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variability of PM_{2.5}
acidity in China**

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**Spatial and seasonal variability of PM_{2.5}
acidity at two Chinese megacities:
insights into the formation of secondary
inorganic aerosols**

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Abstract

Aerosol acidity is one of the most important parameters influencing atmospheric chemistry and physics. Based on continuous field observation from January 2005 to May 2006, both spatial and seasonal variation in $PM_{2.5}$ acidity was investigated at Beijing and Chongqing, two megacities in northern and southwestern China, respectively. $PM_{2.5}$ was generally more acidic at urban and rural sites in Chongqing than Beijing, but a reverse spatial pattern was found within the two cities, with more acidic $PM_{2.5}$ at urban Beijing and rural Chongqing comparing to their rural and urban sites, respectively. $PM_{2.5}$ was more acidic in summer and fall than in winter, while large inter-annual variations were evident during the springs of 2005 and 2006, with Beijing and Chongqing exhibiting opposite trends, however. The higher acidity of $PM_{2.5}$ in the spring of 2006 in Beijing was attributed to the influence of Asian desert dust which significantly enhanced the formation of nitrate relative to sulfate; in contrast, the more acidic aerosols found during the spring of 2005 in Chongqing was mainly due to the greater wet deposition of ammonium, and precipitation was probably one of the key factors that controlled the partition of ammonium in $PM_{2.5}$ and rain water over the surrounding region. Meanwhile, $PM_{2.5}$ became more acidic at both cities from spring into early summer of 2005. The synoptic-scale evolution of its acidity was found to be closely associated with the greater contribution of air masses from between the Northern China Plain to the south of Beijing, and from central China to the east of Chongqing, and was ended by the northward movement of a subtropical high over the northwestern Pacific, a major element of the Asian summer monsoon. Under conditions of high aerosol acidity, heterogeneous reactions may become one of the major pathways for the formation of nitrate at both cities. These findings may also explain the significant variation in inter-annual aerosol acidity observed during other seasons at Beijing, Chongqing and many other cities in China, as reported in previous studies.

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1 Introduction

Acidic aerosols can increase the risks to human health by direct inhalation and indirectly by activating hazardous particulate materials (Amdur and Chen, 1989; Health Effects Institute, 2002), and their wet/dry deposition has also lead to severe degradation of ecosystems (Larssen et al., 2006). Most acidic aerosols are hygroscopic, and as such act to reduce atmospheric visibility (Watson, 2002) as well as disturbing the radiative balance of the atmosphere (Boucher and Anderson, 1995; Crumeyrolle et al., 2008). They are also of great importance to atmospheric chemistry through their influence on many heterogeneous reactions and the behaviors of reactants and oxidants (Seinfeld and Pandis, 1998; Jang et al., 2002).

Acidic aerosol species in cities are usually dominated by sulfate (SO_4^{2-}) and nitrate (NO_3^-), mostly converted from the precursors SO_2 and NO_x , respectively, and are partly or fully neutralized by ammonium (NH_4^+) and basic metals such as Ca^{2+} and Mg^{2+} . Na^+ and Cl^- may also be important species influencing aerosol acidity in coastal area where sea salt plays a role. Aerosol acidity cannot be directly measured due to its low water content (Meng et al., 1995; Nenes et al., 1998), and is generally assessed using three different kinds of parameters, namely, strong acidity, ion-balanced acidity and in situ acidity.

Strong acidity, measured from the aqueous extracts of aerosol samples, represents the absolute acidity of the aerosols, but it cannot show any in situ characteristics due to the large excesses of water (Pathak et al., 2004). Ion-balanced acidity refers to the estimation of H^+ concentration by subtracting the equivalent cations, other than H^+ , from anions (Zhang et al., 2007a). It is more widely used in a relative way to indicate the neutralizing level with the equivalent ratio of cations/anions (Adams et al., 1999; Zhang et al., 2002, 2007a; Chu et al., 2004; Sun et al., 2010; Johansen et al., 1999; Takami et al., 2007; Chou et al., 2008). In situ aerosol acidity, in the form of the concentration of free H^+ or pH in the deliquesced particles at the ambient condition, is most likely to influence the chemical behavior of aerosols. It can be estimated from a variety of

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thermodynamic models, such as E-AIM, SCAPE and GFEMN (Pathak et al., 2004, 2009; Yao et al., 2006; Takahama et al., 2006; Zhang et al., 2007a). However, it should be noted that ion-balanced and in situ aerosol acidity are empirical approaches that both depend on the choice of ion species. For example, due to their low abundance relative to ammonium in fine particles, basic Ca^{2+} and Mg^{2+} are usually ignored in the estimation of aerosol acidity, which might be less appropriate during dust events (Ziemba et al., 2007).

The characteristics of aerosol acidity may vary from region to region due to the spatiotemporal variability in the emission of primary aerosols and gaseous precursors, as well as regional differences in the climatic driving forces. The earliest observations on aerosol acidity in China were initiated in the 1980s in regions in the south and southwest (Huang et al., 1988; Shen et al., 1992; Zhao et al., 1994), but they generally focused on the acidification of fog and cloud in respect to severe acid rain, with most of the sites located in rural and remote areas. In recent years in China, there have been a lot of field observations on aerosol acidity in the megacities of different regions, such as Beijing (Yao et al., 2002; Dillner et al., 2006; Sun et al., 2010), Shanghai (Yao et al., 2002; Xiu et al., 2005; Wang et al., 2006), Hong Kong (Pathak et al., 2003; 2004a,b) and Chongqing (Quan and Zhang, 2008; Aas et al., 2007).

While these studies suggest a general pattern of higher acidity in southern China than in the north, only a few of them presented parallel inter-region comparisons, with little information on seasonal variation. For example, Wang et al. (2006) and Pathak et al. (2009) investigated aerosol acidity at different regions in China, in spring and summer, respectively. Moreover, even for a specific region, there are large discrepancies between the studies. For Shanghai, Xiu et al. (2005) found that aerosols were almost completely neutralized, a finding that is contrary to the results reported by Yao et al. (2002) and Wang et al. (2006) (Chan and Yao, 2008). The discrepancies might be attributed to a variety of factors, including the procedures of sampling analysis and changes in emission strength and meteorological condition. Increasingly there is a need to understand how these factors have influenced the variability of aerosol acidity.

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Along with the increase in domestic NO_x emissions in recent years (Zhang et al., 2007b), the concentration and proportion of NO₃⁻ in aerosols have been found to have increased significantly in most Chinese megacities (Richter et al., 2005; Chan and Yao, 2008; Shen et al., 2008), and become a major concern in the acidity of aerosols as well as their wet/dry deposition (Han et al., 2006; Larssen et al., 2006; Song et al., 2008). The formation pathway of NO₃⁻ depends on not only the availability of NH₄⁺ and on meteorological condition (such as temperature), but also the characteristics of the preexisting particles, such as aerosol acidity, water content and alkaline mineral composition (Pakkanen et al., 1996; Hu and Abbatt, 1997; John et al., 1990; Zhuang et al., 1999). In particular, Pathak et al. (2009) recently reported high concentration of NO₃⁻ with high acidity and low NH₄⁺ at Beijing and Shanghai, with their formation being largely attributed to the hydrolysis of N₂O₅ on the preexisting particles. This differs from the findings of most previous field observations, which have indicated that high concentration of NO₃⁻ are found in association with high NH₄⁺ (Pathak et al., 2009). However, the observations of Pathak et al. (2009) were limited to summertime and therefore it is necessary to investigate the situation during other seasons of the year.

In this study, the aerosol acidity at Beijing and Chongqing, two megacities in northern and southwestern China, respectively, was examined in parallel during a 15-month period of field observation, and the characteristics of fine particles (PM_{2.5}, particles of aerodynamic diameter <2.5 μm) were investigated in detail due to their greater regional influence and higher acidity than coarse particles. Based on the measurement of ion-balanced and in situ acidity, we investigated the spatial and seasonal pattern of PM_{2.5} acidity at these two cities, which showed synchronous variation during the spring and summer of 2005, but an opposite trend for the springs of 2005 and 2006. These variations were attributed to the regional influence from synoptic systems and to desert dust from Asia, and their implications for the formation of nitrate at different aerosol acidities are also discussed.

2 Experimental method and model description

2.1 Sampling and analysis

Weekly PM_{2.5} samples were collected at both urban and rural sites of Beijing and Chongqing using a three-channel low-flow sampler (Aerosol Dynamics Inc., Berkeley, CA). Details of the sampling sites have been provided previously (He et al., 2001; Zhao et al. 2010). In brief, the urban and rural sites at Beijing were inside Tsinghua University (TH, 40°19' N, 116°19' E) and near the Miyun Reservoir (MY, 40°29' N, 116°47' E), respectively, with a distance of 70 km between them. Three sites were selected at Chongqing, including a residential urban site in Jiangbei District (JB, 29°34' N, 106°32' E), an industrial site in Dadukou District (DDK, 29°29' N, 106°29' E), and a rural site near the Jinyun Mountain in the Beibei District (BB, 29°50' N, 106°25' E), which is 30 km and 40 km away from JB and DDK, respectively.

The sampling procedure was also given by He et al. (2001). Operating at a flow rate of 0.4 l min⁻¹, one of the three channels collected PM_{2.5} on a Teflon filter with a Teflon impactor followed by a glass denuder. The glass denuder is coated with a 2% carbonate solution prepared in 50:50 water:methanol to remove the acidic gases. HNO₃ volatilized from the Teflon filter is collected on a nylon filter. Hence water soluble ions are determined from this Teflon filter but the reported particulate NO₃⁻ is the sum of NO₃⁻ on both the Teflon and nylon filters. The other two channels collected PM_{2.5} with a single Teflon filter and quartz filter for measuring elements and carbonaceous components, respectively, which were not used in this study. Each sample was ran continuously and changed every Friday. From 28 January 2005 to 5 May 2006, 106 and 180 PM_{2.5} samples were collected at Beijing and Chongqing, respectively.

Mass concentrations of PM_{2.5} were obtained by weighing on an analytical balance (Mettler Toledo AG285), after stabilizing under constant temperature (20 °C ± 5 °C) and humidity (40 % ± 5 %). Eight ions, including SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, K⁺, Ca²⁺, Na⁺ and Mg²⁺, were measured by ion chromatography (Dionex 600, details in Wang et al.,

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2005).

Hourly meteorological data for both Beijing and Chongqing were obtained from the website <http://www.wunderground.com>, including temperature, dewpoint, wind speed, visibility and precipitation. The spatial distribution of geopotential height was derived from the archived meteorological data of NOAA's Air Resources Laboratory (ARL, <http://www.arl.noaa.gov/READY>).

