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Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere

R. K. Pathak¹, W. S. Wu¹, and T. Wang^{1,2}

¹Department of Civil and Structural Engineering, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, China

²Chinese Research Academy of Environmental Sciences, Beiyuan, Beijing, China

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Abstract. Strong atmospheric photochemistry in summer can produce a significant amount of secondary aerosols, which may have a large impact on regional air quality and visibility. In the study reported herein, we analyzed sulfate, nitrate, and ammonium in PM_{2.5} samples collected using a 24-h filter system at suburban and rural sites near four major cities in China (Beijing, Shanghai, Guangzhou, and Lanzhou). Overall, the PM_{2.5} mass concentrations were high (with a mean value of 55–68 g μg m⁻³), which reflects the long-known particulate pollution in China's large urban centers. We observed very high concentrations of sulfate and nitrate at the Beijing and Shanghai sites, and, in particular, abnormally high levels of nitrate (24-h average concentration up to 42 g μg m⁻³ and contributing up to 25% of the PM_{2.5} mass) in the ammonium-poor samples. The Beijing and Shanghai aerosols were characterized by high levels of aerosol acidity (~220–390 nmol m⁻³) and low levels of in-situ pH (−0.77 to −0.52). In these samples, the formation of the observed high concentrations of particulate nitrate cannot be explained by homogeneous gas-phase reaction between ammonia and nitric acid. Examination of the relation of nitrate to relative humidity and aerosol loading suggests that the nitrate was most probably formed via the heterogeneous hydrolysis of N₂O₅ on the surface of the moist and acidic aerosols in Beijing and Shanghai. In comparison, the samples collected in Lanzhou and Guangzhou were ammonium-rich with low levels of aerosol acidity (~65–70 nmol m⁻³), and the formation of ammonium nitrate via the homogeneous gas-phase reaction was favored, which is similar to many previous studies. An empirical fit has been derived to relate fine nitrate to aerosol acidity, aerosol water content, aerosol surface area, and the precursor of nitrate for the data from Beijing and Shanghai.

1 Introduction

Atmospheric PM_{2.5} (particulate matter with an aerodynamic diameter of 2.5 microns or less) is linked to visibility reduction, adverse health effects, and climate change (Heintzenberg, 1989; Speizer, 1989; Dockery et al., 1993; Charlson and Heintzenberg, 1995; Vedal, 1997). Water-soluble ions often account for a major fraction of PM_{2.5} mass, along with organic and elemental carbon (Andrews et al., 2000; Chow et al., 2006; Seinfeld and Pandis, 2006). Due to the uptake of water vapor by water-soluble ionic species, they play a central role in the earth's radiation balance – directly by scattering incoming solar radiation and indirectly by altering cloud properties (Hillamo et al., 1998).

Sulfate and ammonium are the predominant water-soluble ionic species in PM_{2.5}, whereas nitrate can be found in both PM_{2.5} and coarse mode (>2.5 μm) particles, depending on the atmospheric conditions that support the formation of ammonium nitrate and the presence of coarse mode particles that react with nitric acid (HNO₃), such as sea-salt and crustal aerosols (Seinfeld and Pandis, 2006). Generally, ammonium nitrate is formed in areas with high ammonia (NH₃) and HNO₃ concentrations and low temperatures. The neutralization of acidic sulfate by ammonia is favored over the formation of ammonium nitrate via a homogeneous gas phase reaction between ammonia and nitric acid. Therefore, ammonium nitrate in PM_{2.5} is typically associated with significantly neutralized or ammonium-rich sulfate (Pathak et al., 2004a; Seinfeld and Pandis, 2006). Nitric acid is predominantly formed during the daytime via the homogeneous gas-phase reaction of NO₂+OH or via heterogeneous chemistry that involves the hydrolysis of dinitrogen-pentoxide (N₂O₅) on the aerosol surface at nighttime.

The contributions of various pathways of nitrate formation to PM_{2.5} mass are less known compared to the formation of sulfate, which is dominated by cloud/fog processes (Karamchandani and Venkatram, 1992; Pandis et al., 1992;



Correspondence to: T. Wang
(cetwang@polyu.edu.hk)

Dennis et al., 1993; Seinfeld and Pandis, 2006). The production of sulfate and nitrate and their resulting contributions to PM_{2.5} mass depend on such factors as the emission mix of the precursors (SO₂, NH₃, NO_x), the levels of oxidants in both the gas and aqueous phases, the characteristics of pre-existing aerosols/fog/cloud, and meteorological conditions. These conditions can vary from location to location; thus, it is important to understand how they individually and collectively affect the production of secondary aerosols in different parts of the world.

With China's rapid industrialization and urbanization, its urban and regional air quality is becoming of increasing concern. Large-scale emissions of aerosol precursors can lead to the significant production of secondary aerosols, especially in the summer, when the level of photochemical activities is high and frequent fog/clouds prevail due to the large water-vapor content. Indeed, very high concentrations of sulfate (10–50 μgm⁻³) have been reported in China (He et al., 2001; Hu et al., 2002; Yao et al., 2003; Wang et al., 2004; Zheng et al., 2005; Han et al., 2007). Therefore, there is a need for an improved understanding of the atmospheric distribution of the ionic species and of the formation mechanisms of sulfate and nitrate in the chemically rich atmosphere of China.

From 2004–2006, PM_{2.5} samples were collected during the summer using a 24-h filter-based system at suburban and rural sites near four major cities in China: Beijing, Shanghai, Guangzhou, and Lanzhou. The sampling campaign was part of a larger study that aimed to investigate the impact of Chinese mega-cities on the regional environment. In the current study, we analyzed the water-soluble ionic species in these PM_{2.5} samples. We investigated the acidity characteristics of the sulfate-nitrate-ammonium system and nitrate formation in the four cities, which are situated in the northern, eastern, southern, and north-western regions of China. We found strikingly high concentrations of nitrate (with 24-h average values up to 42 μgm⁻³) in the Beijing and Shanghai samples, and, in these samples, nitrate was associated with high concentrations of sulfate in the ammonium-poor aerosols, which is unusual according to the results of previously published studies. We discuss the possible role of nighttime heterogeneous NO_x/O₃ chemistry in nitrate formation in the ammonia-deficient atmosphere of Beijing and Shanghai.

