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Citation for published version:
Xu, W, Wu, Q, Liu, X, Tang, A, Dore, AJ & Heal, MR 2016, 'Characteristics of ammonia, acid gases, and PM2.5 for three typical land-use types in the North China Plain' Environmental science and pollution research, vol 23, no. 2, pp. 1158-1172. DOI: 10.1007/s11356-015-5648-3

Digital Object Identifier (DOI):
10.1007/s11356-015-5648-3

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Publisher's PDF, also known as Version of record

Published in:
Environmental science and pollution research

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Characteristics of ammonia, acid gases, and PM$_{2.5}$ for three typical land-use types in the North China Plain

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Received: 18 April 2015 / Accepted: 19 October 2015 / Published online: 27 October 2015
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Abstract Air pollution is one of the most serious environmental problems in China due to its rapid economic development alongside a very large consumption of fossil fuel, particularly in the North China Plain (NCP). During the period 2011–2014, we integrated active and passive sampling methods to perform continuous measurements of NH$_3$, HNO$_3$, NO$_2$, and PM$_{2.5}$ at two urban, one suburban, and two rural sites in the NCP. The annual average concentrations of NH$_3$, NO$_2$, and HNO$_3$ across the five sites were in the ranges 8.5–23.0, 22.2–50.5, and 5.5–9.7 μg m$^{-3}$, respectively, showing no significant spatial differences for NH$_3$ and HNO$_3$ but significantly higher NO$_2$ concentration at the urban sites. At each site, annual average concentrations of NH$_3$ and NO$_2$ showed increasing and decreasing trends, respectively, while there was no obvious trend in annual HNO$_3$ concentrations. Daily PM$_{2.5}$ concentrations ranged from 11.8 to 621.0 μg m$^{-3}$ at the urban site, from 19.8 to 692.9 μg m$^{-3}$ at the suburban site, and from 23.9 to 754.5 μg m$^{-3}$ at the two rural sites, with more than 70 % of sampling days exceeding 75 μg m$^{-3}$. Concentrations of water-soluble ions in PM$_{2.5}$ ranked differently between the non-rural and rural sites. The three dominant ions were NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$ and mainly existed as (NH$_4$)$_2$SO$_4$, NH$_4$HSO$_4$, and NH$_4$NO$_3$, and their concentrations averaged 48.6±44.9, 41.2±40.8, and 49.6±35.9 μg m$^{-3}$ at the urban, suburban, and rural sites, respectively. Ion balance calculations indicated that PM$_{2.5}$ was neutral at the non-rural sites but acidic at the rural sites. Seasonal variations of the gases and aerosols exhibited different patterns, depending on source emission strength and meteorological conditions. Our results suggest that a feasible pathway to control PM$_{2.5}$ pollution in the NCP should target ammonia and acid gases together.

Keywords Air pollution · Reactive N · PM$_{2.5}$ · Control strategies · Chemical characteristics · The North China Plain

Introduction

In China, the atmospheric environment has been greatly affected over recent decades by various anthropogenic factors, such as a dramatic economic rise, rapid industrial development, population growth, and construction and demolition projects. The increase of traffic flow is also of central importance. As a consequence, complex air pollution events characterized by regional photochemical smog and haze occur frequently in many regions of China (Wang et al. 2014a), arousing increasing attention from the private citizen as well as environmental scientists and policy makers. The smog and haze largely result from high levels of particulate matter (PM), especially PM$_{2.5}$ (particular matter less than 2.5 μm), which limits atmospheric visibility by light extinction (absorption and scattering) (Sun et al. 2006; Wang et al. 2012a). Several studies focusing on health effects have revealed associations between PM pollution and morbidity and mortality, including
in the USA (Domini et al. 2014) and China (Guo et al. 2009; Wu et al. 2010). It has been estimated that 350,000–400,000 premature deaths can be ascribed to ambient air pollution in China, and the economic burden of premature mortality and morbidity was conservatively estimated at approximately 157 billion RMB (1.16 % of the GDP) in 2003 (Zhang and Smith 2007; WB 2007).

Airborne PM$_{2.5}$ can be directly emitted by anthropogenic sources or generated by gas-to-particle conversion (secondary PM) (Watson 2002). The primary precursors for formation of ammonium sulfate (or bisulfate) and ammonium nitrate are NH$_3$, SO$_2$, and NO$_x$ (NO+NO$_2$). Atmospheric NH$_3$ is emitted primarily from livestock wastes and volatilization of N fertilizers. Other sources include biomass burning, excreta of human and pets, and wastewater (Clarisse et al. 2009). NO$_x$ and SO$_2$ are mainly derived from combustion processes and are subsequently oxidized to HNO$_3$ and H$_2$SO$_4$ in the atmosphere (Sharma et al. 2007).