2.2 Indicators of PM_{2.5} acidity

2.2.1 Ratio of cation/anion

In this study, the equivalent charge ratio (eq/eq) of the major cations NH₄⁺ and Ca²⁺ to anions SO₄²⁻ and NO₃⁻ was used to indicate the neutralizing level of PM_{2.5}, as the other ions generally had little influence on the acidity at Beijing and Chongqing (to be discussed in Sect. 3.1). The equivalent charge ratio was defined as following:

$$R_{C/A} = \frac{NH_4^+ + Ca^{2+}}{SO_4^{2-} + NO_3^-} \quad (1)$$

where all the species denote the concentrations of their equivalent charges (likewise for all the ratios of species without brackets in the following text). In this equation, $R_{C/A} \geq 1$ indicates that most of the acids can be neutralized, while $R < 1$ indicates the aerosol is acidic.

2.2.2 In situ aerosol acidity

Both free H⁺ concentration ($[H^+]_{ins}$, the square brackets indicate the molar concentration of the species inside, used here and henceforth) and in situ pH in the deliquesced particles were used as indicators of aerosol acidity, which can be estimated from a chemical thermodynamic model (E-AIM2, <http://www.aim.env.uea.ac.uk/aim/>). E-AIM2 is a state-of-the-art model that can accurately simulate the liquid and solid phase of

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ionic compositions in the mixing system $\text{H}^+ - \text{NH}_4^+ - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ at a given temperature and relative humidity (Clegg et al., 1998). The model input of E-AIM2 includes weekly averaged temperature, relative humidity, $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$, $[\text{NH}_4^+]$ and total H^+ ($[\text{H}^+]_{\text{Total}}$), which is estimated from the ionic balance of the relevant species (Yao et al., 2006; Zhang et al., 2007a; Pathak et al., 2009):

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

The aerosol pH was calculated as:

$$\text{In situ aerosol pH} = -\log(\gamma \times [\text{H}^+]_{\text{Frac}}) \quad (3)$$

where γ is the activity coefficient on mole fraction basis and $[\text{H}^+]_{\text{Frac}}$ is the molar fractions of aqueous phase H^+ (Zhang et al., 2007a). In addition to these two parameters, $[\text{H}^+]_{\text{Ins}}$ and the concentration of water content ($[\text{H}_2\text{O}]$) were derived from E-AIM2.

The lack of information about the organic acids generally has little influence on the estimation of aerosol acidity due to their low abundance in aerosols (Zhang et al., 2007a; Pathak et al., 2009). However, larger bias may exist because of a lack of information about basic Ca^{2+} and Mg^{2+} , especially in samples containing high concentrations of mineral dust (Ziemba et al., 2007). Although there are models, such as SCAPE, that take into account a system with these basic ions included, they cannot be used in the current study because the required gaseous HNO_3 and NH_3 , the input parameters for the models, were not measured. It should also be noted that the E-AIM2 model only simulates the average results over the whole week without considering the influence from temporal variations in aerosol composition, temperature and relative humidity (Yao et al., 2006).

2.3 Trajectory computation and clustering

Backward trajectories of air masses arriving at Beijing and Chongqing were calculated using the HYSPLIT model (Version 4.8) to investigate the influence of different

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air masses on aerosol composition and acidity. The meteorological data fields used to run the model are 6-hourly FNL archived data, which are available at NOAA's ARL archives. For single trajectory calculation, the model was run 4 times per day (UTC 00:00, 06:00, 12:00 and 18:00) with the arrival level at 500 m (below the boundary layer) or 2000 m (above the boundary layer).

As the typical errors of individual trajectories were estimated to be 20 % of the traveled distance (Stohl, 1998), the trajectories over the whole sampling period were classified into seasonal transport patterns using the HYSPLIT model. A detailed procedure of the clustering analysis is provided in the Supplement according to the model description (Draxler et al., 2006). The percentage change in total spatial variance (TSV) was used to determine what is a reasonable number of clusters in each season: a large increase in TSV indicates that different clusters are being paired and therefore that the cluster process should stop.

3 Results and discussions

3.1 Abundance of ionic species in $PM_{2.5}$

The annual concentrations of $PM_{2.5}$ and ionic species were averaged from March 2005 to February 2006 for Beijing and Chongqing, as shown in Table 1. $PM_{2.5}$ concentration was similar for all the three sites at Chongqing ($\sim 130 \mu\text{g m}^{-3}$), and all were higher than the concentrations at Beijing ($118 \mu\text{g m}^{-3}$ for TH and $68 \mu\text{g m}^{-3}$ for MY), indicating high regional background levels of $PM_{2.5}$ in the surrounding area. As with $PM_{2.5}$ mass, higher concentrations of total ionic species were found at Chongqing ($41.3\text{--}45.0 \mu\text{g m}^{-3}$) than at Beijing ($28.3\text{--}39.1 \mu\text{g m}^{-3}$). The proportion of $PM_{2.5}$ at the urban TH in Beijing (33.0 %) was very close to those at Chongqing (31.8 %–34.9 %), but the higher fraction in MY (41.4 %) suggests a more important role of ionic species in rural areas of Beijing. Components other than ionic species contributed similar amounts to $PM_{2.5}$ at Beijing and Chongqing, i.e., carbonaceous species and crustal dust generally

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accounted for 36 %–40 % and 6 %–8 % of $PM_{2.5}$ mass, respectively (Zhao et al., 2010; He et al., 2011).

SO_4^{2-} , NO_3^- and NH_4^+ dominated the ionic species, with a contribution of up to 85 %–90 % at both Beijing and Chongqing. As with $PM_{2.5}$ at Chongqing, the three species when considered in combination had an even spatial distribution, while at Beijing the relatively small difference in them between MY and TH (MY/TH: 76.8 %) compared to $PM_{2.5}$ (MY/TH: 57.7 %) indicates that they are of greater regional significance than the other aerosol species. Concentrations of SO_4^{2-} for all the sites were higher at Chongqing than at Beijing, whereas NO_3^- showed the opposite spatial pattern with higher concentrations at Beijing than at Chongqing. This is mainly attributed to regional differences in energy structure and meteorology (see Sect. 3.2).

Compared to the above major ionic species, Ca^{2+} , Mg^{2+} , Na^+ , K^+ and Cl^- constituted a minor fraction (10 %–15 %) of ionic species at Beijing and Chongqing. The annual concentrations of basic Ca^{2+} and Mg^{2+} were higher at Chongqing (totalling 0.9–1.5 $\mu g m^{-3}$) than at Beijing (totalling 0.7–1.1 $\mu g m^{-3}$). Their low abundance relative to NH_4^+ suggests that they have only a weak influence on neutralizing the acidic species, as found in most studies on aerosol acidity (Yao et al., 2006; Zhang et al., 2007a; Pathak et al., 2009). However, as an indicator of mineral dust, which was found in high concentrations during the spring and winter at Beijing and Chongqing (Zhao et al., 2010), Ca^{2+} was included in the acidity analysis to get an idea of the regional influence of alkaline dust.

Cl^- was relatively abundant at all the sites (0.4–2.2 $\mu g m^{-3}$), and primarily comes from coal combustion (Yao et al., 2002) and biomass burning (Li et al., 2007, 2009). Similarly, Na^+ (0.3–0.7 $\mu g m^{-3}$) and K^+ (1.4–3.1 $\mu g m^{-3}$) mainly come from coal combustion and biomass burning, respectively, as revealed by our previous study (Zhao et al., 2010). These three ions were excluded in the following acidity analysis due to their neglectable effect on aerosol acidity.

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3.2 Spatiotemporal variations in cation/anion ratio

3.2.1 Spatial distribution

The ratio of cation/anion ($R_{C/A}$) in $PM_{2.5}$ was calculated for all the sites at Beijing and Chongqing according to Eq. (2). As shown in Table 1, annual $R_{C/A}$ from March 2005 to February 2006 approximated 1.0 at TH (0.97) and MY (1.04), both being higher than at the urban and rural sites at Chongqing which were 0.81–0.86 and 0.76, respectively, indicating that the aerosols were much more acidic at Chongqing than at Beijing. This pattern is consistent with Wang et al. (2006), who found that aerosols over southern China were neutralized much less during springtime than aerosols over northern China.

The regional distribution of $PM_{2.5}$ acidity was mainly caused by regional differences in levels of NH_4^+ , as revealed from the low ratio of Ca^{2+}/NH_4^+ at all sites (0.06–0.08, equivalent charge ratio); however, NO_3^- and SO_4^{2-} are identified to play different roles in contributing to the acidity of the two cities. As shown in Table 1, NO_3^-/SO_4^{2-} for Beijing (0.47–0.60) was ~3–4 times higher at all the sites than for Chongqing (0.15–0.17), which indicates a higher contribution from vehicle sources at Beijing (Arimoto et al., 1996; Yao et al., 2002). This is confirmed by Beijing having 4 times the number of vehicles (2.1 million) than Chongqing (0.47 million) in 2005, with comparable coal consumption (~30 million tons; Beijing Statistic Bureau, 2006; Chongqing Statistic Bureau, 2006). Although NO_3^-/SO_4^{2-} may also be influenced by sampling artifacts due to a long sampling duration (Pathak et al. 2004b), the charge ratios were quite close to those previously reported using daily samples for Beijing (0.52 in 2001–2003; Wang et al., 2005) and Chongqing (0.16 in 2003; Aas et al., 2007).

The urban–rural distributions of $R_{C/A}$ for $PM_{2.5}$ at Beijing and Chongqing were opposites. Both NO_3^-/SO_4^{2-} and Ca^{2+}/NH_4^+ were higher at urban sites, possibly due to more vehicle sources and construction activities, however they showed different spatial gradients within the two cities. Compared to the difference of NO_3^-/SO_4^{2-} at Chongqing (<10%; urban: 0.016–0.17, rural: 0.15), the ratio was found ~30% higher at urban TH

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(0.60) than rural MY (0.47) at Beijing. At the meantime, $\text{Ca}^{2+}/\text{NH}_4^+$ showed a larger urban-rural difference at Chongqing (~25 %) than at Beijing (~10 %). Therefore, it was the higher concentrations of NO_3^- within the urban site in Beijing and the lower concentrations of Ca^{2+} within the rural site in Chongqing that made their $\text{PM}_{2.5}$ more acidic. This differs from findings for Pittsburgh where NH_4^+ levels determined the spatial distribution of aerosol acidity at urban and semi-rural sites (Liu et al., 1996).

