-SO4\(^{2-} \) and NO3\(^{-} \) in precipitation. However, the measured annual VWM pH was found to be highly variable, highlighting the role and mechanism of buffering of precipitation acidity by alkaline CaCO3 and gas NH3. Hence, it can be expected that in the near future, the reduction of primary emissions of particles and gas ammonia may lead to increasing acid precipitation at the same sulfur levels in Northern China.

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References


### About the Authors

**Yuesi Wang** is a tenured professor of the State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics at Chinese Academy of Sciences in Beijing, People’s Republic of China.

**Wenpeng Yu** is a Ph.D. candidate in the Institute of Atmospheric Physics at Chinese Academy of Sciences.

**Yuepeng Pan** is an assistant professor in the Institute of Atmospheric Physics at Chinese Academy of Sciences.

**Dan Wu** is an assistant professor in the Department of Environmental Science and Engineering at Nanjing University of Information Science and Technology, Nanjing, People’s Republic of China.