In order to prevent further deterioration of air quality, China has made tremendous efforts since 2005. For example, the 11th Five-Year Plan (FYP) (2006–2010) for national environmental protection required the reduction of annual SO$_2$ emissions in 2010 by 10 % from its 2005 level, which required installation of flue-gas desulfurization systems to coal-fired power plants as a primary control measure and a stronger vehicle emissions standard. As a consequence, national SO$_2$ emissions decreased by 14.3 % from 2005 to 2010 (MEPC 2011). In the 12th FYP (2011–2015), China is mainly focused on the reduction of national NO$_x$ emissions by 10 % in 2015 from the 2010 level, as well as controls on SO$_2$ and primary particle emissions. To achieve this binding target, China’s Ministry of Environmental Protection (MEP) released a new “emission standard of air pollutants for thermal power plants” (GB 13223-2011) in 2011 to further strengthen the NO$_x$ controls. Furthermore, a stricter vehicle emissions standard (equivalent to the European Union’s Euro IV standard) was also released in late 2012. Unfortunately, legislation to simultaneously reduce NH$_3$ emissions has not been implemented in China. Such legislation is urgently needed given that the estimated health costs associated with NH$_3$ emissions were greater than those associated with NO$_x$ emissions in more than 77 % of provinces in China, particularly in the North China Plain (NCP) (Gu et al. 2014).

The NCP is an intensively managed agricultural and economically developed region, which comprises only 8 % of the total area of China but contributes 40 % of the total national GDP (CSY 2014). The consumption of N fertilizer and energy in the NCP accounted for 35 and 34 % of their respective total national consumption (CSY 2014). This makes the NCP one of the greatest emitters of air pollutants (e.g., NH$_3$, NO$_x$, and SO$_2$) nationally and globally (Clarisse et al. 2009; Gu et al. 2009; Zhang et al. 2009; Huang et al. 2012) and a serious PM$_{2.5}$ pollution region in China (Wang et al. 2014b). Some studies have focused on the measurements of atmospheric NO$_2$ and NH$_3$ at various sites in the NCP (Shen et al. 2009, 2011; Meng et al. 2011; Pan et al. 2012; Luo et al. 2013) and on estimating of emissions of NO$_2$ and NH$_3$ from anthropogenic sources (Zhang et al. 2010, 2011b). Very few studies in the NCP have considered ambient HNO$_3$ measurements (Shen et al. 2009; Luo et al. 2013). PM$_{2.5}$ has been systematically analyzed in many studies in the NCP. Most of the studies have provided the general characteristics of the chemical compositions of PM$_{2.5}$ and discussed its seasonal variations, correlations, or sources (Sun et al. 2004; Song et al. 2006). Additionally, the concentration, correlations, sources, or formation of some specific species (e.g., inorganic ions, carbonaceous components, or organic matter) and their spatial variations have been investigated in the NCP (Ianniello et al. 2011; Zhao et al. 2013; Hu et al. 2014). However, few studies have measured NO$_x$, NH$_3$, HNO$_3$, and PM$_{2.5}$ simultaneously. In addition, previous work has mainly included short-term studies before the year 2010 and has been limited to single land-use types (e.g., urban areas). In the absence of long-term and simultaneous observations, the characteristics of these air pollutants and their implications cannot be determined accurately.

In the present study, ambient NO$_x$, NH$_3$, and HNO$_3$ were continuously monitored at five typical sites (two urban, one suburban, and two rural) in the NCP during the period 2011–2014, and PM$_{2.5}$ was sampled at four of the five sites. The objectives of this study were (1) to characterize spatial, seasonal, and annual variations of concentrations for the measured gases and evaluate their pollution status during the period from 2011 to 2014 and (2) to analyze the concentrations and seasonal variations of PM$_{2.5}$ and its secondary inorganic components over different land-use types. The intention of the study was to provide accurate and current insight into the characteristics of air pollutants and to support interpretation of the effectiveness of major national control policies implemented recently in the NCP.

Materials and methods

Sampling sites

Sampling was conducted between January 2011 and December 2014 at five sites in Beijing and in Henan, Shandong, and Hebei provinces (Fig. 1), which are located in the North China Plain. The area has a typical temperate and monsoonal climate with dry winters and wet summers. The prevailing wind direction is from the southeast in the summer and northwest in the winter.

