



HAL
open science

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

Ravi Kant Pathak, Wai Shing Wu, Tao Wang

► **To cite this version:**

Ravi Kant Pathak, Wai Shing Wu, Tao Wang. Summertime PM_{2.5} ionic species in four major cities of China: nitrate formation in an ammonia-deficient atmosphere. *Atmospheric Chemistry and Physics Discussions*, 2008, 8 (3), pp.11487-11517. hal-00304253

HAL Id: hal-00304253

<https://hal.science/hal-00304253>

Submitted on 18 Jun 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

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

Ravi Kant Pathak¹, Wai Shing Wu¹, and Tao 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

Received: 20 May 2008 – Accepted: 28 May 2008 – Published: 11 June 2008

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

Published by Copernicus Publications on behalf of the European Geosciences Union.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 $\mu\text{g m}^{-3}$), 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 $\mu\text{g m}^{-3}$ 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 ($\sim 220\text{--}390 \text{ nmol m}^{-3}$) 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 ($\sim 65\text{--}70 \text{ nmol m}^{-3}$), 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.

ACPD

8, 11487–11517, 2008

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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. At low NH₃ concentrations, the neutralization of acidic sulfate by ammonia is favored over the formation of ammonium nitrate, which involves 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 contribution to the formation of nitrate in PM_{2.5} is relatively less known compared to the formation of sulfate, which is dominated by cloud/fog processes (Karamchandani and Venkatram, 1992; Pandis et al., 1992; Dennis et al., 1993; Seinfeld and Pandis, 2006). The production of sulfate and nitrate and their resulting contributions to PM_{2.5}

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

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 μg m⁻³) have been reported in China (He et al., 2001; Hu et al., 2002; Yao et al., 2002; Wang et al., 2004; Zheng et al., 2005; Han et al., 2007). Nevertheless, 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 central regions of China. We found strikingly high concentrations of nitrate (with 24-h average values up to 42 μg m⁻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 central 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 a.s.l.) 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 m a.g.l. 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 northwestern part of China. It is one of the most polluted cities in China, partly due to its valley topography. The sam-

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



pling 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 18 June to 17 July 2006, when the weather was sunny and dry with weak winds.

5 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 m a.g.l. 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 μ m 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. The filters were stored at 4°C after sampling to minimize artifacts. 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 min. The water extracts were filtered through a 0.2 μ m-pore size 13-mm filter (MFS, 13JP020AN) and then stored in a bottle. The 100 μ L 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).

Summertime $PM_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 ammonium, sulfate, and nitrate in our measurements, based on the knowledge and findings of previous studies.

2.3.1 Sulfate

Positive artifacts for sulfate, which are due to the absorption of SO_2 by the collected particles, can be important, especially in ammonium-rich particles (Tsai and Perng, 1998; Pathak and Chan, 2005). These artifacts have been estimated to be about 7% and 11% in ammonium-rich samples of $\text{PM}_{2.5}$ and PM_{10} , respectively (Tsai and Perng, 1998; Pathak and Chan, 2005). Therefore, in this paper, an average of 7% positive sulfate artifacts is assumed for the ammonium-rich samples (collected mainly in Guangzhou and Lanzhou). The absorption of SO_2 by acidic particles is, however, negligible, which is the case for Beijing and Shanghai.

2.3.2 Nitrate and ammonium

The nitrate artifact on the filter depends on the degree of internal mixing, the aerosol composition, and the gas-aerosol ratio of nitric acid (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).

Summertime $\text{PM}_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



In the Beijing and Shanghai samples, the nitrate-to-sulfate ratios were high, and the samples were ammonium-poor. The particulate nitrate mainly existed in the form of aqueous nitric acid with sulfate in the internally mixed aerosols, as discussed in the following sections of this paper. Therefore, no significant nitrate artifacts were expected in the samples collected in Beijing and Shanghai. The nitrate sampling artifacts for the Lanzhou and Guangzhou samples, in which ammonium nitrate was present, were estimated on the basis of the ammonium-to-nitrate ratios on their filters using the methodology of Pathak and Chan (2005). However, the overall estimated artifacts were small for both sites (Guangzhou ~2%; Lanzhou ~10%). Similarly, the artifacts of ammonium were 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.

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 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) 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^- , which were mea-

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



sured from the aqueous extract of the sampled aerosols, were used as the input in model-II of the E-AIM to obtain the in-situ acidity ($[H^+]_{ins}$), 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 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 $[H^+]_{Total} = [H^+]_{ins} + [HSO_4^-] +$ any $[H^+]$ in the solid phase with sulfate and/or nitrate at equilibrium. The aerosol acidity of PM_{2.5} ($[H^+]_{Total}$) can be estimated using an ionic balance of the relevant inorganic ionic species (Lippmann et al., 2000). In this paper, $[H^+]_{Total}$ is estimated as

$$[H^+]_{Total} = (2 \times [SO_4^{2-}] + [NO_3^-]) - ([NH_4^+]).$$

The in-situ pH of aerosols was estimated as the negative log of activity of the hydrogen ion ($pH = -\text{Log}(\gamma \times [H^+]_{ins} / \text{aerosol solution volume})$) inside the aerosol droplets, where γ is the activity coefficient for $[H^+]_{ins}$ (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 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 $\mu\text{g m}^{-3}$, and the sulfate and nitrate concentrations exceeded 90 and 40 $\mu\text{g m}^{-3}$, respectively. The highest $\text{PM}_{2.5}$ value was six times the new USAEPA standard for 24-h $\text{PM}_{2.5}$ (35 $\mu\text{g m}^{-3}$). Higher loadings of $\text{PM}_{2.5}$ (>100 $\mu\text{g m}^{-3}$) 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 m s^{-1}). In contrast, very low concentrations (<15 $\mu\text{g m}^{-3}$) 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 $\text{PM}_{2.5}$ 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 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 $\text{PM}_{2.5}$ 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 ($[\text{H}^+]_{\text{Total}}$) 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