2 Experiment and methods

2.1 Sampling sites

The PM_{2.5} samples were collected in suburban and rural settings near three of the largest and most economically important mega-cities in Northern, Eastern, and Southern China (i.e., Beijing, Shanghai, and Guangzhou) and near another large city, Lanzhou, which is in the interior region of China and has a drier climate. These sites were carefully chosen to

allow detailed examination of the characteristics of the processed/secondary aerosols from these large urban centers and to sample the regional-scale pollution.

In Beijing, the measurements were conducted at Hei Shan Zhai, a rural mountainous site (40°21'N, 116°18'E, 280 m above sea level) approximately 50 km north of the center of Beijing (Tiananmen Square). The Tianjin Municipality (population: ~10 million) is 150 km southeast. This site is frequently affected by pollution from Beijing and the region, which is brought by the strengthening southerly winds in the afternoon during summer (Wang et al., 2006). The instruments were set up at a height of 5 m, and sampling was conducted from 29 June to 2 August 2005. During the measurement period, the weather was generally humid and cloudy with light winds.

In Shanghai, the largest city in China, the sampling site was located at Tai Cang, which is 44 km to the northwest. Shanghai is home to China's largest petrochemical complex, steel makers, a seaport, and other industries. Although Tai Cang actually belongs to Jiangsu Province, it is often influenced by emissions from Shanghai urban areas under prevailing summertime southeasterly winds. Several coal-fired power plants are situated within 20 km of the site. The sampling instruments were set up on the rooftop of the Tai Cang Meteorological Station (31°27'N, 121°06'E), about 15 meters above ground level. The sampling was conducted from 5 May to 15 June 2005. During the study period, the weather was usually cloudy with moderate winds.

Lanzhou is a major city and industrial center in the north-western part of China. It is one of the most polluted cities in China, partly due to its valley topography. The sampling site was located at Renshoushan Park, a suburban mountainous area with the industrial region to the southwest and the urban area to the east. The measurements were conducted from June 18 to July 17, 2006, when the weather was sunny and dry with weak winds.

Guangzhou is also one of the most polluted cities in China due to its fast growth in population and energy use. The sampling site was located at Wan Qing Sha, which is a suburban area approximately 50 km southeast of Guangzhou City. The sampling instruments were set up on the rooftop of a secondary school at 17 meters above ground level. The measurements were made between 15 and 27 May 2004 when the weather was cloudy and humid with moderate winds.

2.2 Measurements and analysis

The 24-h PM_{2.5} samples were collected on pre-weighed Teflon filters (ZeflourTM, 2 μm pore size and 47 mm diameter, Pall Gelman Inc.) using a Thermo Andersen Chemical Speciation Monitor (Thermo Electron Corporation, RAAS2.5-400) at a flow rate of 7 LPM. Filters were stored at 4°C after sampling at the sampling site and during the transportation as well as in the laboratory until chemical analysis was performed. The PM_{2.5} mass was determined

using the standard gravimetric method at 45% RH. The filters were then extracted with 10 mL of ultra-pure water in an ultrasonic bath for 30 minutes. The water extracts were filtered through a 0.2 μm -pore size 13-mm filter (MFS, 13JP020AN) and then stored in a bottle. The 100 μL extracts were injected into an ion chromatography (IC) system for analysis, the details of which are provided elsewhere (Wu and Wang, 2007).

Several meteorological parameters were also measured at each site. Wind direction and wind speed were recorded by a wind monitor (R. M. Young Company, 05305VM), and the ambient relative humidity and temperature were measured with a relative humidity/temperature probe (R. M. Young Company, 41372VC/CF).

2.3 Sampling artifacts

Artifacts can occur in filter-based sampling, due to interparticle interactions, gas-particle interactions, and the dissociation of semi-volatile species, thus changing the composition of the collected particles. This topic has been well-studied (Appel et al., 1984; Dasch et al., 1989; Harrison et al., 1990; Koutrakis et al., 1992; Zhang and McMurry, 1992; Cheng and Tsai, 1997; Tsai and Perng, 1998; Yao et al., 2001; Pathak et al., 2004a; Pathak and Chan, 2005). Depending on the aerosol composition and the relative humidity and temperature, the sampling artifacts of ammonium and nitrate can be significant. In the following sections, we estimated the magnitude of the artifacts for sulfate, nitrate and ammonium in our measurements, based on the knowledge and findings of previous studies.

2.3.1 Sulfate

The positive artifacts of sulfate are caused by absorption of SO₂ into the ammonium rich sulfate particles collected on the filter while sampling, which is consequently oxidized to form sulfate within the collected particles (Tsai and Perng, 1998; Pathak and Chan, 2005). In previous studies, the positive artifacts of sulfate have been estimated to be about 7% and 11% in the ammonium-rich samples of PM_{2.5} and PM₁₀, respectively (Tsai and Perng, 1998; Pathak and Chan, 2005). Therefore, in this study, an average of 7% positive sulfate artifacts is assumed for the ammonium-rich samples (collected mainly in Guangzhou and Lanzhou). The absorption of SO₂ by acidic particles is, however, negligible (Pathak and Chan, 2005), which is the case for Beijing and Shanghai.

2.3.2 Nitrate and ammonium

Artifacts of nitrate and ammonium occur due to evaporation of semivolatile NH₄NO₃ (NH₄NO₃(s) ↔ NH₃(g) + HNO₃(g)) from the particles collected on the filter due to fluctuations in temperature and RH and/or pressure drop across the filter, which perturb the gas-particle equilibrium (Appel et al., 1984; Dasch et al., 1989; Harrison et al., 1990; Koutrakis

et al., 1992; Zhang and McMurry, 1992; Cheng and Tsai, 1997; Tsai and Perng, 1998; Pathak et al., 2004a; Pathak and Chan, 2005). Nitrate evaporations are also possible due to the mixing of acidic (H₂SO₄) and alkaline particles (Ca(NO₃)₂, NaNO₃, KNO₃ etc.) on the filter (e.g. Ca(NO₃)₂ + H₂SO₄ → 2HNO₃(g) + CaSO₄). The above two processes cause negative bias of the filter data. Positive artifacts of nitrate can occur when HNO₃ is absorbed on the sea salt (or dust) particles collected on the filter (e.g. NaCl + HNO₃(g) ↔ NaNO₃ + HCl(g)) (Tsai and Perng, 1998; Pathak et al., 2004a; Pathak and Chan, 2005). Generally, the evaporations of semivolatile NH₄NO₃ under dry sampling conditions are the major cause for nitrate artifacts (Dasch et al., 1989; Harrison et al., 1990; Koutrakis et al., 1992; Zhang and McMurry, 1992; Cheng and Tsai, 1997; Tsai and Perng, 1998).