3.2.2 Seasonal variation

The seasonal averages of $R_{\text{C/A}}$ of $\text{PM}_{2.5}$ in Beijing and Chongqing are shown in Table 2. In Beijing, $\text{PM}_{2.5}$ at TH was more acidic in the summer of 2005 and spring of 2006 than other seasons ($R_{\text{C/A}} \leq 1$ for all seasons). Similar seasonal variation in $R_{\text{C/A}}$ was also observed at rural MY, but its higher $R_{\text{C/A}}$ indicates that $\text{PM}_{2.5}$ was almost neutral in all seasons ($R_{\text{C/A}} \geq 1$), except for the spring of 2006 ($R_{\text{C/A}} = 0.80$). These results are similar to previous findings that aerosols were more acidic in warm seasons than in cold seasons at Beijing, as indicated from $R_{\text{C/A}}$ reproduced from their reported datasets shown in Table 2. However, no consistent pattern in inter-annual trends can be discerned for each season. During the summer, $R_{\text{C/A}}$ was > 1 in 2001–2003 (Wang et al., 2005) and 2006 (Sun et al., 2010), and < 1 in 1999–2000 (Wang et al., 2000; He et al., 2001) and 2005 (Pathak et al., 2009; this study); for spring, $R_{\text{C/A}}$ was > 1 in 1994–1995 (Wang et al., 2000) and 2001–2003 (Wang et al., 2005), and < 1 in 1999–2000 (He et al., 2001; Dillner et al., 2006) and 2005–2006 (this study); for winter, $R_{\text{C/A}}$ was > 1 in most years except 1999–2000 when it was only 0.63 (He et al., 2001), indicating the aerosols were much more acidic than during other seasons. Similar characteristics in seasonal variation of aerosols are also observed in other northern cities. As shown in Table 2, while they were neutralized in most cases ($R_{\text{C/A}} > 1$), very acidic aerosols were also observed at Yungang (summer of 1988; Wang et al., 2000), Xi'an (winter of 1996–1997; Zhang et al., 2002) and Jinan (spring of 2004–2005; Yang et al., 2007).

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As in Beijing, $R_{C/A}$ was high in winter and low in summer and fall of 2005 at both urban and rural sites of Chongqing. However, the ratios for the two springs were not similar, with much more acidic aerosols being found in 2005 ($R_{C/A} = 0.58\text{--}0.62$) than in 2006 ($R_{C/A} = 0.94\text{--}1.00$). No consistent inter-annual trend in seasonal acidity could be found at Chongqing, either. For example, Liu et al. (1988) found $R_{C/A}$ of PM₂ to be 1.77 in the fall of 1980s, much higher than the ratios from our observation (0.79–1.02). The large difference between the two studies cannot be simply explained by the increased acidity of aerosol over the past 20 years because similarly low $R_{C/A}$ (0.78–1.01) were also measured in TSP by Zhao et al. (1994) during 1987–1988 in Chongqing (the ratio was even lower for fine particles). This phenomenon shifts the likely explanation to factors other than the changes in the emission of acidic aerosols and their precursors. As at Chongqing, aerosol $R_{C/A}$ at other southern cities have also exhibited an inconsistent inter-annual trend in recent years. The $R_{C/A}$ of PM_{2.5} in Shanghai was significantly higher in the summer and winter of 2004 (1.38 and 0.78, respectively; Wang et al., 2006) than in summer of 2005 and winter of 2001 (0.4–0.5; Xiu et al., 2004; Pathak et al., 2009), while for Hong Kong the ratio in winter was also distinctively higher in 2002 (1.06; Cheung et al., 2005) than 2001 (0.73; Louie et al., 2005).

In spite of the uncertainties in using $R_{C/A}$ to compare the aerosol acidity between different studies, such as the variable sampling methods, the representativeness of sampling periods, and analytical procedures, the above findings collectively suggest that the seasonal variation of aerosol acidity in northern and southern China may be influenced by a variety of factors (emission strength, meteorological condition and characteristics of preexisting particles and precursors, etc.). For either long-term or short-term field observations, it is consequently risky to attribute the inter-annual changes of aerosol acidity to any of these factors alone. For example, based on a comparison with the acidic aerosols reported by Dillner et al. (2006) for spring 2001, Sun et al. (2010) simply attributed their fully neutralized aerosols in Beijing during the summer of 2006 to the reduced SO₂ emissions or increased NH₃ emissions in this region.

It is interesting to observe that the inter-annual variation in spring acidity for Chongqing was opposite to that for Beijing. For both cities, their covariation at urban and rural sites indicates that the inter-annual trend was of regional scale. Thus, the weekly $R_{C/A}$ for each city was averaged to investigate the short-period variation in aerosol acidity within each season.

As shown in Fig. 1a, $R_{C/A}$ showed extensive weekly fluctuation for both cities, with larger variation at Beijing ($\times 4$, 0.39–1.60) than at Chongqing ($\times 2$, 0.51–1.13). However, $R_{C/A}$ at Beijing was higher in the spring of 2005 (>1) than in 2006 (<1 , from the week of 24–31 March), while at Chongqing continuously higher $R_{C/A}$ was observed in the spring of 2006 (0.8–1.1) than in 2005 (0.6–0.8). This pattern is better presented as normalized $R_{C/A}$ ($R_{C/A}$ minus the averaged ratio during the whole sampling period, as shown in Fig. 1b), indicating a weak intra-seasonal variation of aerosol acidity for both Beijing and Chongqing during the two springs. Also of note is that $R_{C/A}$ at both Beijing and Chongqing showed a similar decreasing trend during February–June 2005 with a sharp increase at the end, which implies that the aerosol acidity of both cities had been influenced by large-scale driving forces, as discussed in Sect. 4.

3.3 Seasonal variation of in situ aerosol acidity

In situ aerosol pH, $[H^+]_{ins}$ and $[H_2O]$ of $PM_{2.5}$ at Beijing and Chongqing were derived based on E-AIM2, as described in Sect. 2. $[NH_4^+]$, $[SO_4^{2-}]$ and $[NO_3^-]$ were averaged for urban and rural sites and used as the input data to simplify the comparison between the two cities.

The in situ $PM_{2.5}$ acidity showed similar seasonal variation as previously indicated by $R_{C/A}$, and gives additional insight into the hygroscopic properties of aerosols. As shown in Fig. 2a, it was only in summer, fall of 2005 and spring of 2006 that deliquescent aerosols were found to be abundant at Beijing with free H^+ , while most of them remained in solid phase during the spring and winter of 2005. The spring of 2006 at Beijing had the most acidic aerosols, with an in situ pH of only -0.618 to 0.404 , while there were only two weeks in the spring of 2005 when it was found

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acidic. Moreover, although high $[H^+]_{\text{Ins}}$ existed in $PM_{2.5}$ during the summer of 2005 ($0.002\text{--}0.126\ \mu\text{mol m}^{-3}$) and spring of 2006 ($0.006\text{--}0.122\ \mu\text{mol m}^{-3}$), the former was less acidic because of its much higher $[H_2O]$ ($0.100\text{--}8.466\ \mu\text{mol m}^{-3}$) than the latter ($0.034\text{--}0.468\ \mu\text{mol m}^{-3}$).

5 Contrasting with Beijing, $PM_{2.5}$ at Chongqing was deliquescent throughout the year with high $[H^+]_{\text{Ins}}$ and $[H_2O]$, while a significant variation of in situ acidity between the two springs was also clearly evident, as shown in Fig. 2b. The most acidic aerosols were found during February–June 2005, when in situ pH consistently remained at its lowest level ($0.515\text{--}1.384$) due to a faster increase in $[H^+]_{\text{Ins}}$ ($\times 20$) than in $[H_2O]$ ($\times 5$).
10 Interestingly, both parameters simultaneously decreased to their lowest level of the whole observation period in the week of 25 June to 1 July 2005, resulting in a significant increase of in situ pH and thus much less acidic $PM_{2.5}$. This was also coincident with the week when $R_{C/A}$ showed a remarkable increase (Fig. 1).

In contrast to results revealed by $R_{C/A}$, a noteworthy finding for the variation of in situ pH is that $PM_{2.5}$ was more acidic at Beijing than at Chongqing during the springs. This was mainly due to the drier climatology and lower water content in aerosols at Beijing that favored high in situ acidity, even though there might be less free H^+ . Similar finding was also reported in Hong Kong where variation of in situ $PM_{2.5}$ acidity was a function of relative humidity (RH) and even the more neutralized particles could have a high
15 acidity under the influence of dry air masses from the Chinese mainland (Pathak et al., 2004a), and thus highlighted the importance of the in situ acidity relative to other parameters (Pathak et al., 2004b).

In addition, as one of the most important parameters determining the in situ acidity, RH clearly exhibited opposite trends from winter into spring at Chongqing during 2005 and 2006, which can partly explain the inter-annual variation of $PM_{2.5}$ acidity. As shown in Fig. 2b, for the period from February to May, it increased from $\sim 60\%$ to $\sim 80\%$
20 in 2005, but decreased from $\sim 80\%$ to $\sim 50\%$ in 2006. These long-playing reverse seasonal trends were likely to have been influenced by large-scale synoptic system anomalies.

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3.4 Factors influencing the spring–summer variation of PM_{2.5} acidity

As a case study, below we examine the covariation of PM_{2.5} acidity from spring into summer 2005 for Beijing and Chongqing, as well as the opposite inter-annual variation during the springs of 2005 and 2006.

3.4.1 Asian summer monsoon

The covariation of $R_{C/A}$ for PM_{2.5} at Beijing and Chongqing from February to June 2005, with a sharp increase at the end of June, is thought to be associated with the influence of synoptic systems, which generally cover a distance of 2000 km (Roger and Andrew, 2002).

The anomaly of the Asian summer monsoon in June 2005 was the abnormal behavior of the subtropical high over the Northwestern Pacific (Pacific High, in short) and the trough/ridge systems over mid- and high latitudes (Lu et al., 2007; Mu et al., 2008). The northward movement of the Pacific High, which is one of the most important parameters indicating the evolution of spring into summer in East Asia, was delayed until the end of June 2005. As shown in Fig. 3a (Lu et al., 2007), the ridge of the Pacific High remained around 13° N–16° N before 26 June 2005, 3°–5° to the south of the normal position. During 26–28 June, however, it suddenly moved from 17° N to 28° N at a speed of 3°–4° per day, and its representative positions before and after the movement are indicated by the geopotential heights of 500 hPa in Fig. 3b (23 June) and Fig. 3c (29 June), respectively.

The evolution of air mass sources at Beijing and Chongqing was investigated before and after the northward movement of the Pacific High. The period from 4 March to 27 June 2005 was divided into three phases, including 4 March–6 May (to be compared with the same period in the spring of 2006), 7–31 May and 1–27 June. For each phase, backward trajectories of air masses at 500 m a.g.l. of Beijing and Chongqing were classified according to the procedures in Sect. 2.3. Trajectories of longer duration were calculated for Chongqing (120 h) than for Beijing (72 h) because of their different

spread of travel.