Summertime $\text{PM}_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 ammonium to sulfate, plus nitrate equivalents that is less than one indicates the partial neutralization of acidic aerosols. In the Beijing and Shanghai samples, the ammonium-to-sulfate plus nitrate 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 loadings 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 loadings 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

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 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±91 μg m⁻³, 24±26 μg m⁻³, 10±12 μg m⁻³, and 55±68 μg m⁻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, a higher level of aerosol water content frees a larger fraction of aerosol acidity as in-situ acidity, but it dilutes the hydrogen ion concentrations – that is, 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 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).

5 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, which is different from previous studies and indicates the significant amount of PM_{2.5} nitrate that is normally found in an ammonia-rich environment. In this section, we examine in detail the possible causes of this phenomenon.

10 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) loadings of sulfate. In most of the previous studies, the relative abundance of
15 nitrate increased as the ammonium-to-sulfate molar ratio increased in the ammonium-rich samples. This can be represented by $[\text{NH}_4^+]/[\text{SO}_4^{2-}] > 1.5$ and suggests that more particulate nitrate was brought into the sulfate-nitrate-ammonium system by the increase in ammonium concentration. In fact, this excess ammonium, which is defined as the amount of ammonium in excess of that required for $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ equal to 1.5 (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. The scattering of the data can
20 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, illustrate the characteristics of nitrate formed via

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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 concentrations 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.

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 increases pH of aerosol, 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, thus leading to the formation of nitrate on preexisting 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, in the sampled air mass. In this study, NO_y was measured with a chemiluminescence

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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 a 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.

In anticipation of the conducive role played by aerosol acidity, aerosol surface area, relative humidity, and the nitrate precursor in heterogeneous hydrolysis in nitrate production, we attempt to relate nitrate concentration to these parameters. 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.

$$[\text{NO}_3^-] = 8 \times \ln(-\text{pH}) + \frac{40}{3} \times \ln(\text{Aerosol Water}) + \frac{8}{3} \times \ln(\text{Aerosol Mass}) + 8 \times \ln(\text{NO}_y) - 18$$

for $\text{pH} < 0$,

and

$$[\text{NO}_3^-] = 8 \times \ln(\text{pH}) + \frac{40}{3} \times \ln(\text{Aerosol Water}) + \frac{8}{3} \times \ln(\text{Aerosol Mass}) + 8 \times \ln(\text{NO}_y) - 18$$

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. The above relationships show a linear combination of the logarithmic functions of aerosol pH, aerosol water, aerosol mass, and NO_y , which 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.

Summertime $\text{PM}_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



4 Conclusion and implications

The average summertime $\text{PM}_{2.5}$ mass concentrations in the four Chinese cities studied were 55–68 $\mu\text{g m}^{-3}$, 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 loadings. It is believed that the hydrolysis of N_2O_5 on the preexisting aerosols under these favorable conditions was responsible for the production of the observed nitrate. The very acidic $\text{PM}_{2.5}$ aerosols in Beijing and Shanghai add to the atmospheric acidification and affect pH-dependent heterogeneous reactions, such as the oxidation of SO_2 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.

Acknowledgements. We would like to thank Joe Cheung for his help in collecting the filter samples, Yu Ren for her help with part of the chemical analysis, and Steven Poon and Jian Gao for their help with logistics and with setting up the instrumentation in the field. We also thank A. J. Ding for his valuable suggestions and for providing the meteorological data. We thankfully acknowledge the contributions by S. J. Fan, H. C. Zuo, T. J. Wang, and J. Tang in the selection of sampling sites and setting up the instruments. This research was funded by the Research Grants Council of Hong Kong (PolyU 5144/04E), the National Basic Research Program of China (2005CB422203), and the Hong Kong Polytechnic University (1-BB94 and G-YX0K).