In our study, except for Lanzhou, samples in Beijing, Shanghai, and Guangzhou were collected in humid conditions and particles were generally deliquesced (RH > Deliquescence RH for the 24 h average measurements). Pathak and Chan (2005) have shown that nitrate artifacts from the deliquesced particles collected on the filter can be estimated using the following empirical correlations:

For ammonium rich samples:

$$\text{Nitrate loss (\%)} = 30 * [\text{Ln}([\text{NH}_4^+]/[\text{NO}_3^-]) - 1.2]$$

For ammonium poor samples:

$$\text{Nitrate loss (\%)} = 30 * [\text{Ln}([\text{H}^+]/[\text{NO}_3^-]) - 1.2]$$

In this present study, we have used the above methods to estimate the nitrate artifacts for the four city samples. The results show that the average nitrate artifacts were not significant for samples taken in Beijing (3%), Shanghai (10%), and Guangzhou (2%). For Lanzhou, due to its dry conditions, the estimated evaporated loss of 10% should be viewed as a lower limit.

The artifacts of ammonium are found to be small (~7%) in the ammonium-rich samples (Pathak and Chan, 2005). Hence, in this study, an average of 7% positive ammonium errors is considered for the ammonium-rich samples. However, the artifacts of ammonium were negligible (~1%) for the ammonium-poor samples. In this study we have corrected these sampling artifacts in the dataset.

2.4 Thermodynamic model

In this study, such in-situ aerosol properties as acidity and the water content of the aerosols are needed to investigate the aerosol acidity characteristics and the role of heterogeneous chemistry in nitrate formation. Here, in-situ aerosol acidity ([H⁺]_{ins}), is defined as the moles of free hydrogen ions in the aqueous phase of aerosols per unit of air (nmol m⁻³). As these properties cannot be measured directly, a chemical thermodynamic model (Aerosol Inorganic Model: *E-AIM*)

Table 1. Summary of water-soluble ions and acidity in PM_{2.5} and meteorological data for the four cities in China.

Parameter/Species	Beijing	Shanghai	Lanzhou	Guangzhou
Number of samples	25	40	25	13
SO ₄ ²⁻ (μg m ⁻³)	22.6±26.1	15.8±9.8	9.8±5.6	13.1±5.5
NO ₃ ⁻ (μg m ⁻³)	9.9±12.0	7.1±6.7	3.2±2.0	5.2±3.8
NH ₄ ⁺ (μg m ⁻³)	4.7±3.3	4.1±1.5	4.1±2.5	4.8±2.1
Na ⁺ (μg m ⁻³)	0.1	0.4	0.5	0.4
Ca ²⁺ (μg m ⁻³)	0.2	0.2	1.3	0.3
K ⁺ (μg m ⁻³)	1.3	2.3	0.8	1.0
Mg ²⁺ (μg m ⁻³)	0.03	0.06	0.40	0.03
Cl ⁻ (μg m ⁻³)	0.4	1.9	5.5	0.9
NO ₂ ⁻ (μg m ⁻³)	0.7	0.2	2.3	0.6
Sum of ionic species (μg m ⁻³)	40±42	32±21	26±11	27±12
PM _{2.5} (μg m ⁻³)	68±61	67±28	65±29	55±28
(NH ₄ ⁺)/(SO ₄ ²⁻) Molar Ratio	1.03±1.05	1.38±0.38	2.25±1.10	2.10±0.41
(NO ₃ ⁻)/(SO ₄ ²⁻) Molar Ratio	0.69±0.47	0.75±0.42	0.47±0.56	0.65±0.20
Aerosol Acidity ((H ⁺) _{Total} ; nmol m ⁻³)	390±545	220±225	65±44	70±58
in-situ Acidity ((H ⁺) _{ins} ; nmol m ⁻³)	228±344	96±136	7±6	25±29
Aerosol Water (μg m ⁻³)	77±91	24±26	10±12	55±68
pH	-0.52±0.62	-0.77±0.67	-0.38±0.64	0.61±0.71
T (°C)	26±5	22±6	25±5	26±4
RH (%)	63±18	64±12	45±16	79±9
Wind Speed (ms ⁻¹)	0.4±0.2	2.6±1.1	0.7±0.4	1.4±0.8

was used (Clegg et al., 1998). The Aerosol Inorganic Model (*E-AIM*: <http://www.aim.env.uea.ac.uk/aim/aim.php>) is a state-of-the-art aerosol thermodynamic model that can accurately simulate the in-situ acidity ($[\text{H}^+]_{\text{ins}}$), aerosol water content, and activities of ionic species in aqueous aerosols and the solid- and liquid-phase compositions of ionic strength up to about 40 M at equilibrium in the $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$ system (Clegg et al., 1998; Zhang et al., 2000).

The average ambient temperature, relative humidity, and average molar concentrations of total aerosol acidity ($[\text{H}^+]_{\text{Total}}$), NH_4^+ , SO_4^{2-} , and NO_3^- from the aqueous extract of the aerosols collected on the filter were used as the input in model-II of the *E-AIM* to obtain the in-situ acidity ($[\text{H}^+]_{\text{ins}}$), bi-sulfate (HSO_4^-), SO_4^{2-} , NO_3^- , and NH_4^+ in the liquid phase, and/or any salt of these ions that was formed in the solid phase at equilibrium. Here, aerosol acidity ($[\text{H}^+]_{\text{Total}}$), is the total amount of acid contributed by the strong acids, such as sulfuric and/or nitric acid, in the aqueous extract of the aerosols collected on the filter and is defined as $[\text{H}^+]_{\text{Total}} = [\text{H}^+]_{\text{ins}} + [\text{HSO}_4^-] + \text{any } [\text{H}^+]$ in the solid phase with sulfate and/or nitrate at equilibrium. The aerosol acidity of PM_{2.5} ($[\text{H}^+]_{\text{Total}}$) can be estimated using an ionic balance of the relevant inorganic ionic species (Lippmann et al., 2000). In this paper, $[\text{H}^+]_{\text{Total}}$ was estimated as

$$[\text{H}^+]_{\text{Total}} = (2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-]) - ([\text{NH}_4^+]).$$

The in-situ pH of aerosols was estimated as the negative log of activity of the hydrogen ion ($\text{pH} = -\text{Log}(\gamma \times [\text{H}^+]_{\text{ins}} / \text{aerosol solution volume})$) inside the aerosol droplets, where γ is the activity coefficient for $[\text{H}^+]_{\text{ins}}$ (Yao et al., 2006). Aerosol solution volumes (solution volume = (mass of solute ionic species + aerosol water content) / solution densities) were computed using Tang and Munkelwitz's (1994) framework for estimating the solution densities of aqueous aerosols. Hereafter, for simplicity, pH connotes in-situ pH.