Two urban sites were at the China Agricultural University (CAU) and Zhengzhou (ZZ), a suburban site was at Shangzhuang (SZ), and two rural sites were at Quzhou (QZ) and Yucheng (YC). The CAU site is located at the west
NH$_3$ and HNO$_3$ samples were collected using the DELTA (DEnuder for Long-Term Atmospheric sampling) system designed by the Centre for Ecology and Hydrology Edinburgh, UK. The DELTA system has been used widely in Europe and described in detail in many previous studies (e.g., Flechard et al. 2011; Luo et al. 2013; Shen et al. 2013). Briefly, the DELTA sampling “train” consists of two potassium carbonate plus glycerol (1 % (m/v) K$_2$CO$_3$ + 1 % (m/v) glycerol in methanol)-coated denuders in series for the simultaneous collection of HNO$_3$, followed by two citric acid (5 % (m/v) citric acid in methanol)-coated denuders for NH$_3$. A low-volume pump (D210, TCS Micropumps Ltd., UK) in the DELTA system was used to sample ambient air at a rate of 0.2–0.4 L min$^{-1}$. When the air passes through a denuder filter train, HNO$_3$ and NH$_3$ in the air are absorbed by the coated chemical solutions in sequence. With a monthly sampling period, the detection limit of the DELTA system for gaseous HNO$_3$ and NH$_3$ was determined as 0.03 $\mu$g HNO$_3$m$^{-3}$ and 0.01 $\mu$g NH$_3$m$^{-3}$. Two denuders in series are used for every sample to check capture efficiency for HNO$_3$ and NH$_3$. When the value is less than 75 %, an imperfectly coated film or some other sampling problems can be assumed to have occurred in the DELTA system (Tang et al. 2009). Across the five sites, collection efficiencies in the first of the two denuders for HNO$_3$ and NH$_3$ averaged 83.2 % (95 % confidence interval 81.5–84.9 %) and 82.7 % (81.3–84.1 %), respectively, during the entire period. Thus, we can be assured that both of measured gases were effectively captured in both denuders. It should be noted that nitrous acid (HONO) could cause a positive bias in the long-term measurement of HNO$_3$ using the DELTA system (Tang et al. 2009). This is of importance in urban areas whereas HONO interference (as well as possible NO$_2$ and PAN interference) should be negligible in rural areas. In this study, glycerol was added to the coating of the denuder for HNO$_3$ sampling in order to increase adhesion and reduce volatilization of the carbonate coating and also to minimize oxidation of nitrite to nitrate which can occur when ozone is present (Allegrini et al. 1987; Perrino et al. 1990; Tang et al. 2009). In addition, the average denuder capture efficiency for HNO$_3$ was 83.2 % in the first denuder as noted earlier, indicating little evidence of significant NO$_2$ or PAN capture (Tang et al. 2009).
Nevertheless, measured HNO₃ concentrations may be overestimated to some extent at the urban CAU site but could reflect actual levels at suburban and rural sites. In future work, HNO₃ should be selectively removed from the sampling air by first using a sodium fluoride or sodium fluoride-coated denuder as widely used in previous studies (Allegrini et al. 1987; Spataro et al. 2013). For NH₃ sampling, Perrino and Gherardi (1999) have highlighted that in the case of citric acid, about 8% of the collected ammonia was released after 2 h and more than 40% after 12 h. In contrast, phosphorous acid is a suitable coating layer for a denuder line intended to determine gaseous ammonia in the atmosphere (Perrino and Gherardi 1999). However, an intercomparison study conducted by Tang et al. (2009) showed that the 14-day mean NH₃ concentration from citric acid-coated denuders of a DELTA system was about 9% lower than that from H₃PO₃-coated denuders of an Annular Denuder System. Given this, together with an overall 82.7% NH₃ capture efficiency as noted earlier, NH₃ concentrations sampled at the five sites should be reasonable and acceptable, albeit with some degree of underestimation.

NO₂ samples were collected by Gradko diffusion tubes (Gradko International Limited, UK). Each sampler consists of a 71.0-mm long × 11.0-mm internal diameter acrylic tube with colored and white thermoplastic rubber caps. Three NO₂ samplers at each site were exposed under a PVC shelter which protected the samplers from precipitation and direct sunshine. The NO₂ was absorbed into a 20% triethanolamine/deionized water solution coated onto two stainless steel wire meshes within the colored cap. As indicated by the manufacturer (Gradko International Ltd, UK), the uptake rate of the tube is 68.8 × 10⁻⁶ m⁻³ h⁻¹, the desorption efficiency is 0.98, the limit of detection is 1.6 μg N O₂ m⁻³ over a 2-week exposure period, and the analytical expanded measurement uncertainty is ±10%. Over the entire period, the standard deviations of each sampling across all sites ranged from 0.01 to 2.9 μg N O₂ m⁻³ and averaged 0.8 μg N O₂ m⁻³ (95% confidence interval 0.7–0.9).

All the samplers were exposed for 1 month at each site and returned to the laboratory for analysis. In the laboratory, all the exposed samples were stored at 4°C and analyzed at 1-month intervals. The HNO₃ denuders were extracted with 10 mL 0.05% H₂O₂ solution. The NH₃ denuders were extracted with 10 mL high-purity water. Ammonium and nitrate in the extracted solutions were measured with an AA3 continuous-flow analyzer (Bran+Luebbe GmbH, Norderstedt, Germany). The detection limits were determined as 0.01 mg N L⁻¹ for NH₄⁺ and NO₃⁻. The meshes from the NO₂ diffusion tubes were extracted with a solution containing sulfanilamide, H₃PO₄, and N-1-naphthylethylene-diamine, and the NO₂ content in the extract determined using a colorimetric method by absorption at a wavelength of 542 nm. The detection limit for NO₂ was 0.01 mg N L⁻¹.

### Table 1

| Monitoring site                     | Species                  | Monitoring period          | Measurement height (m) and underlying surface | Population density (persons km⁻²) | Surrounding environment and possible emission sources |
|-------------------------------------|--------------------------|---------------------------|-----------------------------------------------|--------------------------------|-----------------------------------------------------|
| China Agricultural University (CAU) | NH₃, HNO₃, NO₂, PM₂.₅   | Jan. 2011–Dec. 2014       | 2                                             | 7616                           | Densely occupied residences, small-scale urban agriculture, and traffic roads. |
| Shanghai (SH)                      | NH₃, HNO₃, NO₂, PM₂.₅   | Mar. 12–Nov. 2014         | 2                                             | 519                            | Small towns, traffic roads, and farmland.             |
| Quzhou (QZ)                        | NH₃, HNO₃, NO₂, PM₂.₅   | Jan. 2011–Dec. 2014       | 2                                             | 606                            | Small villages, a traffic road, and dense farmland.  |
| Yucheng (YC)                       | NH₃, HNO₃, NO₂, PM₂.₅   | Apr. 12–Nov. 2014         | 2                                             | 495                            | Small villages, a road, and dense farmland.          |
| Zhengzhou (ZZ)                     | NH₃, HNO₃, NO₂           | Jan. 2011–Dec. 2014       | 2                                             | 17,069                         | Densely occupied residences and traffic roads.       |

a NH₃, HNO₃, and NO₂ were measured.