Summertime $\text{PM}_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



References

- Alastuey, A., Querol, X., Rodríguez, S., Plana, F., Lopez-Soler, A., Ruiz, C., and Mantilla, E.: Monitoring of atmospheric particulate matter around sources of secondary inorganic aerosol, *Atmos. Environ.*, **38**, 4979–4992, 2004.
- 5 Allen, A. G. and Miguel, A. H.: Indoor organic and inorganic pollutants: In-situ formation and dry deposition in southeastern Brazil, *Atmos. Environ.*, **29**, 3519–3526, 1995.
- Andrews, E., Saxena, P., Musarra, S., Hildemann, L. M., Koutrakis, P., McMurry, P. H., Olmez, I., and White, W. H.: Concentration and composition of atmospheric aerosols from the 1995 SEAVS experiment and a review of the closure between chemical and gravimetric measurements, *J. Air Waste Manage. Assoc.*, **50**, 648–664, 2000.
- 10 Anttila, T., Kiendler-Scharr, A., Tillmann, R., and Mentel, T. F.: On the reactive uptake of gaseous compounds by organic-coated aqueous aerosols: Theoretical analysis and application to the heterogeneous hydrolysis of N_2O_5 , *J. Phys. Chem.*, **110A**, 10435–10443, 2006.
- 15 Appel, B. R., Tokiwa, Y., Haik, M., and Kothny, E. L.: Artifact of particulate sulfate and nitrate formation on filter media, *Atmos. Environ.*, **18**, 409–416, 1984.
- Chameides, W. L. and Stelson, A. W.: Aqueous-phase chemical processes in deliquescent sea-salt aerosols: A mechanism that couples the atmospheric cycles of S and sea-salt, *J. Geophys. Res.*, **97**, 20565–20580, 1992.
- 20 Charlson, R. J. and Heintzenberg, J.: *Aerosol Forcing of Climate*, Wiley, England, 363–382, 1995.
- Cheng, Y. H. and Tsai, C. J.: Evaporation loss of ammonium nitrate particles during filter sampling, *J. Aerosol Sci.*, **28**, 1553–1567, 1997.
- Chow, J. C., Antony Chen, L.-W., Watson, J. G., Lowenthal, D. H., Magliano, K. A., Turkiewicz, K., and Lehrman, D. E.: $\text{PM}_{2.5}$ chemical composition and spatiotemporal variability during the California Regional $\text{PM}_{10}/\text{PM}_{2.5}$ Air Quality Study (CRPAQS), *J. Geophys. Res.*, **111**, D10S04, doi:10.1029/2005JD006457, 2006.
- 25 Clegg, S. L., Brimblecombe, P., and Wexler, A. S.: A thermodynamic model of the system $\text{H}^+ - \text{NH}_4^+ - \text{Na}^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{Cl}^- - \text{H}_2\text{O}$ at 298.15 K, *J. Phys. Chem.*, **102A**, 2155–2171, 1998.
- 30 Dasch, J. M., Cadle, S. H., Kennedy, K. G., and Mulawa, P. A.: Comparison of annular denuders and filter packs for atmospheric sampling, *Atmos. Environ.*, **23**, 2775–2782, 1989.
- Dennis, R. L., McHenry, J. N., Barchet, W. R., Binkowski, F. S., and Byun, D. W.: Correcting

Summertime $\text{PM}_{2.5}$ ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

RADM's sulfate under prediction: Discovery and correction of model errors and testing the corrections through comparison against field data, *Atmos. Environ.*, 27A, 975–997, 1993.

Dockery, D. W., Pope III, C. A., Xu, X., Spengler, J. D., Ware, J. H., Fay, M. E., Ferris Jr., B. G., and Speizer, F. E.: An association between air pollution and mortality in six US cities, *New Engl. J. Med.*, 29, 1753–1759, 1993.

Fridlind, A. M. and Jacobson, M. Z.: A study of gas-aerosol equilibrium and aerosol pH in the remote marine boundary layer during the first aerosol characterization experiment (ACE-1), *J. Geophys. Res.*, 105, 17 325–17 340, 2000.

Gao, S., Ng, N. L., Keywood, M., Varutbangkul, V., Bahreini, R., Nenes, A., He, J., Yoo, K. Y., Beauchamp, J. L., Hodyss, R. P., Flagan, R. C., and Seinfeld, J. H.: Particle phase acidity and oligomer formation in secondary organic aerosol, *Environ. Sci. Technol.*, 38, 6582–6589, 2004.

Giroux, J. E., Arnaud, C., and Jacques, J.: Chalk Analysis of levels of nitrates and derivatives of ammonia in an urban atmosphere, *Sci. Total Environ.*, 196, 247–254, 1997.

Hallquist, M., Stewart, D. J., Stephenson, S. K., and Cox, R. A.: Hydrolysis of N₂O₅ on sub-micron sulfate aerosols, *Phys. Chem. Chem. Phys.*, 5, 3453–3463, 2003.

Han, L., Zhuang, G., Cheng, S., and Li, J.: The mineral aerosol and its impact on urban pollution aerosols over Beijing, China, *Atmos. Environ.*, 41, 7533–7546, 2007.

Harrison, R. M., Sturges, W. T., Kitto, A. M. N., and Li, Y.: Kinetics of evaporation of ammonium chloride and ammonium nitrate aerosols, *Atmos. Environ.*, 24A, 1883–1888, 1990.

He, K., Yang, F., Ma, Y., Zhang, Q., Yao, X. H., Chan, C. K., Cadle, S. H., Chan, T., Mulawa, P. A.: The characteristics of PM_{2.5} in Beijing, China, *Atmos. Environ.*, 35, 4959–4970, 2001.

Heintzenberg, J.: Fine particles in global troposphere – A review, *Tellus*, 41B, 149–160, 1989.