3 Results and discussion

3.1 Concentrations and composition of PM_{2.5}

Table 1 summarizes the average concentrations of the ionic species of PM_{2.5} in the four Chinese cities. The average summertime PM_{2.5} mass concentrations at the Beijing, Shanghai, Lanzhou, and Guangzhou sampling sites were $68 \pm 61 \mu\text{g m}^{-3}$, $67 \pm 28 \mu\text{g m}^{-3}$, $65 \pm 29 \mu\text{g m}^{-3}$, and $55 \pm 28 \mu\text{g m}^{-3}$, respectively. Although the average summertime PM_{2.5} concentrations were roughly the same at all of the sites, there were large variations within each site, from a couple of hundred to a few $\mu\text{g m}^{-3}$, especially at the Beijing

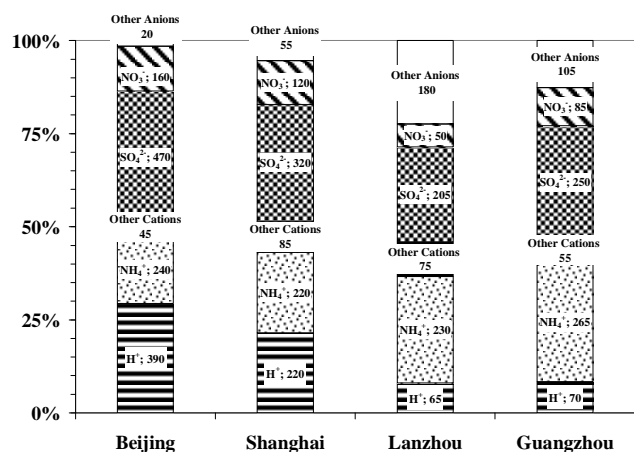


Fig. 1. Relative distributions among water-soluble ionic species in PM_{2.5} in the four cities. The numbers shown in the figure are the average nano-equivalent concentrations (neqm⁻³).

rural site. On several days during the study period, very high particulate concentrations were observed: the 24-h average PM_{2.5} mass was up to 212 μg m⁻³, and the sulfate and nitrate concentrations exceeded 90 and 40 μg m⁻³, respectively. The highest PM_{2.5} value was six times the new USA EPA standard for 24-h PM_{2.5} (35 μg m⁻³). Higher concentrations of PM_{2.5} (>100 μg m⁻³) were usually observed at all of the sites when the winds blew from the direction of the major urban area and/or the wind speeds were low (<1 ms⁻¹). In contrast, very low concentrations (<15 μg m⁻³) were observed when the sites received background air.

Water-soluble ionic species, including sulfate, nitrate, chloride, ammonium, and crustal species, contributed to a large fraction (40–60%) of the PM_{2.5} mass, as shown in Table 1. These concentrations of sulfate and nitrate were generally much higher than those that have been observed at Hong Kong, US, Indian, Brazilian, and European sites (Allen and Miguel, 1995; Pathak et al., 2003; Ho et al., 2006; Pandey et al., 2006; Sillanpaa et al., 2006; Lee et al., 2008).

In general, sulfate, nitrate, and ammonium together contributed to more than 80% of the total inorganic ionic species mass at all of the sites, which indicates the predominance of these three ions in the total water-soluble ions, as can be seen in Fig. 1. Other cations (sodium, potassium, magnesium, and calcium) and anions (nitrite and chloride) contributed to a minor fraction of the water-soluble species (~2–10% each) at all of the sites, except for chloride (~20%) in the Lanzhou samples, which was not balanced by the small concentrations of crustal species. Such high concentrations of chloride in PM_{2.5} may be associated with organic halides from local industrial sources.

We also examined the acidity of aerosols, estimated using the method described in Sect. 2.4. The average aerosol acidity concentrations ([H⁺]_{Total}) in the Beijing, Shanghai, Lanzhou, and Guangzhou samples were 390, 220, 65, and

70 nmol m⁻³, respectively. It is interesting to note that there were almost the same average concentrations of ammonium (~240±20 nmol m⁻³) at all of the sites. However, ambient ammonia could neutralize only a small fraction (~40–50%) of the acidic sulfate and nitrate aerosols at the Beijing and Shanghai sites. In contrast, sulfate and nitrate were almost fully neutralized by ammonia in the Lanzhou and Guangzhou samples. In these samples, the nitrate concentrations were low to moderate (45–85 nmol m⁻³) and were largely tied up with ammonium, as discussed in Sect. 3.3. However, the nitrate distributions were quite unique in the Beijing and Shanghai samples. Such high nitrate concentrations (120–160 nmol m⁻³) with concomitant high levels of acidity (220–390 nmol m⁻³) are not normally observed elsewhere. We discuss the possible mechanism for the production of such a high nitrate concentration in an ammonia-poor environment in Sect. 3.3.

3.2 Characteristics of acidity, sulfate, and ammonium

The acidic characteristics of atmospheric aerosols are determined by the extent of the neutralization of acidic sulfate and nitrate by ammonia. In PM_{2.5}, a ratio of the equivalents of ammonium to the sum of sulfate plus nitrate that is less than one indicates the partial neutralization of acidic aerosols. In the Beijing and Shanghai samples, this ratio was much less than one, especially at higher concentrations of sulfate and nitrate, as shown in Fig. 2. This indicates that the PM_{2.5} samples were significantly acidic when the atmospheric concentrations of sulfate and nitrate were high. In other words, the complete neutralization of sulfate and nitrate was not achieved in the Beijing and Shanghai samples, and these samples were, therefore, ammonium-poor. In contrast, sulfate and nitrate was almost fully neutralized, and the aerosols were ammonium-rich, in most of the Lanzhou and Guangzhou samples. We also compared the data from the four cities in this study with data on the acidity, sulfate, and ammonium characteristics of samples from previously published studies. As shown in Fig. 2, sulfate and nitrate were almost completely neutralized, which indicates an ammonium-rich environment in most of the samples from the previous studies included in this paper. Interestingly, the highest atmospheric concentrations of ammonium in this study and those in the previous studies were comparable. However, the maximum sulfate and nitrate concentrations were higher by a factor of 2–3, which led to the ammonium deficiency in the Beijing and Shanghai samples. This result obviously distinguishes the PM_{2.5} acidity characteristics in the Beijing and Shanghai samples from those in Lanzhou and Guangzhou and from those in the previous studies.