b Population density was estimated by dividing population by area of the town/district/city, where the monitoring site is located.

c Population data were sourced from the sixth census of China in 2010.
samples were extracted and analyzed using the same methods as the exposed samples. After correcting for the corresponding blanks, the results were used for the calculation of concentrations for all measured gases.

Samples of PM$_{2.5}$ were collected by medium-volume samplers (TH-150CIII, 100 L min$^{-1}$, Tianhong Co., Wuhan, China) onto 90-mm quartz fiber filters (Whatman QM/A, Maidstone, UK) at all sites except ZZ because only four particle samplers were available. The quartz fiber filters were baked at 500 °C for 4 h prior to sampling to remove contaminants. The PM$_{2.5}$ samples were collected on a 24-hourly basis from 08:00 hours to 08:00 hours the next day. More than 25 valid samples were obtained for most seasons during the sampling period at each site. Owing to precipitation or occasional sampler failure, a number of seasons have less than 20 samples.

Before and after sampling, the filters were equilibrated for 24 h in a desiccator at 25 °C and 40±5 % relative humidity and then weighed with a microbalance (Sartorius, precision 10 μg). The PM$_{2.5}$ concentrations were calculated by weight differences divided by sampling air flows. A quarter of each filtrate was put into a 50-mL beaker with 10 mL of high-purity water (18.2 MΩ resistivity). After a 30-min ultrasonic extraction, the extracts were filtered using 0.22-μm syringe filters, and the filtrates were stored in clean tubes at 4 °C until analyzed within 1 month of extraction. The cations (NH$_4^+$, Na$^+$, Ca$^{2+}$, K$^+$, Mg$^{2+}$) and anions (NO$_3^-$, SO$_4^{2-}$, F$^-$, Cl$^-$) in the filtrates were determined by Dionex-600 and Dionex-2100 Ion Chromatograph (Dionex Inc., Sunnyvale, CA, USA), respectively. Details of the instruments and detection limits have been provided elsewhere (Zhang et al. 2011a; Tao et al. 2014). Field blank measurements were made each month or each season at all sites.

Meteorological data

Hourly wind speed (WS), temperature ($T$), relative humidity (RH), and daily precipitation for each site for 2011–2014 were taken from Weather Underground (http://www.weatherunderground.com/). The monthly and annual WS, $T$, RH and precipitation are respectively displayed in Fig. S1 and Table S1 in the Supplementary Information (SI). Year-to-year variations in all meteorological parameters were not significant at each site (all $p>0.05$) except RH for CAU, SZ, and QZ.

Statistical analyses

One-way analysis of variance (ANOVA) and paired-sample $t$ tests were used to decide the significance of the differences in annual average gas (i.e., NH$_3$, NO$_2$, and HNO$_3$) concentrations and annual average meteorological data among sites or years, as well as daily average PM$_{2.5}$ concentrations among seasons at each site. Pearson correlation and linear regression analyses were conducted for the water-soluble inorganic ions in PM$_{2.5}$. All statistical analyses were performed using SPSS 11.5 (SPSS Inc., Chicago, IL, USA), and significance was defined as $p<0.05$.