Hillamo, R., Allegrini, I., Sparapani, R., and Kerminen, V. -M.: Mass size distributions and precursor gas concentrations of major inorganic ions in Antarctica aerosol, *Int. J. Environ. Anal. Chem.*, 71, 357–369, 1998.

Ho, K.F., Lee, S. C., Cao, J. J., Chow, J. C., Watson, J. G., and Chan, C. K.: Seasonal variations and mass closure analysis of particulate matter in Hong Kong, *Sci. Total Environ.*, 355, 276–287, 2006.

Hu, J. H. and Abbatt, J. P. D.: Reaction probabilities for N₂O₅ hydrolysis on sulfuric acid and ammonium sulfate aerosols at room temperature, *J. Phys. Chem. A*, 101, 871–878, 1997.

Hu, M., He, L.-Y., Zhang, Y.-H., Wang, M., Kim, Y. P., and Moon, K. C.: Seasonal variation of ionic species in fine particles at Qingdao, China, *Atmos. Environ.*, 36, 5853–5859, 2002.

**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

- Kane, S. M., Caloz, F., and Leu, M.-T.: Heterogeneous uptake of gaseous N₂O₅ by (NH₄)₂SO₄, NH₄HSO₄, and H₂SO₄ aerosols, *J. Phys. Chem. A*, 105, 6465–6470, 2001.
- Karamchandani, P. and Venkatram, A.: The role of non-precipitating clouds in producing ambient sulfate during summer: results from simulations with the Acid Deposition and Oxidant Model (ADOM), *Atmos. Environ.*, 26A, 1041–1052, 1992.
- Keeler, G. J., Spengler, J. D., and Castillo, R. A.: Acid aerosol measurements at a suburban Connecticut site, *Atmos. Environ.*, 25A, 681–690, 1991.
- Koutrakis, P., Thompson, K. M., Wolfson, J. M., Spengler, J. D., Keeler, G. J., and Slater, J. L.: Determination of aerosol strong acidity losses due to interactions of collected particles: Results from laboratory and field studies, *Atmos. Environ.*, 26A, 987–995, 1992.
- Lee, T., Yu, X.-Y., Ayres, B., Kreidenweis, S. M., Malm, W. C., and Collett Jr., J. L.: Observations of fine and coarse particle nitrate at several rural locations in the United States, *Atmos. Environ.*, 42, 2720–2732, doi:10.1016/j.atmosenv.2007.05.016, 2008.
- Lin, J. J.: Characterization of the major chemical species in PM_{2.5} in the Kaohsiung City, Taiwan, *Atmos. Environ.*, 36, 1911–1920, 2002.
- Lippmann, M., Xiong, J. Q., and Li, W.: Development of a continuous monitoring system for PM₁₀ and components of PM_{2.5}, *App. Occup. Environ. Hyg.*, 15, 57–67, 2000.
- Liu, S. L. J., Burton, R. M., Wilson, W. E., and Koutrakis, P.: Comparison of aerosol acidity in urban and semi-rural environments, *Atmos. Environ.*, 30, 1237–1254, 1996.
- Lonati, G., Giugliano, M., Butelli, P., Romele, L., and Tardivo, R.: Major chemical components of PM_{2.5} in Milan (Italy), *Atmos. Environ.*, 39, 1925–1934, 2005.
- Martinez, M., Perner D., Hackenthal, E. -M., Kulzer, S., and Schutz, L.: NO₃ at Helgoland during the NORDEX campaign in October 1996, *J. Geophys. Res.*, 105, 22 685–22 695, 2000.
- McLaren, R., Salmon, R. A., John-Liggio, J., Hayden, K. L., Anlauf, K. G., and Leaitch, W. R.: Nighttime chemistry at a rural site in the Lower Fraser Valley, *Atmos. Environ.*, 38, 5837–5848, 2004.
- Mehlmann, A. and Warneck, P.: Atmospheric gaseous HNO₃, particulate nitrate, and aerosol size distributions of major ionic species at a rural site in western Germany, *Atmos. Environ.*, 29, 2359–2373, 1995.
- Meng, Z., Seinfeld, J. H., Saxena, P., and Kim, Y. P.: Contribution of water to particulate mass in the south coast air basin, *Aerosol Sci. Technol.*, 22, 111–123, 1995.
- Nemitz, E., Sutton, M. A., Wyers, G. P., and Jongejan, P. A. C.: Gas-particle interactions above a Dutch heathland: I surface exchange fluxes of NH₃, SO₂, HNO₃, HCl, *Atmos. Chem. Phys.*,

4, 989–1005, 2004,

<http://www.atmos-chem-phys.net/4/989/2004/>.

Pandey, S. K., Tripathi B. D., Mishra, V. K., and Prajapati, S. K.: Size fractionated speciation of nitrate and sulfate aerosols in a sub-tropical industrial environment, *Chemos.*, 63, 49–57, 2006.

Pandis, S. N., Seinfeld, J. H., and Pilnis, C.: Heterogeneous sulfate production in an urban fog, *Atmos. Environ.*, 26A, 2509–2522, 1992.

Pathak, R. K., Yao, X. H., Lau, A. K. H., and Chan, C. K.: Acidity and concentration of ionic species of PM_{2.5} in Hong Kong, *Atmos. Environ.*, 37, 1113–1124, 2003.