The in-situ acidity of aerosols is an important parameter, as it affects many of the acidity-dependent heterogeneous chemical processes on the aerosol surfaces, such as the oxidation of SO₂, the hydrolysis of N₂O₅, and the formation of organic aerosols (Chameides and Stelson, 1992; Sievering et

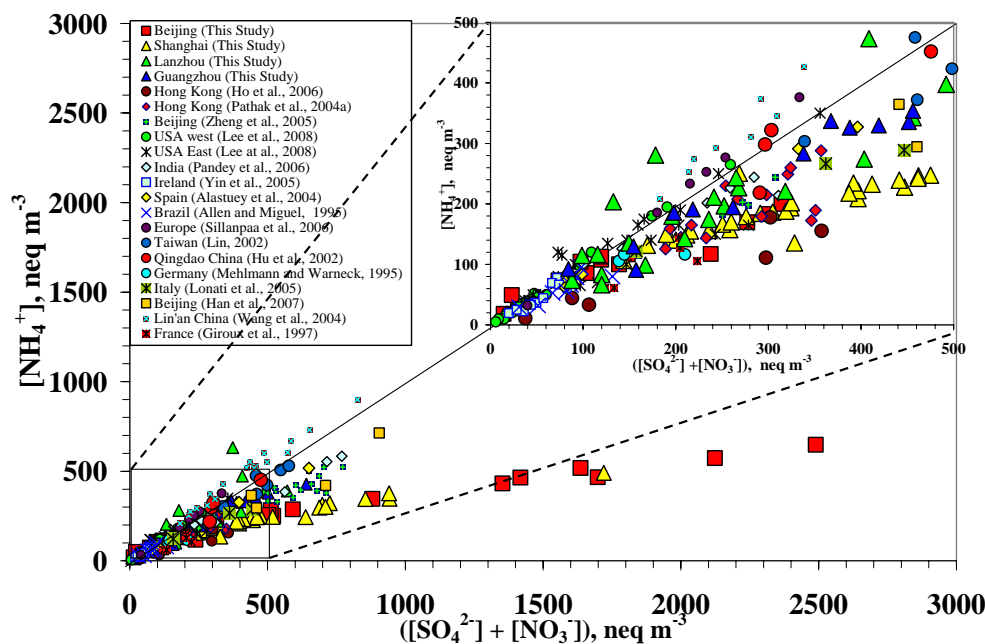


Fig. 2. Ammonium concentration as a function of sum of the sulfate and nitrate equivalent concentrations in the PM_{2.5} samples.

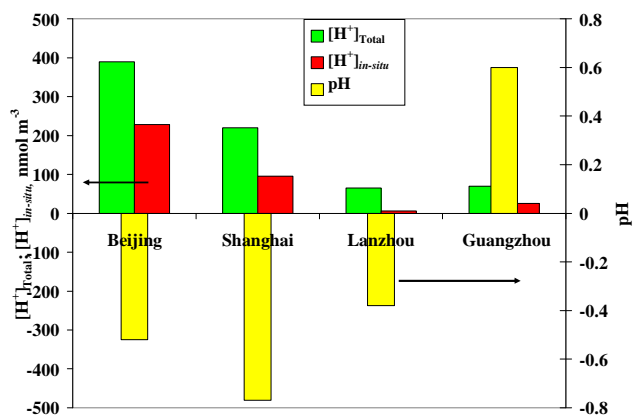


Fig. 3. Acidity characteristics of PM_{2.5} in the four cities.

al., 1995; Van Oss et al., 1998; Gao et al., 2004; Nemitz et al., 2004; Surratt et al., 2007). In-situ acidity in the PM_{2.5} samples was estimated using the thermodynamic model (*E-AIM*) described in Sect. 2.4.

Figure 3 shows the average in-situ acidity ($[H^+]_{ins}$), aerosol acidity ($[H^+]_{Total}$), which is also determined using the method described in Sect. 2.4, and the pH levels in the four city samples. A high level of aerosol acidity (390–220 nmol m⁻³) was found in the samples from Beijing and Shanghai. The acidity characteristics of the Lanzhou and Guangzhou aerosols were much different from those in the Beijing and Shanghai samples. As previously discussed, PM_{2.5} was almost fully neutralized in the former

two city samples. Therefore, a low level of aerosol acidity was found in the Lanzhou (~65 nmol m⁻³) and Guangzhou (~70 nmol m⁻³) samples. The average aerosol acidity levels of PM_{2.5} measured in Hong Kong (~75 nmol m⁻³) and the US (Connecticut ~42 nmol m⁻³; North US ~45 nmol m⁻³) were comparable to those in the ammonium-rich samples of Lanzhou and Guangzhou, but much lower than those in the Beijing and Shanghai samples (Pathak et al., 2003; Speizer, 1989; Keeler et al., 1991; Liu et al., 1996).

The in-situ acidity ($[H^+]_{ins}$) was 228 nmol m⁻³ (59% of $[H^+]_{Total}$), 96 nmol m⁻³ (43% of $[H^+]_{Total}$), 6 nmol m⁻³ (9% of $[H^+]_{Total}$), and 25 nmol m⁻³ (35% of $[H^+]_{Total}$) in the Beijing, Shanghai, Lanzhou, and Guangzhou samples, respectively. On average, a large fraction (59%) of aerosol acidity was released as in-situ acidity (228 nmol m⁻³) due to the high levels of aerosol water content in the Beijing samples. The average aerosol water content was $77 \pm 91 \mu\text{gm}^{-3}$, $24 \pm 26 \mu\text{gm}^{-3}$, $10 \pm 12 \mu\text{gm}^{-3}$, and $55 \pm 68 \mu\text{gm}^{-3}$ in the Beijing, Shanghai, Lanzhou, and Guangzhou samples, respectively. Aerosol water content can be critical in determining in-situ acidity (Pathak et al., 2004b). For instance, although a higher level of aerosol water content frees more $[H^+]$ ions from H₂SO₄ and/or HSO₄⁻ molecules in the aqueous aerosol leading to higher in-situ acidity, but overall it dilutes the hydrogen ion concentrations [moles/ mole of aerosol water] – that increases the pH of the aerosols – thus making the aerosol less acidic. The average pH was -0.52, -0.77, -0.38, and 0.61 in the Beijing, Shanghai, Lanzhou, and Guangzhou samples, respectively, which is comparable to the values reported in the literature: the pH of aerosols