Results and discussion

Spatial and annual variations of NH$_3$, NO$_2$, and HNO$_3$

Monthly mean concentrations of NH$_3$, NO$_2$, and HNO$_3$ at the five sites are shown in Fig. 2. The concentrations of NH$_3$, NO$_2$, and HNO$_3$ across all sites were in the ranges of 1.2–42.3, 10.6–81.3, and 0.3–22.1 μg m$^{-3}$, respectively. Their concentrations varied greatly across sites for all measured gases. The mean annual concentrations of NH$_3$, NO$_2$, and HNO$_3$ at the five sites for the years between 2011 and 2014 are also presented in Fig. 2. The annual NH$_3$ concentrations varied from 8.5±3.7 μg m$^{-3}$ at ZZ in 2011 to 23.7±7.2 μg m$^{-3}$ at QZ in 2014 (Fig. 2a). The year-to-year variations in annual concentrations of NH$_3$ were sometimes significant at all sites except CAU and YC (details are given in Table S2). However, it is important to note that annual NH$_3$ levels show a slight increasing trend at the five sites. This finding is consistent with the increasing trend of NH$_3$ emissions during recent years in the NCP due to intensified agricultural activities (Zhang et al. 2010, 2011b). The largest annual mean NH$_3$ concentration was observed at QZ (16.9±5.9 μg m$^{-3}$), followed by YC (13.8±1.5 μg m$^{-3}$), CAU (13.1±1.0 μg m$^{-3}$), ZZ (11.1±2.0 μg m$^{-3}$), and SZ (10.5±1.1 μg m$^{-3}$) (Fig. S2). This is likely due to the fact that QZ is a typical agricultural rural site with excessive N fertilizer input (about 500–600 kg N ha$^{-1}$ year$^{-1}$) over a large amount of agricultural land (75 % of the total land), which is the main source of NH$_3$ (Clarisse et al. 2009). However, the difference in the annual NH$_3$ concentrations during 2011–2014 across the five sites was not significant. High NH$_3$ concentration in urban areas is associated with NH$_3$ emissions from biological sources, such as humans, sewage systems, and garbage containers (Reche et al. 2002). NH$_3$ is a secondary pollutant in gasoline vehicle emissions that results from the reaction which occurs in the catalytic converter between NO and H (Moeckli et al. 1996). Between 2006 and 2013, the number of civil vehicles increased from 2.39 to 5.17 million in Beijing and from 0.46 to 1.72 million in Zhengzhou (CSY 2007–2014), which could result in elevated NH$_3$ emissions. In addition, large cities in China (e.g., Beijing and Zhengzhou) can receive large amounts of agricultural NH$_3$ from the suburban areas (Gu et al. 2014; Xu et al. 2014). In the present study, annual NH$_3$ concentrations at the five sites were 4–11 times higher than the annual background atmospheric NH$_3$ in North China (ca. 2.1 μg m$^{-3}$) reported by Meng et al. (2010). NH$_3$ levels at different urban, suburban, and rural sites in the world are listed in Table S3.
The average concentrations of NH₃ measured at the rural and urban sites in this study were far higher than those reported in southern China (e.g., Yang et al. 2010; She et al. 2013) and in other countries (e.g., Walker et al. 2004; Trebs et al. 2006; Endo et al. 2011) but were comparable to previous measurements in the NCP (e.g., Meng et al. 2011; Luo et al. 2013). NH₃ concentrations at the suburban site (SZ) were close to those observed at suburban sites with serious NH₃ pollution worldwide (Singh et al. 2001; Alebic-Juretic 2008; Cao et al. 2009). Our findings suggest that the NCP is still experiencing serious NH₃ pollution in present-day China, which is closely related to the high NH₃ emissions from N fertilizer application, intensive livestock production facilities, and high population density. For example, typical application rates of N fertilizer are 500–600 kg N ha⁻¹ year⁻¹ for high yields of maize and wheat in rural and suburb areas. However, less than 30 % of the N fertilizer applied is taken up by the crops and more than 20 % (ca. 100 kg N ha⁻¹ year⁻¹) is lost by NH₃ emissions (Pan et al. 2012). This makes a significant contribution to high NH₃ concentrations in the whole region. Moreover, North China is witnessing a rapid increase in livestock production facilities in suburban areas. Populations of the main livestock (pig and cattle) have increased at an annual rate of 2 % from 1996 to 2013 in North China (CSY 1997–2014). This will also result in large emissions of NH₃.

The annual average NO₂ concentrations ranged from 22.2 ± 6.2 µg m⁻³ at SZ in the suburb of Beijing in 2014 to 50.5 ± 8.3 µg m⁻³ at CAU in the city area in 2011 (Fig. 2b). The annual concentrations at each site varied to a different extent among the years and overall exhibited a decreasing trend during the period 2011–2014 (Fig. 2b and Table S2). This finding is in accordance with the modeling results of Wang et al. (2014b) who calculated that ambient NO₂ concentration will decrease by 8 % during the 12th Five-Year Plan period (2011–2015) as a consequence of national NOₓ control policies (e.g., new emission standards for power plants and vehicles).
interesting to observe that the year-to-year variation exhibited the same characteristic at CAU and SZ, i.e., monthly mean values were significantly lower ($p<0.05$) in 2014 than in 2011 but were not significantly different ($p>0.05$) between other years (Table S2). This result suggests that NO$_2$ produced in the area of the urban site can greatly affect NO$_2$ concentration at the suburban site. As for inter-site comparisons, annual NO$_2$ concentrations at the urban sites (CAU and ZZ, average 43.9±1.0 μg m$^{-3}$) were significantly higher ($p<0.05$) than those at the rural and suburban sites (QZ, YC, and SZ, average 27.5±3.2 μg m$^{-3}$). Differences in annual average values between the suburban and rural sites were not significant ($p>0.05$) (Fig. S2). It is commonly accepted that NO$_2$ is a ubiquitous air pollutant in urban regions derived mainly from fossil fuel combustion processes including power plants, transportation, and industry (Streets et al. 2003). The background concentration of atmospheric NO$_2$ was only about 3.7 μg m$^{-3}$ in North China (Meng et al. 2010). In the present study, annual NO$_2$ concentrations at the rural sites (23.2–31.4 μg m$^{-3}$) were lower than those obtained in a rural area with serious NO$_2$ pollution in eastern China (average 42 μg m$^{-3}$) (Yang et al. 2010) but were much greater than those obtained in the studies of Aas et al. (2007) and Shen et al. (2013) at several rural sites in south China (Table S3), and exceed (or are close to) the annual mean NO$_2$ guideline value of 30 μg m$^{-3}$ set by the World Health Organization (WHO 2000). Annual NO$_2$ concentrations at the urban sites (38.3–50.5 μg m$^{-3}$) exceeded the WHO guideline and mostly exceeded the Chinese annual exposure limit for humans of 40 μg m$^{-3}$ for NO$_2$ (MEPC 2012). Compared to urban sites in other studies (Table S3), the urban NO$_2$ concentrations in this study were similar to those obtained at most capital cities reported by Wang et al. (2014b) for the period of 2013–2014 in China and were higher than values reported for Thessaloniki, Greece (Anatolaki and Tsitouridou 2007). Combining these findings, we conclude that many large cities in China, and rural and suburban regions in the NCP, are suffering from serious NO$_2$ pollution, which mainly results from high NO$_2$ emission from the construction of new power plants and the rapid increase of vehicle numbers. According to Wang and Hao (2012), China increased its thermal power generation by 195% and vehicle production by 300% during 2000–2010 and NO$_2$ emissions from power plants and transport increased by over 100 and 200%, respectively, over the same period. The increased NO$_2$ emissions from newly built large power plants in North China can even be observed by satellite (Wang et al. 2012b).