The increasing aerosol acidity from March to June 2005 at the two cities was closely associated with the contribution of air masses from areas between the Northern China Plain to the south of Beijing and from central China to the east of Chongqing. As shown in Fig.4, Beijing was gradually dominated by air masses originating from south of the city, which increased from 13% in March–April (cluster 5 in Fig. 4a) to 41% in May (clusters 4 and 5 in Fig. 4c) and 59% in June (clusters 3 and 4 in Fig. 4d). At the same time, Chongqing was dominated by air masses from the east of the city, which increased from 50% in March–April (cluster 4 in Fig. 5a) to 65% in May (clusters 1 and 3 in Fig. 5c) and 73% in June (clusters 1, 4 and 5 in Fig. 5c). As indicated by the aerosol optical depth (AOD) shown in the Supplement Fig. S1a–c, these source regions were found to have high aerosol loading from March to June in 2005, which clearly suggested that the aerosol acidity was increasing over a broad region of mainland China, with a stronger influence in the south than in the north.

Along with the northward movement of the Pacific High at the end of June 2005, the acidic aerosols over Beijing and Chongqing were removed by the clean air from the northwest and southeast, respectively, which coincided with the simultaneous decrease of $PM_{2.5}$ acidity at both cities. This effect was also evident from significantly weakened AOD during 29–30 June over a wide region that used to be covered by highly acidic aerosols (Supplement Fig. S1d). In July, Beijing was again dominated by air masses from the south with a monthly contribution (65% of all air masses) and $[H^+]_{Ins}$ level comparable to those in June. However, the Asian summer monsoon was found to have a much greater significance in Chongqing, where the air masses in July were dominated by those having been transported over long distances from the south of China and from southeastern Asia, with high monthly contribution (74% of all air masses,) but low aerosol acidity.

These lines of evidence collectively suggest the major role of the Asian summer monsoon in determining the regional evolution of $PM_{2.5}$ acidity from the spring to the summer of 2005 for Beijing and Chongqing. However, it can not explain the inter-

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annual variation of $PM_{2.5}$ acidity during the springs of 2005 and 2006, since no obvious difference was found between the transport patterns of their air mass trajectories. As shown in Fig. 4b and Fig. 5b, respectively, the dominant air masses for Beijing and Chongqing from 3 March to 5 May 2006 were also from the northwest and east of China, a situation that was similar to that from 4 March to 6 May 2005 (Figs. 4a and Fig. 5a, respectively).

3.4.2 Asian desert dust

Mineral dust can affect aerosol acidity by either directly neutralizing the acidic aerosol or increasing the surface area of heterogeneous reaction for the acids. As an indicator of mineral dust, higher Ca^{2+} as well as higher ratios of Ca^{2+}/NH_4^+ were observed in spring of 2005 and 2006 for Chongqing and Beijing, respectively. This is consistent with the findings of Wu et al. (2009) who reported that emission of Asian desert dust was more active in the spring of 2006 than in the spring of 2005 for Beijing, and our related study (Zhao et al., 2010) found Asian dust to be more active in the spring of 2005 than of 2006 for Chongqing.

In order to compare the $R_{C/A}$ and ionic species of the two springs in parallel, data of weekly samples from 4 March to 6 May 2005 and 3 March to 5 May 2006 were averaged to represent the spring of 2005 and 2006 for each site, respectively. As shown in Fig. 6a, the Ca^{2+} concentration at Beijing was 23.8 % to 30.6 % higher in the spring of 2006 than of 2005, while the concentrations of SO_4^{2-} and NO_3^- also increased by 11.3 % to 23.3 % and 1.9 % to 8.8 %, respectively, with little variation for NH_4^+ . Due to the small contribution of neutralization from mineral components, the increased SO_4^{2-} and NO_3^- in the spring of 2006 remained acidic. Meanwhile, a significant increase (45.5 %) was also found for NO_3^-/SO_4^{2-} at urban TH in the spring of 2006 compared to 2005, which strongly suggests the influence from enhanced production of NO_3^- on the surface of mineral particles. It is well known that the reactions with alkaline mineral components are of several magnitudes faster for gaseous HNO_3 than for NO_2 and SO_2 (Oooki and

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Uematsu, 2005; Vlasenko et al., 2006), which were all abundant in the atmosphere of Beijing (Bergin et al., 2001). When Asian dust was transported to Beijing, CaCO₃ could firstly react with HNO₃ to form Ca(NO₃)₂, providing more hygroscopic surfaces for the heterogeneous reaction with SO₂ and NO₂, as has been directly observed by single particle analysis during dust storms at Beijing (Li and Shao, 2009). However, NO₃⁻/SO₄²⁻ showed little increase (~1.5%) at MY in the spring of 2006 compared to 2005, as seen in Fig. 6a. This is perhaps due to the lack of precursors of NO₃⁻, which was more concentrated in urban area of Beijing, and the unstable nature of NH₄NO₃, which could easily be decomposed into gaseous NH₃ and HNO₃ during transport from the urban area to MY.

On the other hand, compared to 2005 a higher increase in SO₄²⁻ was observed at MY (23.3%) than at TH (11.3%) in the spring of 2006. The more elevated SO₄²⁻ concentration at the rural MY than at the urban TH (a pattern not observed for NO₃⁻ or NO₃⁻/SO₄²⁻) can be explained by coupling the SO₄²⁻ formation with the inter-annual variation in transport pathways during spring. Compared to the transport pattern in the spring of 2005 (Fig. 4a), polluted air masses were more frequently transported from the west and south of Beijing in the spring of 2006 (Fig. 4b), which favored a higher regional contribution of SO₄²⁻ at MY than during periods when other transport pathways were in play (Jia et al. 2008; Zhao et al., 2009). Moreover, faster transformation of local SO₂ to SO₄²⁻ at Beijing could also lead to higher increase of SO₄²⁻ in MY due to the more acidic and hygroscopic aerosols in the southern and southwestern air masses. However, it should be noted that the difference in NH₄⁺ concentrations between the two springs was nearly the same for the two sites at Beijing, perhaps because of the recapture of decomposed NH₃ from NH₄NO₃ by the unneutralized SO₄²⁻ or HSO₄⁻ during transport.

Although the influence of Asian dust at Beijing may partly explain the inter-annual variation of PM_{2.5} acidity for the springs of 2005 and 2006, this does not seem to be an explanatory factor at Chongqing. Firstly, it was a significant decrease in NH₄⁺ concentration in the spring of 2005, which was 28.0% to 30.2% lower than that for the spring of 2006 (Fig. 6b), that essentially led to the elevation of aerosol acidity. The

increased concentration of mineral dust might have changed the gas-particle equilibrium of $\text{NH}_3/\text{NH}_4^+$ by limiting the transfer of NH_3 to NH_4^+ in fully neutralized aerosols (Luo et al., 2007), but it could hardly influence the highly acidic aerosols at Chongqing during the spring of 2005. Secondly, significant monthly variation in the transport of northwestern air masses was found from March through June 2005 at either the boundary layer (Fig. 5) or the higher atmosphere (Supplement Fig. S2), but the $\text{PM}_{2.5}$ acidity at Chongqing (as indicated by $R_{\text{C/A}}$ in Fig. 1 and $[\text{H}^+]_{\text{ins}}$ in Fig. 2) remained at a consistently high level, and indeed showed a slight increase.

3.4.3 Wet deposition of NH_4^+

Particulate NH_4^+ mainly comes from the gaseous NH_3 , with residence times of 4–6 days and 1 day, respectively (Adams et al., 1999). The variation in NH_4^+ concentration at Chongqing for the two springs might be influenced by many factors, including the emission strength of precursor NH_3 , the gas-particle equilibrium of $\text{NH}_3/\text{NH}_4^+$, and patterns of atmospheric transport, diffusion and deposition. (Asman et al., 1998).

NH_3 emissions from natural sources, including animal waste, natural and fertilized soils, and vegetation, usually depend on temperature, which showed little difference between the two springs in Chongqing, as shown in Fig. 6b. Anthropogenic sources, such as industrial process, are considered to be stable during all seasons. The gas-particle equilibrium of $\text{NH}_3/\text{NH}_4^+$ is usually related to NH_4NO_3 and NH_4Cl , which are unstable; however these were not the major form of NH_4^+ in Chongqing due to the high $\text{PM}_{2.5}$ acidity dominated by SO_4^{2-} .

The influence of atmospheric transport, diffusion and deposition on NH_4^+ concentration at Chongqing can be assessed from the variation in air mass trajectories and meteorological factors. For the two springs at Chongqing, little difference was observed in the patterns of air mass backward trajectories, as previously discussed. Meanwhile, as shown in Fig. 6b, surface temperature, wind speed and relative humidity also showed weak variation. Together they suggest that atmospheric transport and diffusion at Chongqing play a minor role in explaining the significant inter-annual variation

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of NH_4^+ during the springs of 2005 and 2006.

In contrast to all the above factors, the amount of precipitation was 35.5 % higher in the spring of 2005 than of 2006, which is comparable to the differences for NH_4^+ (28.0 %–30.2 %) and $R_{\text{C/A}}$ (26.3 %–30.7 %). As shown in Fig. 7a, the precipitation was negatively correlated with NH_4^+ in $\text{PM}_{2.5}$ at the JB site from February 2005 to April 2006 ($R = -0.63, p = 0.01$), indicating that the wet scavenging of NH_4^+ was favored by the increase in precipitation. In fact, southwestern China experienced a long drought from the fall of 2005 to the spring of 2006, and the number of days on which rain fell during spring 2005 was 20 % to 50 % more than in the spring of 2006 for most cities in the Sichuan Basin (Supplement Fig. S3; meteorological data from <http://www.wunderground.com>). Although the precipitation in spring at Beijing also showed large inter-annual variation (Fig. 6a), a similar effect of increased precipitation was not in evidence due to the much smaller amounts that fell during both springs (40 mm and 11 mm in 2005 and 2006, respectively).

Along with these lines of evidence, the chemistry of wet deposition at Chongqing, derived from the Acid Deposition Monitoring Network in East Asia (<http://www.eanet.cc/product/index.html>), also suggests the significant influence of precipitation on the variation of NH_4^+ in $\text{PM}_{2.5}$. Since NH_4^+ and SO_4^{2-} were the major species determining $\text{PM}_{2.5}$ acidity at Chongqing, the ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ (eq/eq) was used to better present the chemical behavior of NH_4^+ in determining the acidity of $\text{PM}_{2.5}$ and precipitation. As shown in Fig. 7b, during February–November 2005 when precipitation was relatively abundant, the ratios of $\text{NH}_4^+/\text{SO}_4^{2-}$ in the precipitation and $\text{PM}_{2.5}$ were significantly negatively correlated with each other at Chongqing ($R = -0.88, 0.001$). However, only a weak correlation ($R=0.44, p = 0.38$) was found for the dry seasons from November 2005 to April 2006, possibly due to the fact that the two datasets became less suitable for comparison as the period covered by the rain samples was much shorter than that of the $\text{PM}_{2.5}$ samples.