Pathak, R. K., Yao, X. H., and Chan, C. K.: Sampling artifacts of acidity and ionic species in PM_{2.5}, *Environ. Sci. Technol.*, 38, 254–259, 2004a.

Pathak, R. K., Liou, P. K. K., and Chan, C. K.: Characteristics of aerosol acidity in Hong Kong, *Atmos. Environ.*, 38, 2965–2974, 2004b.

Pathak, R. K. and Chan, C. K.: Inter-particle and gas-particle interactions in sampling artifacts of PM_{2.5} in filter-based samplers, *Atmos. Environ.*, 39, 1597–1607, 2005.

Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd ed., John Wiley & Sons, New York, 2006.

Sievering, H., Gorman, E., Ley, T., Pszenny, A. A. P., Spring-Young, M., Boatman, J. F., Kim, Y., Nagamoto, C., and Wellman, D. L.: Ozone oxidation of sulfur in sea-salt aerosol particles during the Azores marine aerosol and gas exchange experiment, *J. Geophys. Res.*, 100, 23 075–23 081, 1995.

Sillanpaa, M., Hillamo, R., Saarikoski, S., and Frey, A., et al.: Chemical composition and mass closure of particulate matter at six urban sites in Europe, *Atmos. Environ.*, 40, 212–223, 2006.

Speizer, F. E.: Studies of acid aerosols in six cities and in new multi-city investigations: Design issues, *Environ. Heal. Persp.*, 79, 61–67, 1989.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, 41, 517–527, doi:10.1021/es062081q, 2007.

Tang, I. N. and Munkelwitz, H. R.: Water activities, densities and refractive indices of aqueous sulfates and sodium nitrate droplets of atmospheric importance, *J. Geophys. Res.*, 99, 18 801–18 808, 1994.

ACPD

8, 11487–11517, 2008

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- Tsai, C. J. and Perng, S. N.: Artifacts of ionic species for Hi- Vol PM₁₀ and PM₁₀ dichotomous samplers, *Atmos. Environ.*, 32, 1605–1613, 1998.
- Van Oss, R., Duyzer, J., and Wyers, P.: The influence of gas to particle conversion on measurements of ammonia exchange over forest, *Atmos. Environ.*, 32, 465–471, 1998.
- 5 Vedal, S.: Critical review – ambient particles and health: Lines that divide, *J. Air Waste Manage. Assoc.*, 47, 551–581, 1997.
- Wang, T., Ding, A., Gao, J., and Wu, W. S.: Strong ozone production in urban plumes from Beijing, China, *Geophys. Res. Lett.*, 33, L21806, doi:10.1029/2006GL027689, 2006.
- Wang, T., Wong, C. H., Cheung, T. F., and Blake, D. R. et al.: Relationships of trace gases and aerosols and the emission characteristics at Lin'an, a rural site in eastern China, during spring 2001, *J. Geophys. Res.*, 109, D19S05, doi:10.1029/2003jd004119, 2004.
- 10 Wu, W. S. and Wang, T.: On the performance of a semi-continuous PM_{2.5} soleplate and nitrate instrument under high loadings of particulate and sulfur dioxide, *Atmos. Environ.*, 41, 5442–5451, 2007.
- 15 Yao, X. H., Chan, C. K., Fang, M., Cadle, S. H., Chan, T., Mulawa, P. A., He, K., and Ye, B.: The water-soluble ionic composition of PM_{2.5} in Shanghai and Beijing, China, *Atmos. Environ.*, 36, 4223–4234, 2002.
- Yao, X., Ling, T. Y., Fang, M., and Chan, C. K.: Comparison of thermodynamic predictions for in situ pH in PM_{2.5}, *Atmos. Environ.*, 40, 2835–2844, 2006.
- 20 Yao, X. H., Fang, M., and Chan, C. K.: Experimental study of the sampling artifact of chloride depletion from collected sea salt aerosols, *Environ. Sci. Technol.*, 35, 600–605, 2001.
- Yin, J., Allen, A. G., Harrison, R. M., et al.: Major component composition of urban PM₁₀ and PM_{2.5} in Ireland, *Atmos. Res.*, 78, 149–165, 2005.
- Zhang, X. Q. and McMurry, P. H.: Evaporative loss of fine particulate nitrates during sampling, *Atmos. Environ.*, 26A, 3305–3312, 1992.
- 25 Zhang, Y., Seigneur, C., Seinfeld, J. H., Jacobson, M., Clegg, S. L., and Binkowski, F. S.: A comparative review of inorganic aerosol thermodynamic equilibrium modules: similarities, differences, and their likely causes, *Atmos. Environ.*, 34, 117–137, 2000.
- Zheng, M., Salmon, L. G., Schauer, J. J., Limin Zeng, L., Kiang, C. S., Zhang, Y., and Cass, G. R.: Seasonal trends in PM_{2.5} source contributions in Beijing, China, *Atmos. Environ.*, 39, 3967–3976, 2005.
- 30

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 (μgm ⁻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} ; nmolm ⁻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±2	22±3	25±3	26±2
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