NH$_3$ and NO$_2$ are two primary reactive N species in air which mainly come from human activity. The monthly mean molar ratio of NH$_3$ to NO$_2$ were in the ranges of 0.11–1.92 at the urban sites (CAU and ZZ), 0.15–2.55 at the suburban site, and 0.11–7.38 at the rural sites (QZ and YC), with overall annual values of 0.81, 1.19, and 1.74, respectively (Fig. S3). These results indicate that the concentrations of gaseous N compounds in the air are predominantly influenced by fossil fuel combustion in urban areas and by agricultural activity in non-urban areas.

In contrast to NH$_3$ and NO$_2$, the annual mean concentrations of HNO$_3$ at the five sites were lower and less variable, ranging from 5.5±4.1 μg m$^{-3}$ (at ZZ in 2011) to 9.7±4.5 μg m$^{-3}$ (at CAU in 2014) (Fig. 2c). The year-to-year variation in annual averages was comparatively small at each site except that ZZ and SZ showed a significant difference ($p<0.05$) in monthly mean values between 2014 and 2011 and 2012, respectively (Table S2). Annual HNO$_3$ concentrations were not significantly different ($p>0.05$) among the five sites, with mean values of 8.9, 8.3, 7.1, 7.6, and 7.3 μg m$^{-3}$ at CAU, ZZ, SZ, QZ, and YC, respectively (Fig. S2). This finding is not surprising because HNO$_3$ is produced through many pathways in the atmosphere, including photodissociation of NO$_2$ with OH, reaction of NO$_3$ with VOC, hydrolysis of N$_2$O$_5$, and dissociation of NH$_4$NO$_3$ aerosol (Khoder 2002). The fate of HNO$_3$ is controlled by the reaction with NH$_3$, which is influenced by ambient temperature, relatively humidity, and NH$_3$ concentrations (Sharma et al. 2007). Therefore, the absence of significant spatial difference of HNO$_3$ in this study is likely linked to the differences among sites in the extent of oxidation of NO$_2$, the contribution from other sources, and the ratio of HNO$_3$ and NH$_3$. For example, the correlations between monthly mean concentrations of NO$_2$ and HNO$_3$ were not significant at each site except for a significantly negative correlation for ZZ (Fig. S4). Moreover, NH$_3$ and HNO$_3$ were found to be highly positively corrected at ZZ, QZ, and YC (Fig. S5), suggesting that dissociation of NH$_4$NO$_3$ is the important contributor for the ambient HNO$_3$. Average HNO$_3$ concentrations in this study were comparable to those measured at two sites in the NCP reported by Luo et al. (2013) but much higher than those observed at three sites in south China (Shen et al. 2013) and at many sites worldwide (e.g., Endo et al. 2011; Trebs et al. 2006) (Table S3). The NCP has some of the highest air pollution in China due to the large amounts of coal combustion for industry and power plants and residential heating leading to high HNO$_3$ concentrations from oxidation of NO$_2$.