Interestingly, the influence of the Asian summer monsoon on wet deposition of NH_4^+ is also evident in Fig. 7b. The ratio of $\text{NH}_4^+/\text{SO}_4^{2-}$ increased from February to June in

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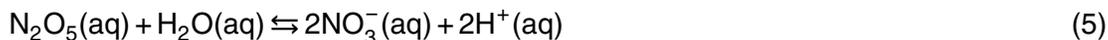
2005, decreased and remained at a low level after the arrival of the prevailing summer monsoon in July, and returned to a higher level in October when the winter monsoon started to prevail. All of these collectively suggest that precipitation was one of the key factors that dominated the partition of NH_4^+ in $\text{PM}_{2.5}$ and rain water at Chongqing, and the enhanced wet deposition of NH_4^+ may be responsible for the lower NH_4^+ and higher acidity of $\text{PM}_{2.5}$ during the spring of 2005 compared to that of 2006. Our findings have important implications for the interpretation of large-scale variability of airborne $\text{NH}_3/\text{NH}_4^+$. For example, large inter-annual variation of NH_3 was recently observed at a rural site in southwestern China, the cause of which remained undetermined, however (Meng et al., 2010).

3.5 Formation of NO_3^- at different levels of aerosol acidity

As SO_4^{2-} competes with NO_3^- for NH_4^+ during its formation, the relationship between NO_3^- and NH_4^+ at different levels of SO_4^{2-} , which are expressed as $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, is indicative of the pathway of NO_3^- formation (Pathak et al., 2004a, 2009). For a variety of cities worldwide, linear correlation between $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ in NH_4^+ -rich conditions ($[\text{NH}_4^+]/[\text{SO}_4^{2-}] \geq 1.5$, molar ratio) suggested the homogenous formation of NO_3^- :



while no relationship was observed in NH_4^+ -poor conditions ($[\text{NH}_4^+]/[\text{SO}_4^{2-}] < 1.5$) and the high level of NO_3^- was attributed to its formation from the hydrolysis of N_2O_5 on the preexisting aerosols (Pathak et al., 2009):



However, our study found significant correlations during both NH_4^+ -rich and NH_4^+ -poor conditions at Beijing and Chongqing. Thus aerosol acidity, in terms of the ratio

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$R_{C/A}$, was used instead as the key parameter to investigate the relationship between $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, as well as the formation pathways of NO_3^- . Considering the uncertainties in representing the neutralization level of $\text{PM}_{2.5}$, a $R_{C/A}$ ratio of 0.9 was used to divide the samples into a group of more acidic aerosols ($R_{C/A} < 0.9$) and a group of less acidic aerosols ($R_{C/A} \geq 0.9$), which gave the prospect of a good fit in the regression analysis as discussed below.

$[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ is plotted against $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ at different acidities for both Beijing and Chongqing in Fig. 8a. For less acidic samples ($R_{C/A} \geq 0.9$), although their $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ showed a clear intercity variation, with higher ratios at Beijing (≥ 0.6) than at Chongqing (≤ 0.6), together they were significantly correlated with $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ ($R^2 = 0.71$, $p < 0.001$) with the regression function:

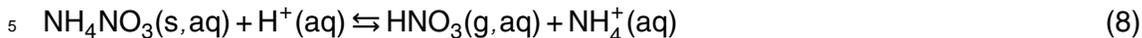
$$\frac{[\text{NO}_3^-]}{[\text{SO}_4^{2-}]} = 0.80 \times \frac{[\text{NH}_4^+]}{[\text{SO}_4^{2-}]} - 1.33 \quad (6)$$

The intercept of the regression line with the axis of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ (1.66) was quite close to that (1.5) found by Pathak et al. (2009), indicating that NO_3^- in these less acidic samples was mainly formed from Eq. (4) between HNO_3 and the excess NH_3 , which became available after neutralizing most of the SO_4^{2-} and HSO_4^- . Excess NH_4^+ associated with the formation of NO_3^- can be derived from the following equation:

$$[\text{NH}_4^+]_{\text{Excess}} = \left(\frac{[\text{NH}_4^+]}{[\text{SO}_4^{2-}]} - 1.66 \right) \times [\text{SO}_4^{2-}] \quad (7)$$

For both Beijing and Chongqing, significant a correlation ($R^2 = 0.70$, $p < 0.001$) was found between the excess NH_4^+ and NO_3^- when $[\text{NH}_4^+]_{\text{Excess}} \geq 30 \text{ nmol m}^{-3}$, as shown in Fig. 9. The slope of regression line for NO_3^- against excess NH_4^+ at Beijing equaled 1.0, which is consistent with the molar ratio for the reaction between HNO_3 and NH_3 . However, a shallower slope (0.65) was found for Chongqing, which indicates that in

PM_{2.5} there was approximately 35 % excess NH₄⁺ bounded to species other than NO₃⁻. Some of which might exist in the form of NH₄Cl, while others could be associated with acidic SO₄²⁻ or HSO₄⁻, which could recapture the decomposed NH₃ from NH₄NO₃, as shown by the following equation:



For the more acidic samples ($R_{C/A} < 0.9$), a significant correlation ($R^2 = 0.59$, $p < 0.001$) also existed between $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, although R^2 was a little lower than that of the less acidic samples. Its regression equation was:

$$\frac{[\text{NO}_3^-]}{[\text{SO}_4^{2-}]} = 0.59 \times \frac{[\text{NH}_4^+]}{[\text{SO}_4^{2-}]} - 0.42 \quad (9)$$

10 Its intercept with the axis of $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ (0.71) was much smaller than that for the less acidic samples (1.66). However it is notable that the two lines approximated each other as $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ increased over 1.66, indicating that the homogeneous reaction for HNO₃ and NH₃ was also favored with abundant NH₄⁺ in the acidic samples. On the other hand, along with decreasing $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, a large NH₄⁺ deficit ($[\text{NH}_4^+]_{\text{Excess}}$ of up to -350 nmol m^{-3} , calculated according to Eq. 7) was evident in these more acidic samples (Fig. 9), and the reaction of Eq. (4) was supposed to be constrained. However, markedly high concentrations of NO₃⁻ were still found at Chongqing (up to 169 nmol m^{-3}) and Beijing (up to 318 nmol m^{-3}), which suggests the dominance of heterogeneous reactions without involving NH₃, most likely the hydrolysis of N₂O₅ on the preexisting aerosols (Pathak et al., 2009).

20 The close correlation between $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ for the more acidic aerosols (which is in contrast to the weak correlation reported by Pathak et al., 2009) can be explained in at least two ways. Firstly, due to the long sampling duration of our study (~ 1 week), NO₃⁻ in each sample had formed from both homogenous

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and heterogeneous reactions, and thus a good correlation between $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ and $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ might exist even for those dominated by the latter pathway. Secondly, with an increase in aerosol acidity and a decrease in $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, NO_3^- tends to partition into coarse particles with abundant alkaline mineral components (Pakkanen et al., 1996; Zhuang et al., 1999), consequently there is a resultant decrease in $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ that is positively correlated with $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ in fine particles (Sun et al., 2006).

These hypotheses are further suggested by coupling the variation of aerosol water content with the two compositional ratios. As shown in Fig. 8b, aerosol samples with $[\text{NH}_4^+]/[\text{SO}_4^{2-}] < 1.66$ contained high amounts of water, indicating the vital role of the liquid phase reactions of Eq. (5), while the water content was much less in most of the other samples ($[\text{NH}_4^+]/[\text{SO}_4^{2-}] \geq 1.66$), in which NO_3^- was dominated by the gaseous reaction of Eq. (1). However, relatively high water content was also found in some of the less acidic samples with high $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$, which were mainly collected during the winter in Chongqing and the summer in Beijing. Their NO_3^- may be attributable to NH_4NO_3 formation on the existing particles and/or to in-cloud processes (Yao et al., 2003).

It should be noted that there were, respectively, 5 and 2 outliers excluded in the regression analysis of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ against $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ for the less acidic and the more acidic samples, as shown in Fig. 8a. These outliers, all collected during spring and winter in Beijing, were found to have significantly higher $[\text{Ca}^{2+}]/[\text{NH}_4^+]$ than other samples with low water content (Fig. 8b), and suggests that heterogeneous reactions on the dry surface of fine mineral particles was also an important pathway during these periods at Beijing.

4 Conclusions and atmospheric implications

The spatial and seasonal variations of $\text{PM}_{2.5}$ acidity were investigated for both rural and urban sites of Beijing and Chongqing from January 2005 to May 2006. With similar

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levels of NH_4^+ at each site, $\text{PM}_{2.5}$ was generally more acidic at Chongqing than at Beijing due to its higher levels of SO_4^{2-} , which indicates a significant contribution from coal combustion in southwestern China, while Chongqing's lower levels of NO_3^- suggest that vehicle sources play a more important role in Beijing. The intra-city comparison of $\text{PM}_{2.5}$ acidity showed a reverse pattern for Beijing and Chongqing, with higher levels of NO_3^- and lower levels of Ca^{2+} making $\text{PM}_{2.5}$ more acidic in urban areas of Beijing and in rural areas of Chongqing.

$\text{PM}_{2.5}$ was more acidic in the summer and fall than in winter of 2005 at Beijing and Chongqing, but large inter-annual variation was found during the springs of 2005 and 2006, with the cities exhibiting opposite trends. The greater acidity of $\text{PM}_{2.5}$ in the spring of 2006 at Beijing was attributed to the influence of Asian desert dust with significant enhancement of the formation of NO_3^- relative to SO_4^{2-} , both of which were not completely neutralized by the increase in alkaline dust, however. For Chongqing, the greater acidity of $\text{PM}_{2.5}$ in the spring of 2005 was mainly due to increased wet deposition of NH_4^+ , and precipitation was probably one of the key factors that controlled the partition of NH_4^+ in $\text{PM}_{2.5}$ and in rain water over the surrounding region. As revealed by a variety of previous studies, significant inter-annual variation in aerosol acidity was also found during other seasons at Beijing, Chongqing and many other cities in China, with no consistent long-term trend. These variations may be influenced by a variety of factors, such as emission strength, meteorological conditions and the characteristics of preexisting particles and precursors.