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

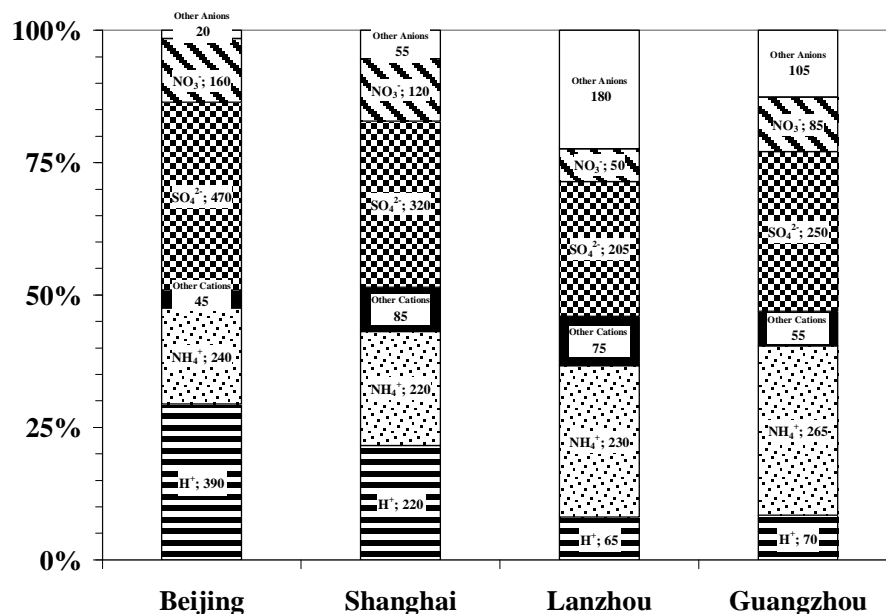


Fig. 1. Relative distributions among water-soluble ionic species in PM_{2.5} in the four cities. The numbers shown in the figure are the average nano-equivalent concentrations (neqm^{-3}).

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

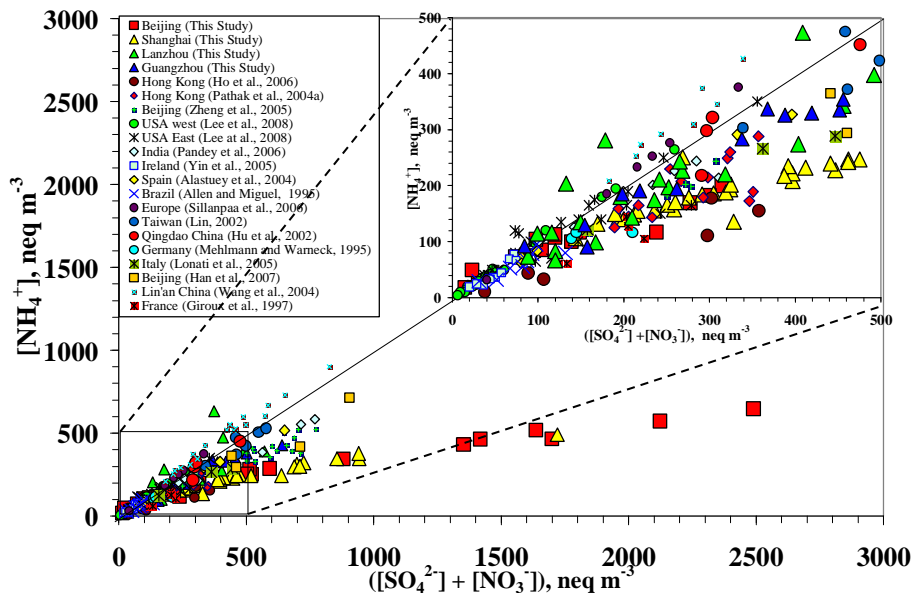


Fig. 2. Ammonium concentration as a function of the sum of the sulfate and nitrate equivalent concentrations in the PM_{2.5} samples.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

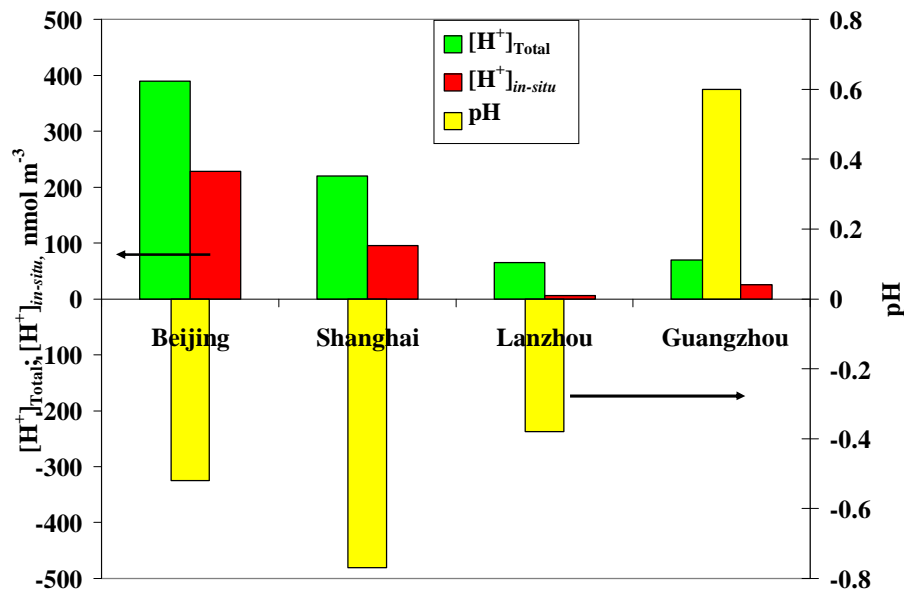
Printer-friendly Version

Interactive Discussion



**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

**Fig. 3.** Acidity characteristics of PM_{2.5} in the four cities.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Summertime PM_{2.5} ionic species in four major cities of China

Ravi Kant Pathak et al.