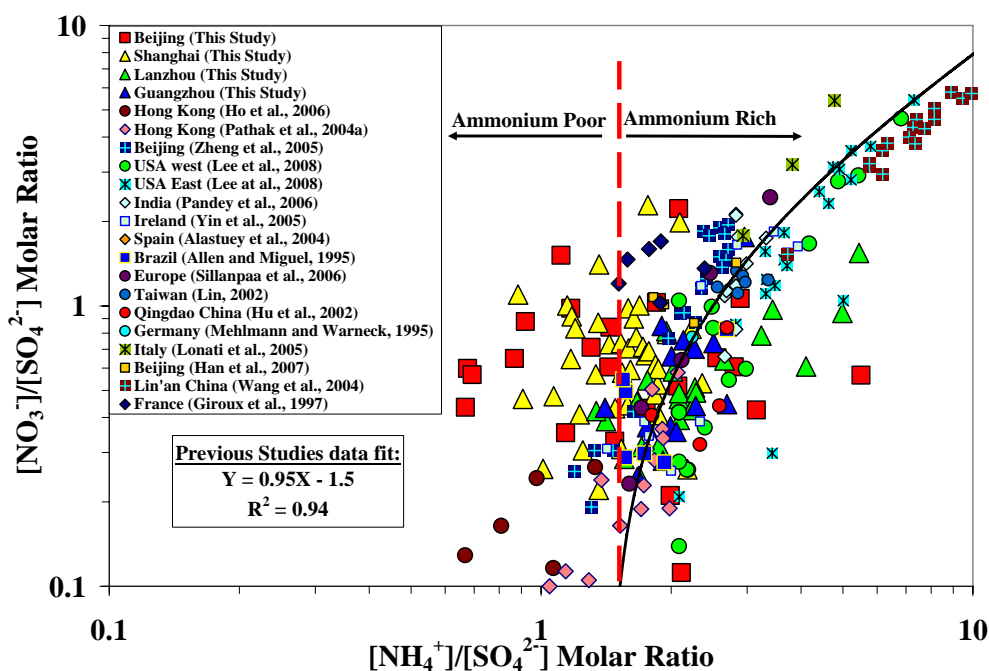


Fig. 4. Nitrate to sulfate molar ratio as a function of as a function of ammonium to sulfate molar ratio.

ranged from -1 to 3 in Hong Kong and the US (Pathak et al., 2004b; Yao et al., 2006; Fridlind and Jacobson, 2000; Meng et al., 1995; Seinfeld and Pandis, 2006).

3.3 Characteristics and formation of nitrate

One important finding of this study is the high concentrations of nitrate found in the ammonium-deficient samples from the Beijing and Shanghai sites, which is different from previous studies, where significant amount of PM_{2.5} nitrate was normally found in an ammonia-rich environment. In general, the atmospheric conditions at the Beijing and Shanghai sites were quite different from the other sites included in this study in terms of chemical mix and weather conditions. The pollution levels observed at the Beijing and Shanghai sites were much higher than at the other sites. The weather was generally humid. The samples with high concentrations of nitrate were collected during humid and hazy weather, which were associated with high sulfate and acidity. In this section, we examine in detail the possible causes of high nitrate in acidic samples of PM_{2.5}.

Figure 4 shows the nitrate-to-sulfate molar ratio ($[\text{NO}_3^-]/[\text{SO}_4^{2-}]$) as a function of the ammonium-to-sulfate molar ratio ($[\text{NH}_4^+]/[\text{SO}_4^{2-}]$) for the samples in our four cities and for those from previous studies. These ratios are used to show the reaction between ammonia and nitric acid and the other formation processes of nitrate in different (relative) concentrations of sulfate. In most of the previous studies, the relative abundance of nitrate increased as the ammonium-to-sulfate molar

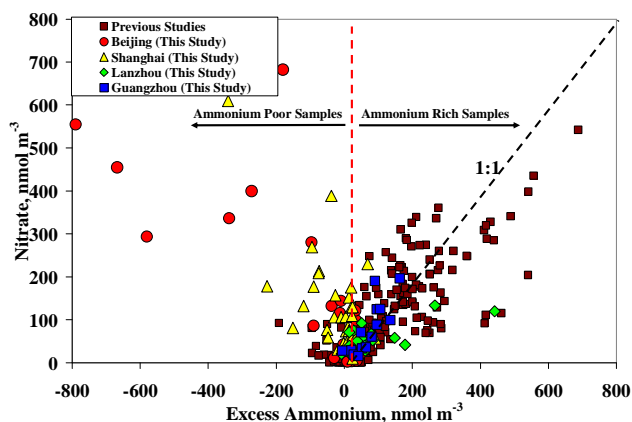


Fig. 5. Nitrate concentration as a function of “Excess Ammonium”. The data from previous studies include all of the studies mentioned in Figs. 2 and 4.

ratio increased in the ammonium-rich samples. This suggests that at $[\text{NH}_4^+]/[\text{SO}_4^{2-}]=1.5$ nitrate formation via gas-phase reaction $\text{NH}_3+\text{HNO}_3 \leftrightarrow \text{NH}_4\text{NO}_3$ becomes evident in the $\text{NH}_3-\text{H}^+-\text{SO}_4^{2-}-\text{H}_2\text{O}$ system in aerosol (Pathak et al., 2004a, 2005). In fact, “excess ammonium” defined as the amount of ammonium in excess of that required for $[\text{NH}_4^+]/[\text{SO}_4^{2-}]=1.5$ (i.e., excess $[\text{NH}_4^+]=([\text{NH}_4^+]/[\text{SO}_4^{2-}]-1.5) \times [\text{SO}_4^{2-}]$) was similar to the nitrate concentration, as shown in Fig. 5. This suggests that the nitrate concentration increased with an almost similar increase in excess ammonium via the gas-phase