The impact of the Asian monsoon systems can explain well the synoptic-scale evolution of $\text{PM}_{2.5}$ acidity at Beijing and Chongqing. For both cities, $\text{PM}_{2.5}$ acidity increased from spring to early summer of 2005, a trend that was closely associated with an increased contribution of air masses from between the Northern China Plain to the south of Beijing and from central China to the east of Chongqing. The regionally acidic aerosols were replaced by more neutralized aerosols at the end of June 2005, coupled with the northward movement of a subtropical high over the northwestern Pacific, which is a major element of the Asian summer monsoon. Previous studies have

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found a seasonal influence of the Asian monsoon on the concentrations of aerosol and gaseous pollutants in China (e.g. He et al., 2001; Ye et al., 2003; Wai and Turner, 2005; Xin et al., 2007; Zhang et al., 2010), but few of them, if any, have related its behavior to large-scale variability in aerosol acidity. Moreover, a recent study using modeling suggests that the strength of the Asian monsoon could influence the inter-annual variation in aerosols in eastern China mostly by altering wet deposition and aerosol transport (Zhang et al., 2010), which we believe is also likely to explain the inter-annual variation of aerosol acidity during the springs of 2005 and 2006. For example, RH, one of most important parameters influencing in situ aerosol acidity, exhibited opposite trends from winter into spring at Chongqing during 2005 and 2006, a situation that was likely influenced by large-scale synoptic system anomalies. In the meantime, more air masses from northwestern Asian deserts were transported to the south of the country in the spring of 2005 than of 2006, while the reverse trend was found for the air masses influencing the Northern China Plain (not shown). This may also have been related to variation of the strength of the Asian monsoon, which was found to have greater bearing on the transport pathway of dust to the Asian subcontinent than to dust production itself (Gong et al., 2006). Clearly, these are important subjects of future work.

PM_{2.5} acidity was closely related to the formation of NO₃⁻ at both Beijing and Chongqing. NO₃⁻ formation in more neutralized PM_{2.5} was favored by the homogeneous reaction of HNO₃ and NH₃, while heterogeneous reactions (such as the hydrolysis of N₂O₅ on preexisting aerosols with a higher water content) may become major pathways when particulates are more acidic. In addition, the formation of NO₃⁻ on the relatively dry surface of mineral dust could also be an important pathway during winter and spring at Beijing.

Aerosol acidity has also frequently been linked to the formation of secondary organic aerosols (Jang et al., 2002; Takahama et al., 2006; Zhang et al., 2007a). In addition to the inorganic aerosols discussed in this study, we also observed significantly higher ratios of Organic carbon to Elemental carbon (OC/EC) in the spring of 2005 than of 2006 at the rural sites of both Beijing and Chongqing (unpublished data); a pattern which

was not in evidence at the urban sites, however. This phenomenon probably indicates the different levels of oxidation of organic aerosols in the background air masses, and more detailed investigation is required.

Supplementary material related to this article is available online at:

**[http://www.atmos-chem-phys-discuss.net/11/25557/2011/
acpd-11-25557-2011-supplement.pdf](http://www.atmos-chem-phys-discuss.net/11/25557/2011/acpd-11-25557-2011-supplement.pdf)**

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Table 1. Annual concentrations of PM_{2.5}, its major ionic species and their equivalent ratios at Beijing and Chongqing from March 2005 to February 2006.

PM _{2.5} species	Chongqing			Beijing	
	JB	DDK	BB	TH	MY
Number of samples	48	49	43	43	42
PM _{2.5} (μg m ⁻³)	129.0 ± 42.6	133.7 ± 44.1	126.1 ± 43.4	118.5 ± 40.6	68.4 ± 24.7
SO ₄ ²⁻ (μg m ⁻³)	25.5 ± 9.1	23.4 ± 8.4	23.9 ± 8.9	15.7 ± 10.5	13.0 ± 9.3
NO ₃ ⁻ (μg m ⁻³)	5.3 ± 3.6	5.0 ± 3.3	4.8 ± 3.0	10.1 ± 6.2	6.4 ± 4.9
NH ₄ ⁺ (μg m ⁻³)	7.9 ± 3.8	7.7 ± 3.5	7.3 ± 3.9	7.4 ± 4.2	6.1 ± 3.4
Ca ²⁺ (μg m ⁻³)	1.1 ± 0.7	1.2 ± 0.6	0.7 ± 0.4	0.9 ± 0.4	0.5 ± 0.3
Cl ⁻ (μg m ⁻³)	1.8 ± 1.8	1.6 ± 1.5	0.8 ± 0.9	2.2 ± 2.3	0.4 ± 0.6
Na ⁺ (μg m ⁻³)	0.7 ± 0.2	0.7 ± 0.24	0.5 ± 0.1	0.5 ± 0.2	0.3 ± 0.2
Mg ²⁺ (μg m ⁻³)	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
K ⁺ (μg m ⁻³)	2.5 ± 0.9	2.6 ± 1.3	3.1 ± 1.5	2.1 ± 1.2	1.4 ± 0.8
Sum of ionic species (μg m ⁻³)	45.0 ± 28.7	42.5 ± 26.2	41.3 ± 24.6	39.1 ± 22.1	28.3 ± 20.3
Sum of SO ₄ ²⁻ , NO ₃ ⁻ , NH ₄ ⁺ in ionic species (%)	0.86 ± 0.06	0.85 ± 0.06	0.87 ± 0.07	0.85 ± 0.07	0.90 ± 0.09
Ionic species in PM _{2.5} (%)	0.31 ± 0.08	0.27 ± 0.07	0.28 ± 0.06	0.27 ± 0.11	0.36 ± 0.15
(NH ₄ ⁺ + Ca ²⁺)/(SO ₄ ²⁻ + NO ₃ ⁻) (μeq/μeq)	0.81 ± 0.23	0.86 ± 0.19	0.76 ± 0.19	0.97 ± 0.16	1.04 ± 0.21
Ca ²⁺ /NH ₄ ⁺ (μeq/μeq)	0.08 ± 0.06	0.08 ± 0.06	0.06 ± 0.04	0.07 ± 0.05	0.06 ± 0.05
NO ₃ ⁻ /SO ₄ ²⁻ (μeq/μeq)	0.16 ± 0.08	0.17 ± 0.08	0.15 ± 0.07	0.60 ± 0.32	0.47 ± 0.28

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Table 2. Seasonal $R_{C/A}$ at multiple sites in the northern and southern China (spring \equiv MAM, summer \equiv JJA, fall \equiv SON, winter \equiv DJF).

Observational sites	PM size	Year	Spring	Summer	Fall	Winter	References	
Beijing	Urban (TH)	PM _{2.5} 2005–2006	0.95/0.80	0.83	1.00	0.99	This study	
	Rural (MY)		1.24/0.89	1.01	1.07	1.19		
	Urban	PM ₁ 2006		1.04			Sun et al. (2010)	
	Rural	PM _{2.5} 2005		0.43			Pathak et al. (2009)	
	Urban/rural	PM _{2.5} 2001–2003	1.03	1.06	0.99	1.06	Wang et al. (2005)	
	Urban	PM _{2.5} 2001	< 1				Dillner et al. (2006)	
Northern	Urban	PM _{2.5} 1999–2000	0.98	0.84	0.79	0.63	He et al. (2001)	
	Urban	PM _{2.5} 1994–1995	1.20	0.87		0.98	Wang et al. (2000)	
	Lanzhou	Rural	PM _{2.5} 2006		1.14		Pathak et al. (2009)	
	Xi'an	Urban	PM _{2.5} 1996–1997	1.26	1.11	1.12	0.96	Zhang et al. (2002)
	Jinan	Urban	PM _{2.5} 2004–2005	0.89	1.20	1.47	1.19	Yang et al. (2007)
	Yungang	Urban	PM _{2.5} 1988		0.84			Wang et al. (2000)
Jiaozuo	Urban	PM ₁₀ 2002–2003	4.48	3.90		2.68	Feng et al. (2007)	
	Rural		4.62	3.52		2.37		
Chongqing	Urban (JB)	PM _{2.5} 2005–2006	0.60/1.00	0.85	0.80	1.00	This study	
	Urban (DDK)		0.58/0.97	0.96	1.02	1.07		
	Rural (BB)		0.62/0.94	0.70	0.79	0.92		
	Urban	PM _{2–10} PM ₂ 1980s			2.02		Liu et al. (1988)	
	Urban	TSP 1987–1988	1.01				Zhao et al. (1994)	
	Rural		0.78					
Shanghai	Urban	PM _{2.5} 2000–2001	0.60			0.52	Xiu et al. (2004)	
	Rural		0.72			0.41		
	Urban	TSP PM _{2.5} 2004	0.86	1.08	1.16	1.36	Wang et al. (2006)	
Southern	Rural	PM _{2.5} 2005		0.54			Pathak et al. (2009)	
	Urban	PM _{2.5} 2001			1.12	1.38	Yang et al. (2005)	
	Rural					1.02		
	Urban	PM _{2.5} 1988	0.90				Wang et al. (2000)	
	Rural	PM _{2.5} 2004		0.79			Pathak et al. (2009)	
	Urban	PM ₁₀ 1993–1994				0.78	Wu et al. (2006)	
Rural	PM _{2.5} 2002				1.06	Cheung et al. (2005)		
Hong Kong	Urban	PM _{2.5} 2001–2002	0.75	0.77	0.82	0.86	Louie et al. (2005a)	
	Rural		0.59	0.58	0.67	0.73		
Liu Zhou	Urban	PM _{2.5} 1988	0.98				Wang et al. (2000)	
Xiamen	Urban	PM _{2.5} 1993	0.61					
Haikou	Urban	PM ₁₀ 1989–1990	1.55					
Sanya	Urban	PM ₁₀ 1988			2.90		Wu et al. (2006)	
Yongxing	Rural	PM ₁₀ 1988			2.20			
Heng Mountain	Rural	TSP 1988/1989	0.97/1.18				Wang et al. (1992)	
Lion Mountain	Rural	TSP 1988/1989	1.18/0.88					

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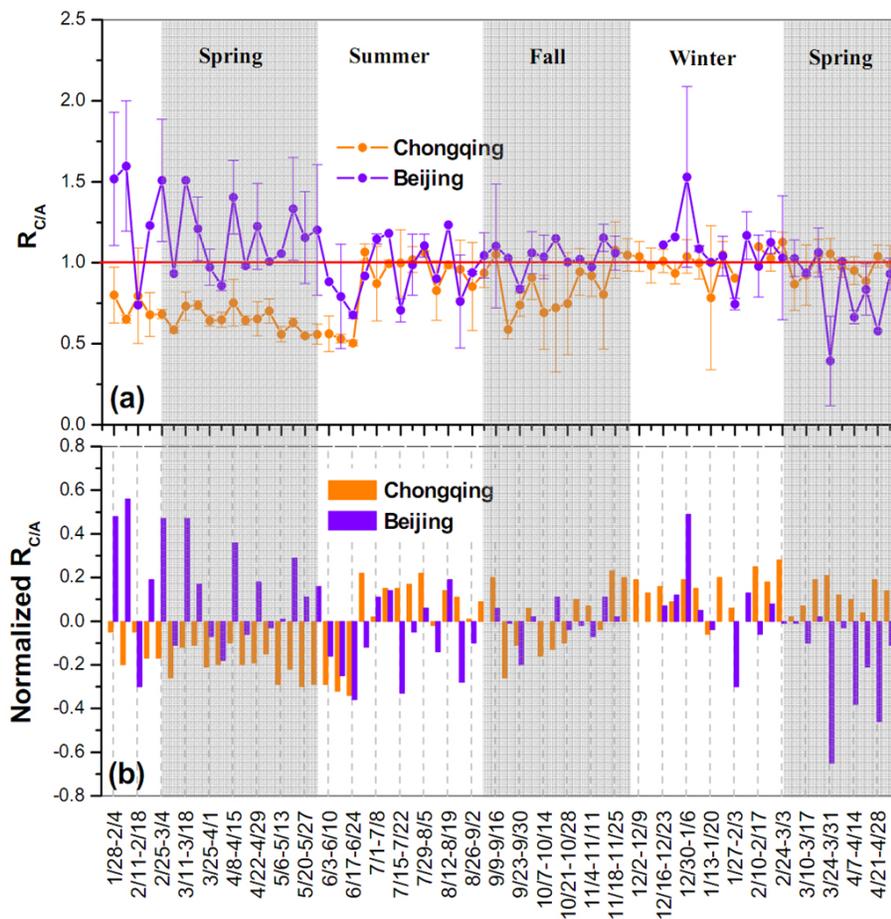


Fig. 1. Seasonal variations of (a) $R_{C/A}$ and (b) normalized $R_{C/A}$ of PM_{2.5} at Beijing and Chongqing.