### Seasonal variation of gaseous NH$_3$, NO$_2$, and HNO$_3$

The seasonal concentrations of NH$_3$, NO$_2$, and HNO$_3$ are dependent on their source strength and meteorological conditions. Figure 3 shows the monthly statistics of NH$_3$, NO$_2$, and HNO$_3$ concentrations, averaged over the 4-year period, measured at the five sites (2-year observation at YC). NH$_3$ concentrations across all sites were higher in March or April, especially at the rural sites (Fig. 3(a)). This can be partly explained by the enhanced NH$_3$ emission from natural and agricultural sources and city garbage, caused by the abrupt temperature increase after winter (Fig. S1a); every 5 °C...
temperature increase nearly doubles the volatilization potential of ammonia (Sutton et al. 2013). The highest concentrations of NH₃ at all sites were in summer (June–August), which is due to the fact that high temperatures together with ammonium-N fertilizer use induce high NH₃ emissions from fertilizers. As shown in Fig. 4, NH₃ concentrations increased exponentially with the increase in air temperature at the sampling sites. The lowest concentrations of NH₃ in winter can be ascribed to the reduced NH₃ volatilization at low air temperature, high snow coverage, and infrequency of agricultural activities in winter (Cao et al. 2009). The highest NO₂ concentrations at all sites were observed in autumn (September–November) or winter (December–February) with the exception of SZ, which showed comparable values between spring and winter (Fig. 3(b)). Increased NO₂ emissions from the greater coal combustion for domestic heating (from middle November to middle March) in Northern China is the main reason for high NO₂ concentrations in autumn/winter. Moreover, agricultural crop residues in North China are not only burned as domestic fuel but are also burned directly in the field during harvest seasons (e.g., autumn), which can also cause serious local and regional NO₂ pollution (Duan et al. 2004). In addition, stable atmospheres and low temperatures appeared more frequently during autumn and winter (Fig. S1a, b), which are unfavorable meteorological conditions for air pollution dilution and dispersion (Chai et al. 2014). The lowest NO₂ concentrations were observed in summer at ZZ, SZ, and YC; in spring at QZ; and were comparable between spring and summer at CAU. In summer, stronger atmospheric mixing leads to a deeper boundary layer and a dilution of pollutants emitted from the surface, and the increased photochemistry increases the oxidation of NO₂ and its conversion rate to nitrate by reaction with OH (Yang et al. 2010). Consequently, NO₂ concentrations were lowest in summer at most sites. In contrast, the relatively high NO₂ concentration in summer at QZ and CAU is probably due to high NO₂ emissions from road traffic. The seasonal pattern of HNO₃ changes somewhat across the five sites, with the highest HNO₃ concentrations observed in winter at CAU and SZ, in summer at QZ and ZZ, and in autumn at YC (Fig. 3(c)). Different seasonal patterns of atmospheric HNO₃ in China were also reported.

**Fig. 3** The statistics of monthly average concentrations of a NH₃, b NO₂, and c HNO₃ during the sampling periods at the five sites. The arrows denote N fertilizer application for the maize-wheat crop rotation system at SZ, QZ, and YC.

**Fig. 4** Correlation between monthly average air temperature and monthly average NH₃ concentration across all five sites.
in previous studies (Li et al. 2013; Luo et al. 2013; Shen et al. 2013).

**Mass concentrations of PM$_{2.5}$ and water-soluble ions**

Table 2 presents the summary statistics for daily average PM$_{2.5}$ concentrations during the sampling periods at the four sites. The concentrations of PM$_{2.5}$ were in the range 11.8–621.0, 19.8–692.9, 23.9–754.5, and 27.9–455.0 μg m$^{-3}$ at CAU, SZ, QZ, and YC, respectively (data for each season per site during the sampling period are provided in Table S4). Daily average PM$_{2.5}$ concentrations were not significantly different between the sites with the exception of significantly higher PM$_{2.5}$ concentrations at CAU than at SZ. The average PM$_{2.5}$ concentration at the urban site (CAU, 159.4 μg m$^{-3}$) was comparable to the annual mean value of 123.5 μg m$^{-3}$ in 2009/2010 in the urban area of Beijing (Zhao et al. 2013). Also, the average daily PM$_{2.5}$ concentration at the suburban (SZ, 141.5 μg m$^{-3}$) and rural (153.9 μg m$^{-3}$ at QZ and 141.8 μg m$^{-3}$ at YC) sites was similar to those obtained at sites with corresponding land-use types in the NCP (Shen et al. 2011). The daily average PM$_{2.5}$ concentration was a factor of 2.1 (95% confidence interval 1.99–2.25), 1.9 (1.72–2.04), 2.1 (1.89–2.21), and 1.9 (1.75–2.03) greater than the Chinese Grade II standard for daily PM$_{2.5}$ concentration (75 μg m$^{-3}$, MEPC 2012) at CAU, SZ, QZ, and YC, respectively. When compared to the WHO guideline for daily PM$_{2.5}$ concentration (25 μg m$^{-3}$, WHO 2005), the ratios were even higher, being 6.4 (5.99–6.76) at CAU, 5.7 (5.18–6.14) at SZ, 6.2 (5.67–6.64) at QZ, and 5.7 (5.24–6.11) at YC. More than 70% of the sampling days had daily average PM$_{2.5}$ concentration above the Chinese Grade II standard at the four sites, especially at YC (94%). Compared with the WHO standard for daily average PM$_{2.5}$, almost all (>98%) of the daily PM$_{2.5}$ concentration exceeded the standard. Obviously, severe PM$_{2.5}$ pollution not only existed in the urban area but also in suburban and rural areas in the NCP.