homogeneous reaction between the ambient ammonia and nitric acid in the ammonium-rich samples, thus forming nitrate or the nitrate-sulfate salts of ammonium. In other words, when the “excess ammonium” is >0 , homogenous gas-phase formation of nitrate is significant, as shown in Fig. 5. The scattering of the data can be attributed to the minor influences of other atmospheric processes, such as ammonium chloride and sodium nitrate formation. The data from previous studies, coupled with the solid line shown in Fig. 4, which is the best fit to the pooled data from other studies, illustrate the characteristics of nitrate formed via the homogenous gas-phase reaction between ammonia and nitric acid. The nitrate-to-sulfate molar ratio, in contrast, was very low and scattered at $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ below 1.5 for the few samples from Hong Kong, Beijing, the Great Smoky Mountains in the eastern US, and a few European sites in the previous studies. This suggests that nitrate formation was not important in the ammonium-poor samples from the previous studies. The small amount of nitrate observed in these samples may be associated with crustal species in PM_{2.5}. A few samples from France and Brazil were outliers, and thus the nitrate formation in these samples cannot be explained by the homogeneous gas-phase mechanism that involves a reaction between ammonia and nitric acid.

In this study, most of the samples from Lanzhou and Guangzhou were ammonium-rich, and their nitrate characteristics are similar to those found in ammonium-rich conditions. The nitrate from the Lanzhou and Guangzhou samples shows a strong association with ammonium, as is clearly shown in Figs. 4 and 5, thus suggesting that the PM_{2.5} nitrate was primarily produced via the homogeneous gas-phase reaction between the ambient ammonia and nitric acid. Some of the scattering in the Lanzhou data may be due to the association of ammonium with the observed high chloride concentrations.

In the Beijing and Shanghai samples collected for the present study, the nitrate showed strikingly different compositional characteristics than those described above. Most of these samples were ammonium-poor, but contained high concentrations of nitrate. Figure 4 clearly shows that most of the samples fall in the region with an ammonium-to-sulfate molar ratio lower than 1.5, yet with a high nitrate-to-sulfate ratio. Figure 5 further shows that the nitrate concentration increased with a decrease in excess ammonium, thus indicating that nitrate is associated with acidity. These results suggest that the high nitrate concentrations in Beijing and Shanghai cannot be explained by the homogeneous gas-phase reaction that involves ammonia and nitric acid.

Evidence exists to indicate that the nighttime heterogeneous hydrolysis of N₂O₅ on the moist surface of the pre-existing aerosols was responsible for the formation of the high PM_{2.5} nitrate in the ammonium-poor samples from Beijing and Shanghai. In the following section, we examine the parameters that are critical to hydrolysis in the atmosphere and their connection to the observed nitrate concentration.

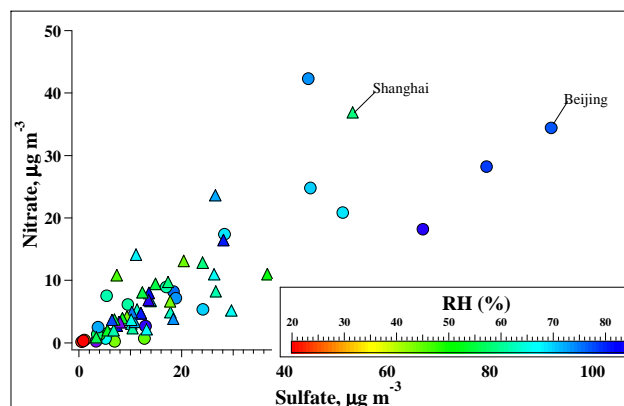


Fig. 6. Nitrate concentration as a function of sulfate concentration and ambient RH.

Laboratory and field studies have shown that greater hygroscopicity, surface area, and acidity of the preexisting particles promote the heterogeneous hydrolysis of N₂O₅ (Anttila et al., 2006; Martinez et al., 2000; Hu and Abbatt, 1997; McLaren et al., 2004; Hallquist et al., 2003). The N₂O₅ uptake coefficients increase as the acid weight fraction increases (or the pH decreases) in the sulfuric acid aerosols (Hu and Abbatt, 1997). Other laboratory studies have reported larger N₂O₅ uptake coefficients at higher levels of RH (Kane et al., 2001; Hallquist et al., 2003). Water plays a vital role in the heterogeneous hydrolysis of N₂O₅ on the aerosol surface in a complex way. On the one hand, higher levels of RH aid in producing greater aerosol water content and surface area, which promotes N₂O₅ uptake on the aerosol surfaces. On the other hand, an increase in aerosol water content decreases in-situ aerosol acidity, which reduces N₂O₅ uptake.

The high concentration of PM_{2.5} mass and the large fractions of water-soluble ionic species in PM_{2.5}, with sulfate as the main component, in Beijing and Shanghai suggest that the aerosols were largely hygroscopic with large surface areas. In addition, these aerosols were highly acidic, as discussed in the previous section. These conditions would favor the hydrolysis of N₂O₅ under reasonably high concentration of NO_x, thus leading to the formation of nitrate on pre-existing aerosols. Indeed, a strong positive correlation between sulfate and nitrate was observed, and high concentrations of nitrate and sulfate were found at high levels of RH (see Fig. 6). These results can be interpreted as nitrate being produced on the preexisting sulfate aerosols, which could provide sufficient surface area, aerosol water content, and aerosol acidity (lower pH level) for the hydrolysis of N₂O₅.

An additional indication of the role played by hydrolysis in the production of nitrate can be seen from the scatter plot between nitrate and the total reactive nitrogen (NO_y; NO_y=NO_x + HNO₃ + PAN + HONO + NO₃ + HO₂NO₂ + N₂O₅ + NO₃⁻) shown in Fig. 7. Here, NO_y represents the initial emission strength of the precursor of nitrate, NO_x,

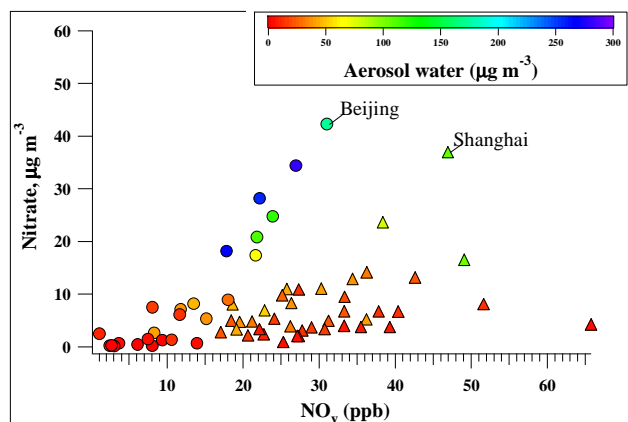


Fig. 7. Nitrate concentration as a function of total reactive nitrogen (NO_y), representing the precursor strength for N_2O_5 , and aerosol water.