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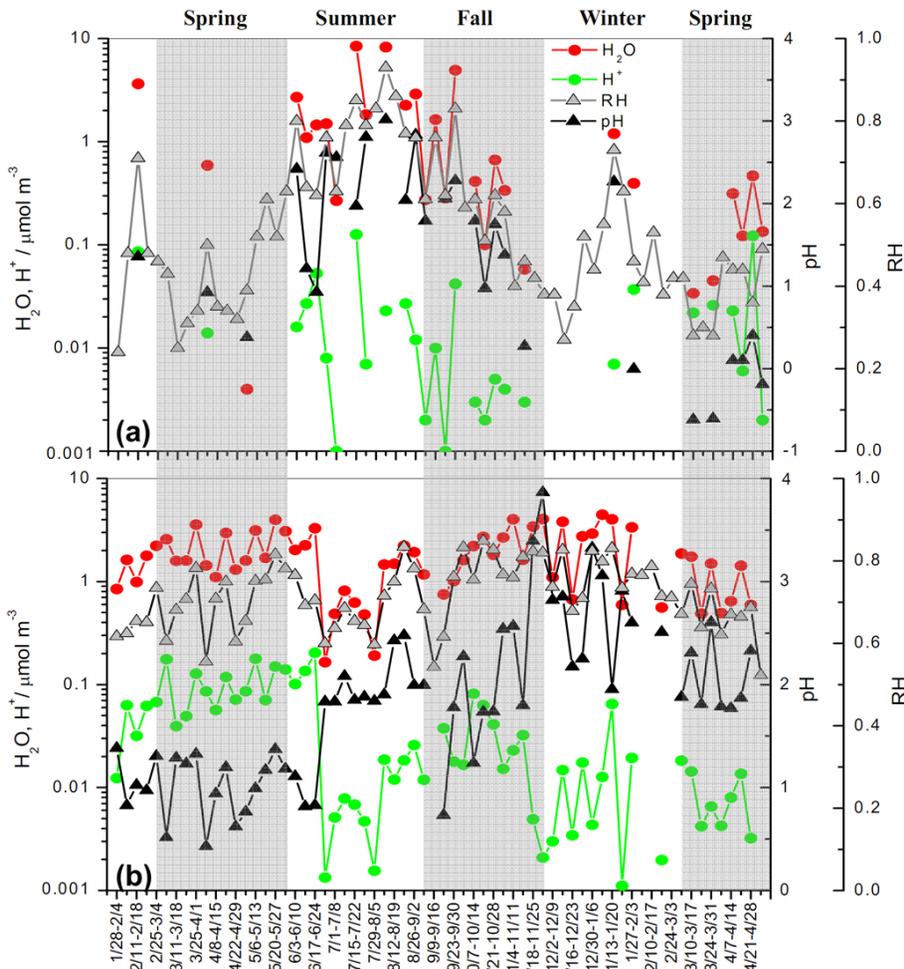


Fig. 2. Seasonal variations of in situ PM_{2.5} pH, [H⁺]_{Insr}, [H₂O] and RH at Beijing and Chongqing.



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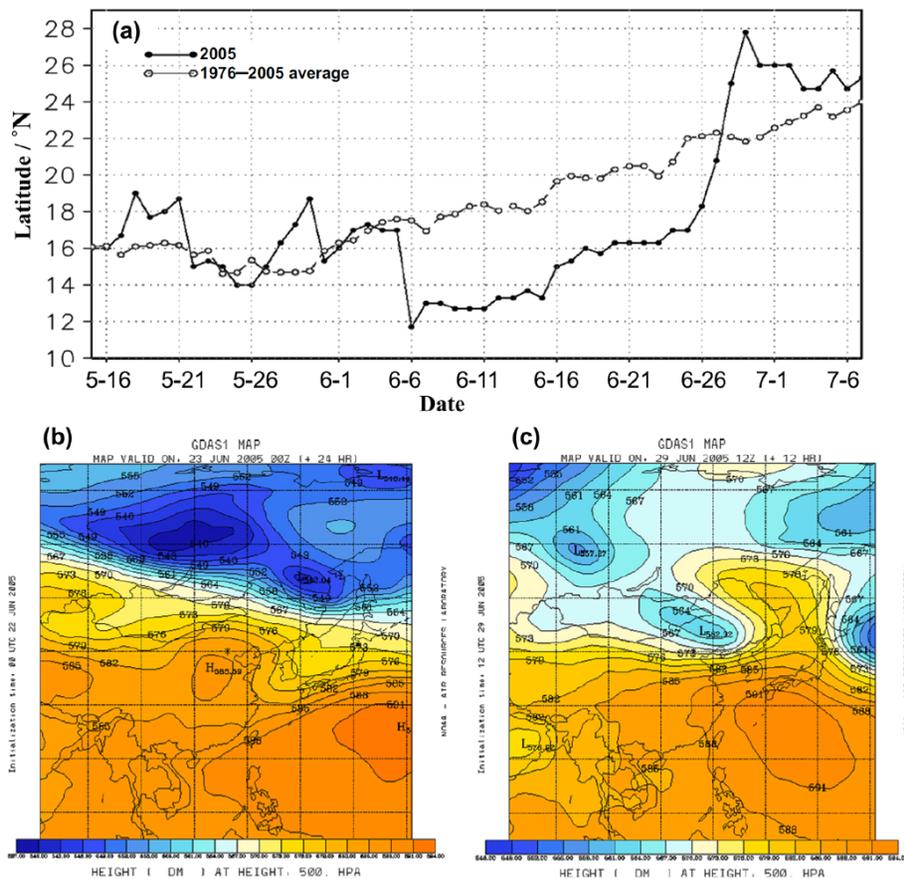


Fig. 3. (a) Daily variation in the subtropical high over the northwestern Pacific between 110°E–130°E (Lu et al., 2007); (b) the geopotential heights of 500 hPa at 23 June 2005, 08:00 UTC over East Asia; (c) the geopotential heights of 500 hPa at 29 June 2005, 12:00 UTC over East Asia.

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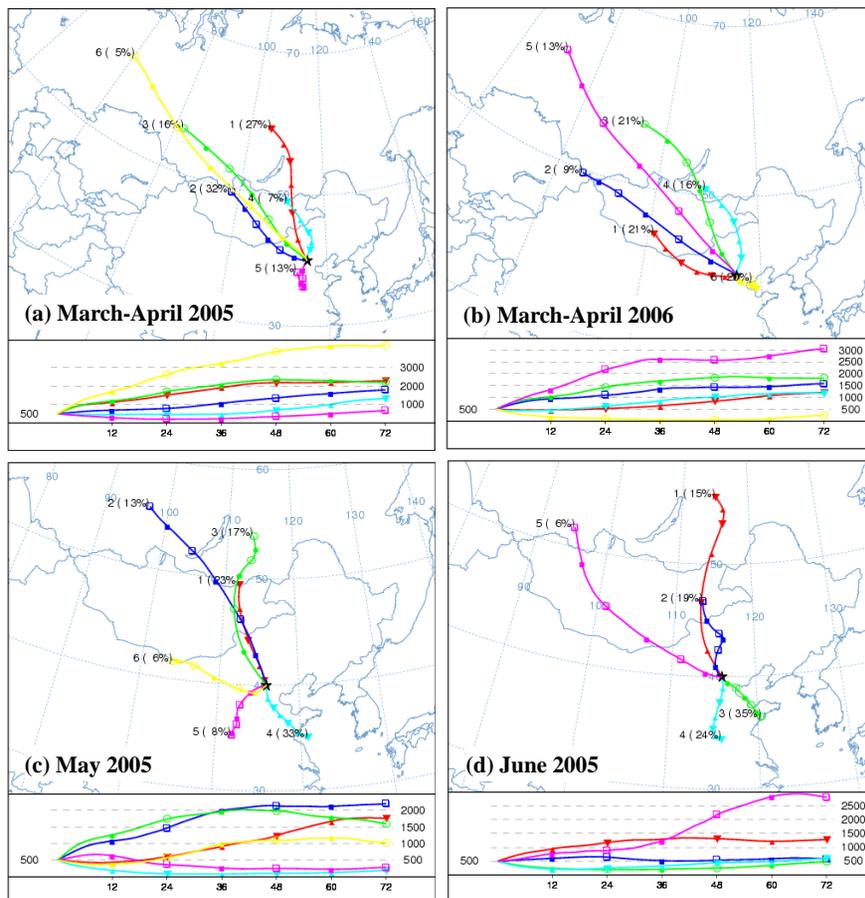


Fig. 4. Clusters of air mass backward trajectories arriving at 500 m a.g.l. at Beijing for **(a)** 4 March–6 May, **(c)** 7–31 May, **(d)** 1–27 June in 2005 and **(b)** 3 March–5 May in 2006.