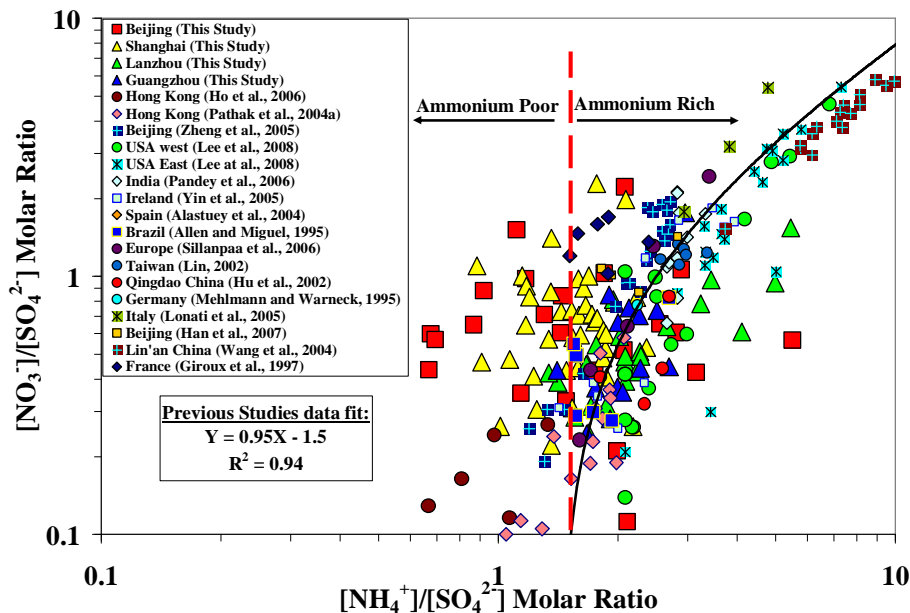


Fig. 4. Nitrate-to-sulfate molar ratio as a function of the ammonium-to-sulfate molar ratio.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Summertime PM_{2.5}
ionic species in four
major cities of China

Ravi Kant Pathak et al.

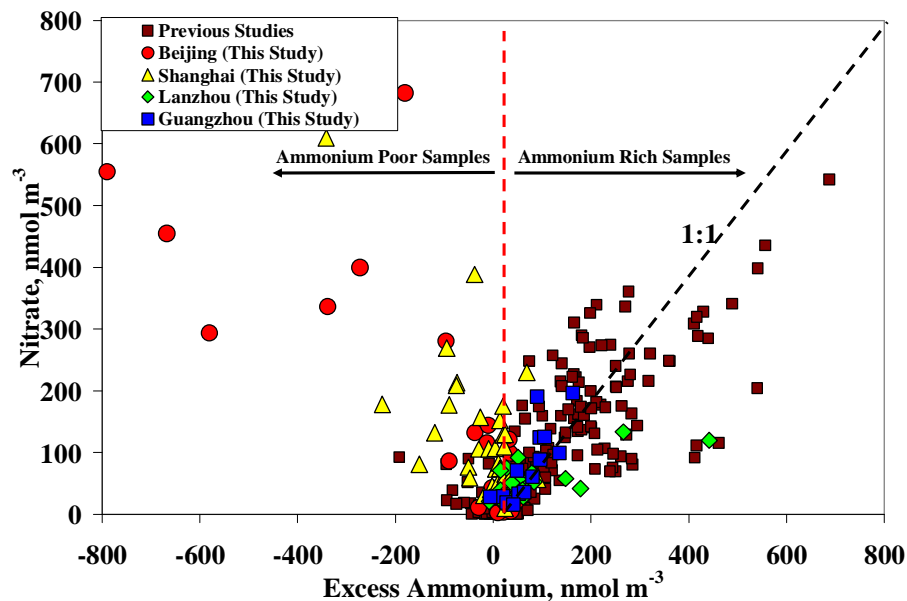


Fig. 5. Nitrate concentration as a function of “Excess Ammonium.” The data from previous studies include all of the studies mentioned in Figs. 2 and 4.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