in the sampled air mass. In this study, NO_y was measured with a chemiluminescence detector with an externally placed Mo catalytic converter (Wang et al., 2006). Figure 7 shows that the high concentrations of nitrate were mostly associated with large aerosol water content and were less dependent on NO_y , which indicates the importance of heterogeneous hydrolysis in the production of nitrate in these samples. It should be noted that since the samples with high concentrations of nitrates were collected during humid and hazy weather, the nitrate formed via hydrolysis would mostly partition in the aqueous aerosol phase.

We attempt to relate nitrate concentration to aerosol acidity, aerosol surface area, relative humidity, and the nitrate precursor as they are important to nitrate production via heterogeneous hydrolysis. As aerosol surface area was not measured in this study, we use the term $(\text{aerosol mass})^{2/3}$ as a proxy for surface area, which can be calculated as $k_1 \times N^{1/3} \times [\text{Aerosol Mass}]^{2/3} / \rho^{2/3}$, where N is the aerosol number concentration, ρ is the aerosol density, and k_1 is a constant. Here, we assume that N and ρ were constant. The following formulation gives the best empirical fit, with a correlation coefficient (R^2) of 0.75, as shown in Fig. 8.

$$[\text{NO}_3^-] = 8 \times \text{Ln}(-\text{pH}) + \frac{40}{3} \times \text{Ln}(\text{Aerosol Water}) + \frac{8}{3} \times$$

$$\text{Ln}(\text{Aerosol Mass}) + 8 \times \text{Ln}(\text{NO}_y) - 18 \text{ for } \text{pH} < 0,$$

and

$$[\text{NO}_3^-] = 8 \times \text{Ln}(\text{pH}) + \frac{40}{3} \times \text{Ln}(\text{Aerosol Water}) + \frac{8}{3} \times$$

$$\text{Ln}(\text{Aerosol Mass}) + 8 \times \text{Ln}(\text{NO}_y) - 18 \text{ for } \text{pH} \geq 0,$$

where Aerosol Mass is the measured mass ($\mu\text{g m}^{-3}$) of the sulfate, nitrate, and ammonium in $\text{PM}_{2.5}$, which is used to represent the surface area of the major water-soluble ions.

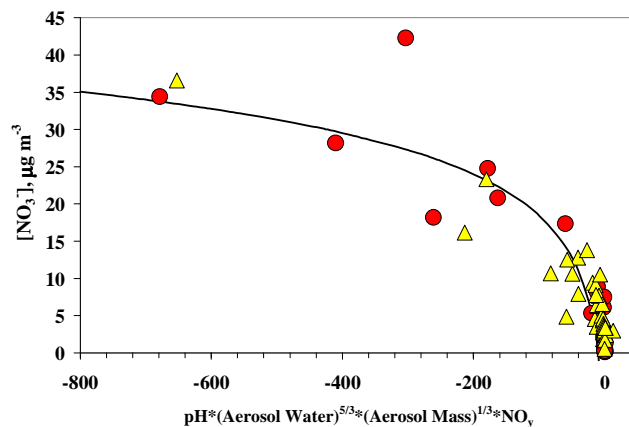


Fig. 8. Nitrate concentration as a function of aerosol pH, water, mass, and NO_y concentrations. Beijing and Shanghai data are shown by solid circles and triangles, respectively.

The formulation indicates that nitrate formation was linked to the parameters that are believed to be important to heterogeneous chemistry and shows a linear combination of the logarithmic functions of aerosol pH, aerosol water, aerosol mass, and NO_y . This empirical fit was obtained after we have tried different combinations of the desired parameters in order to get the best fit to the observation data. Although it is difficult to explain the exact form of this formula, it is consistent with our current understanding of hydrolysis, that is, the formation of nitrate via hydrolysis is enhanced with increasing acidity, surface area, water content, and concentration of total reactive nitrogen. The formula can be used to estimate the contribution of pH, aerosol water content, aerosol mass, and total reactive nitrogen to nitrate production in the samples from Beijing and Shanghai.

Some studies have reported that increase in nitrate concentrations inhibit the uptake of N_2O_5 on the aerosol droplet surface (Hallquist et al., 2003). The nitrate inhibiting effect can be seen in Fig. 8 which shows leveling off concentrations of nitrate at higher nitrate concentration despite high acidity, surface areas, and nitrate precursors concentration that act to promote hydrolysis.

4 Conclusion and implications

The average summertime $\text{PM}_{2.5}$ mass concentrations in the four Chinese cities studied were $55\text{--}68\mu\text{g m}^{-3}$, which are high when compared to the new USAEPA 24-h ambient air quality standard ($35\mu\text{g m}^{-3}$). Overall, $\text{PM}_{2.5}$ was highly acidic in Beijing and Shanghai, but was almost fully neutralized in Lanzhou and Guangzhou. Very high concentrations of nitrate (with a 24-h average value up to $42\mu\text{g m}^{-3}$) were found in the ammonium-poor samples in Beijing and Shanghai, which is in sharp contrast to many previous studies, which have normally found high $\text{PM}_{2.5}$

nitrate concentrations in ammonia-rich environments, as was the case for Lanzhou and Guangzhou. The high nitrate concentrations in the Beijing and Shanghai samples were observed in humid weather, with high levels of aerosol acidity and large aerosol concentrations. It is believed that the hydrolysis of N₂O₅ on the preexisting aerosols under these favorable conditions was responsible for the production of the observed nitrate. Sulfate is likely to play an important role because higher sulfate produces higher acidity, aerosol surface area and aerosol water content, which are believed to promote the heterogeneous hydrolysis. The very acidic PM_{2.5} aerosols in Beijing and Shanghai add to the atmospheric acidification and affect pH-dependent heterogeneous reactions, such as the oxidation of SO₂ to sulfate and the formation of secondary organic aerosols. The strong production of nitrates via hydrolysis can also change the atmospheric lifetime of NO_x, thereby affecting the photochemical production of ozone.

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