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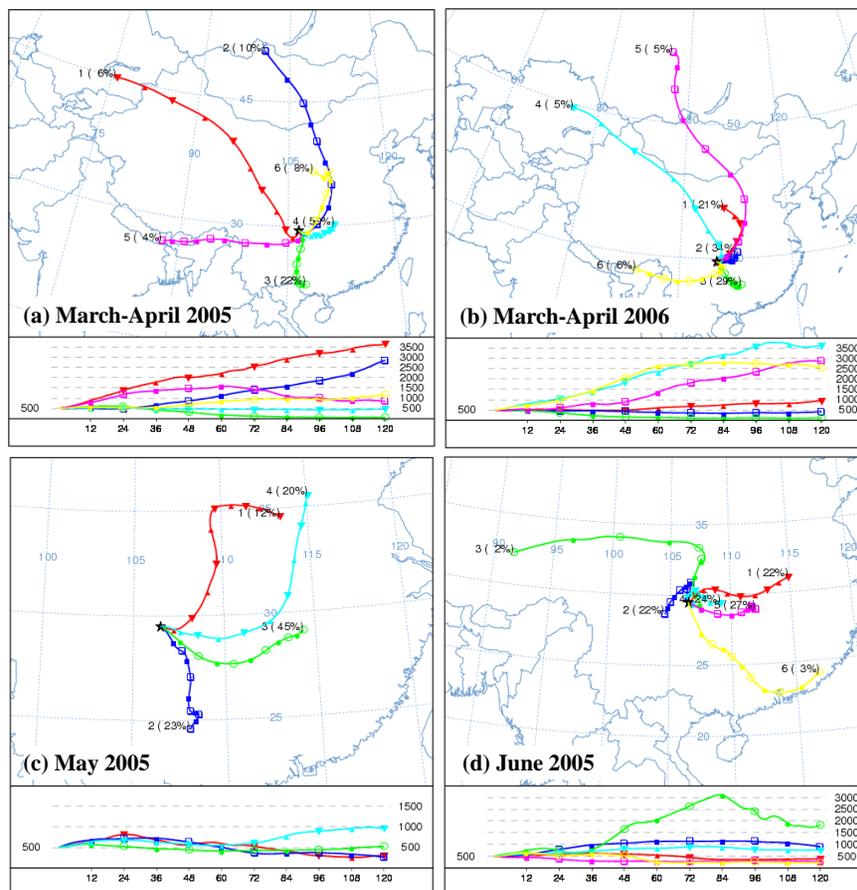


Fig. 5. Clusters of air mass backward trajectories arriving at 500 m a.g.l. at Chongqing for **(a)** 4 March–6 May, **(c)** 7–31 May, **(d)** 1–27 June in 2005 and **(b)** 3 March–5 May in 2006.

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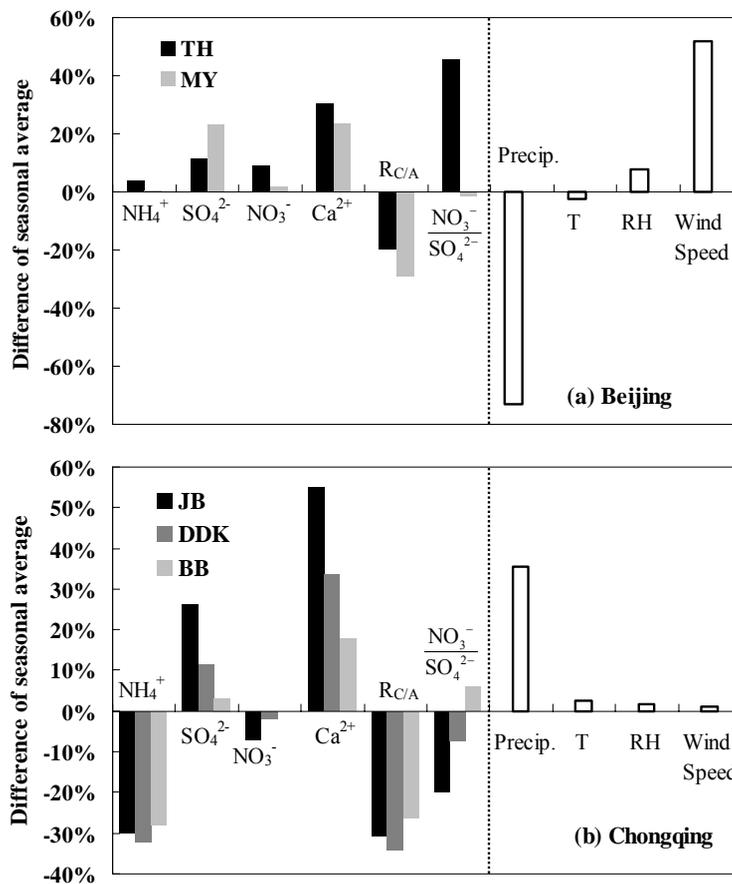


Fig. 6. Differences of $R_{C/A}$, $\text{NO}_3^-/\text{SO}_4^{2-}$, concentrations of associated ionic species and meteorological factors between the two springs of 2005 and 2006 for **(a)** Beijing (TH and MY) and **(b)** Chongqing (JB, DDK and BB), which were calculated based on (2005–2006)/2006 and (2006–2005)/2005, respectively.

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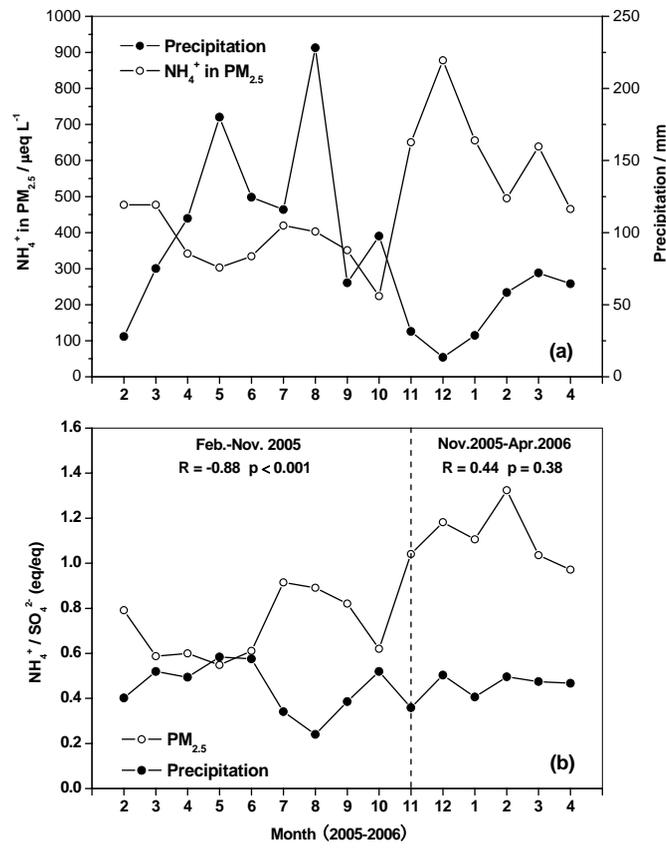


Fig. 7. Monthly variations of (a) amount of precipitation vs. concentration of NH_4^+ in $\text{PM}_{2.5}$ and (b) equivalent charge ratios of $\text{NH}_4^+/\text{SO}_4^{2-}$ in $\text{PM}_{2.5}$ vs. precipitation at Chongqing from February 2005 to April 2006.

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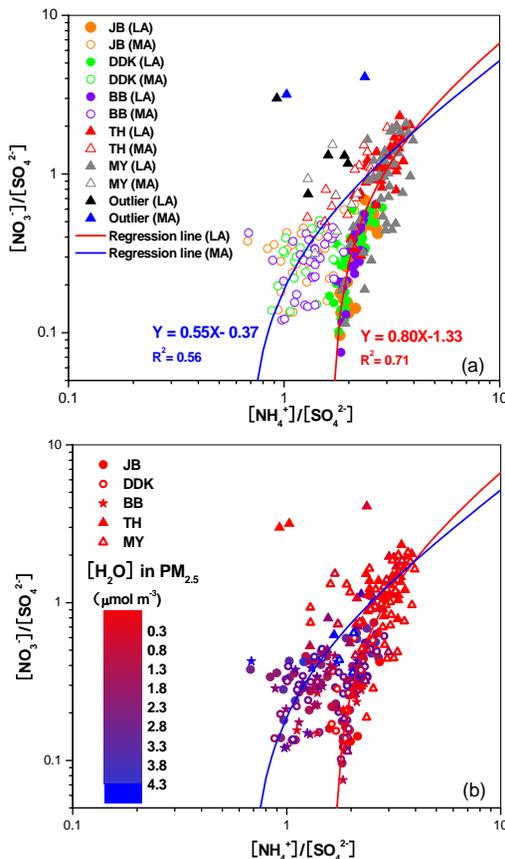


Fig. 8. Molar ratios of $[\text{NO}_3^-]/[\text{SO}_4^{2-}]$ vs. $[\text{NH}_4^+]/[\text{SO}_4^{2-}]$ at different **(a)** acidity and **(b)** water content ($[\text{H}_2\text{O}]$) in $\text{PM}_{2.5}$ at Beijing (TH and MY) and Chongqing (JB, DDK and BB). LA, less acidic. MA, more acidic.

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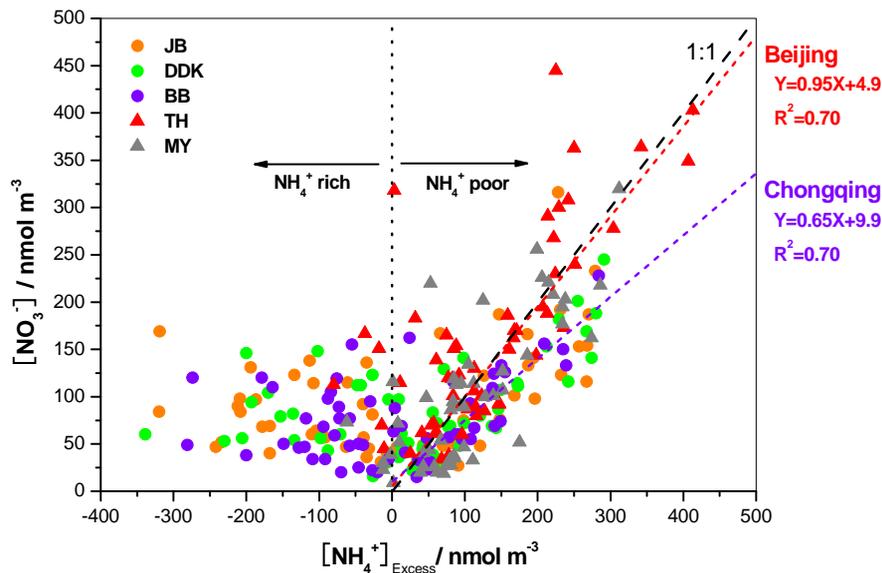


Fig. 9. Relationships between molar concentrations of $[\text{NO}_3^-]$ and $[\text{NH}_4^+]_{\text{Excess}}$ in PM_{2.5} at Beijing (TH and MY) and Chongqing (JB, DDK and BB).

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