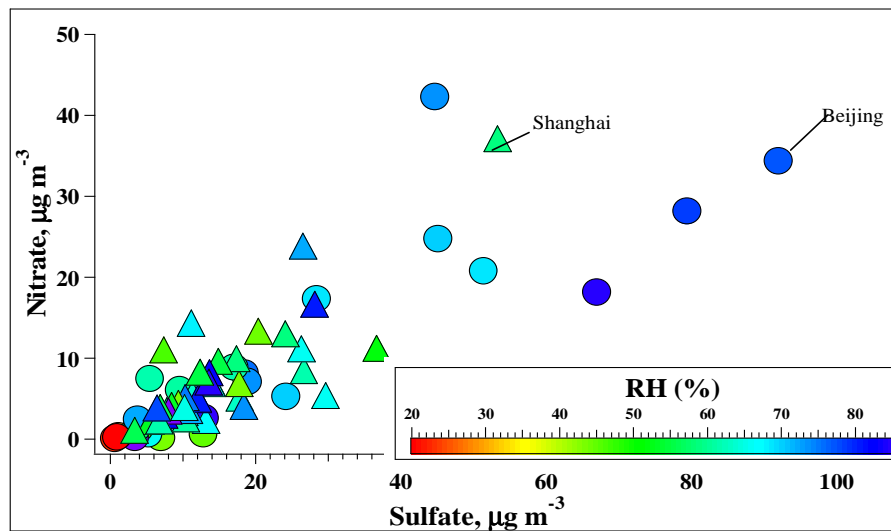


Fig. 6. Nitrate concentration as a function of sulfate concentration and ambient RH.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[I◀](#)[▶I](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

Summertime PM_{2.5}
ionic species in four
major cities of China

Ravi Kant Pathak et al.

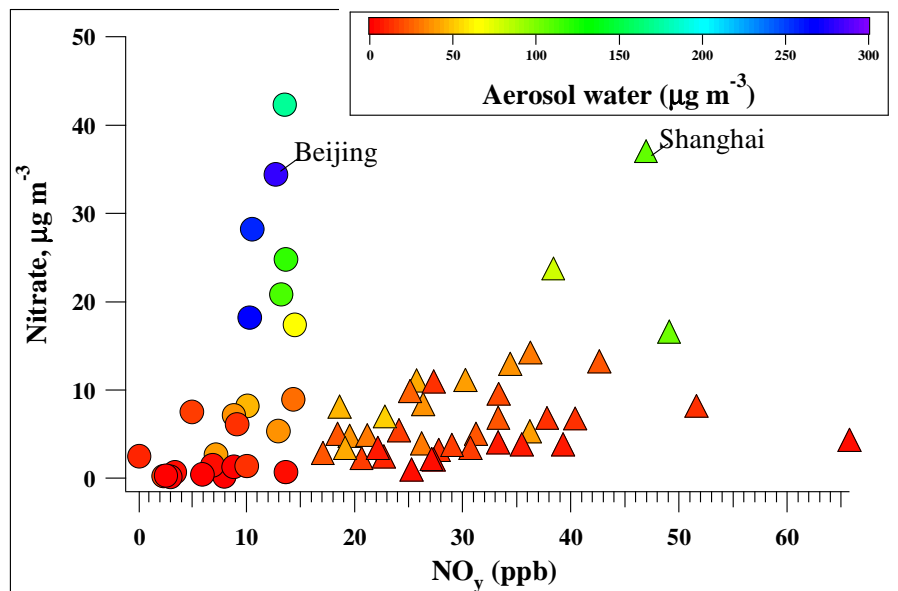


Fig. 7. Nitrate concentration as a function of total reactive nitrogen (NO_y), representing the precursor strength for N_2O_5 and aerosol water.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

**Summertime PM_{2.5}
ionic species in four
major cities of China**

Ravi Kant Pathak et al.

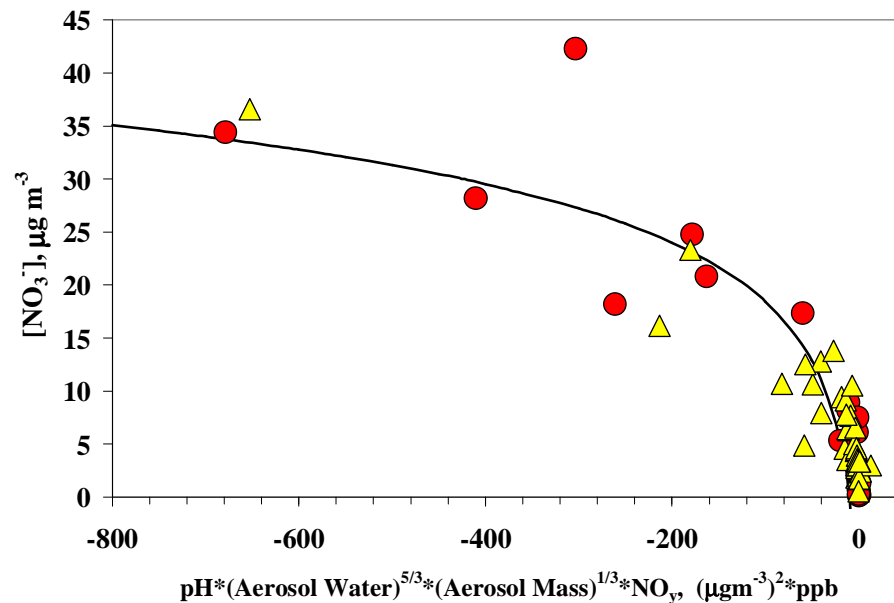


Fig. 8. Nitrate concentration as a function of aerosol pH, water, mass, and NO_y concentrations. Beijing and Shanghai data are shown by solid circles and triangles, respectively.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