At four sites, the daily PM$_{2.5}$ concentrations during summer were lower than those in other seasons (Fig. 5). Higher rainfall in summer at all sites (Fig. S1d) promotes the scavenging of particles by wet deposition. In addition, higher temperatures during summer (Fig. S1a) favor the volatilization of fine particle nitrate to NH$_3$ and HNO$_3$ (Seinfeld and Pandis 2006). Different seasonal characteristics for highest PM$_{2.5}$ concentrations were found in the present study. At CAU, the maximum concentrations were in spring and winter, with no significant difference between the two seasons. This seasonal pattern is consistent with that for the period 2005–2008 in Beijing investigated by Yu et al. (2011) but is different from the finding of Zhao et al. (2013) who reported similar seasonal PM$_{2.5}$ concentrations across seasons in Beijing in 2009/2010, ascribed to the promotion of electricity and natural gas use. So, our result may imply that combustion of fossil fuel is still the important source of PM$_{2.5}$ in Beijing, regardless of differences in meteorological conditions (e.g., wind direction, wind speed) during experiment periods between the two studies. At QZ and SZ, the concentrations were not significantly different between spring, autumn, and winter. As revealed by Yu et al. (2011), high PM$_{2.5}$ concentrations in spring in Beijing were mainly dominated by geogenic particles from the west and northwest of China via atmospheric transport. In contrast, high concentrations of PM$_{2.5}$ in winter and autumn resulted from the combination of coal and biomass burning for domestic home heating and direct burning of agricultural residues in the field (Hu et al. 2014). Moreover, stable meteorological conditions during autumn and winter (see “Seasonal variation of gaseous NH$_3$, NO$_2$, and HNO$_3$”) also lead to the accumulation of air pollutants. The PM$_{2.5}$ concentrations at YC were significantly higher only in winter as compared to the other three seasons, among which there was no significant difference in PM$_{2.5}$ concentration. Low PM$_{2.5}$ concentration in spring at YC is associated with a combination of fewer samples collected in the spring of 2013 (Table S4) and missing days with serious particle pollution.

The average concentrations of water-soluble ionic species during the sampling period at the four sites are presented in Table 3. The proportion of the water-soluble ions in PM$_{2.5}$ was similar for the urban site (36%), the suburban site (34%), and the rural sites (average 40%). The concentrations of ions at the urban and suburban sites were both in the order NH$_4^+$ > Ca$^{2+}$ > K$^+$ > Na$^+$ > Mg$^{2+}$ for the cations and NO$_3^-$ > SO$_4^{2-}$ > Cl$^-$ > F$^-$ for the anions. At the rural sites, the concentration order was NH$_4^+$ > K$^+$ > Ca$^{2+}$ > Na$^+$ > Mg$^{2+}$ for the cations and SO$_4^{2-}$ > NO$_3^-$ > Cl$^-$ > F$^-$ for the anions. The SO$_4^{2-}$, NO$_3^-$, and NH$_4^+$ are the dominant ionic species, contributing 29–39% of the average PM$_{2.5}$ mass across the four sites (Table 3). The

| Table 2 | Summary statistics for daily average PM$_{2.5}$ concentrations (μg m$^{-3}$) during the sampling period at the four sites |
|---|---|
| | CAU | SZ | QZ | YC |
| Mean | 159.4 | 141.5 | 153.8 | 141.8 |
| Median | 137.3 | 110.3 | 126.4 | 127.7 |
| Min | 11.8 | 19.8 | 23.9 | 27.9 |
| Max | 621.0 | 692.9 | 754.5 | 455.0 |
| SD | 95.8 | 105.9 | 101.5 | 68.4 |
| N | 384 | 299 | 270 | 155 |
| ECGS (%)$^a$ | 80.5 | 72.6 | 79.6 | 93.5 |
| EWHOS (%)$^b$ | 98.2 | 99.7 | 99.6 | 100 |

$^a$Number of sampling days
$^b$The proportion of sampling days which had concentrations of PM$_{2.5}$ exceeded the Chinese Grade II standard

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The average PM$_{2.5}$ mass across the four sites (Table 3).
sampling sites in the present study were located in Beijing and its neighboring provinces (far from the ocean), where the contribution to aerosols from sea salt spray could be ignored (Yuan et al. 2004). The inconsistent order of Ca\(^{2+}\) and K\(^{+}\) between non-rural and rural sites is likely due to the differences in contributions from road and soil dust and biomass burning, as the fine mode Ca\(^{2+}\) and K\(^{+}\) are widely regarded as indicators of mineral dust and biomass burning, respectively (Zhao et al. 2010). The average mass ratios of NO\(_3^-\)/SO\(_4^{2-}\) were 1.15±0.90, 1.10±0.82, 0.81±0.53, and 0.81±0.49 for CAU, SZ, QZ, and YC, respectively. The higher ratios at CAU and SZ indicate a greater fraction of particles sourced from automobile exhaust. Lower NO\(_3^-\)/SO\(_4^{2-}\) ratio at QZ and YC could reflect the dominant coal combustion sources for particles.

Figure 6 illustrates the acid-base balance of the inorganic ions in PM\(_{2.5}\) at the four sites. The ion balance expresses the equivalent concentration (\(\mu\text{eq} \text{m}^{-3}\)) of total inorganic anions (sum of NO\(_3^-\), SO\(_4^{2-}\), Cl\(^-\), F\(^-\)) to cations (sum of NH\(_4^+\), Ca\(^{2+}\), K\(^+\), Na\(^+\), and Mg\(^{2+}\)). The correlation coefficients for the anion versus cation concentration data stratified by season all were greater than 0.92 at all sites, suggesting a common origin of the ions in PM\(_{2.5}\). The slopes (anion/cation) of the linear regressions for all PM\(_{2.5}\) samples were equal to the theoretical

### Table 3  Average mass concentrations of PM\(_{2.5}\) species during the sampling period at the four sites

|                  | CAU Mean±SD | SZ Mean±SD | QZ Mean±SD | YC Mean±SD |
|------------------|-------------|------------|------------|------------|
| PM\(_{2.5}\) (\(\mu\text{g} \text{m}^{-3}\)) | 159.40±95.76 | 141.50±105.89 | 153.85±101.53 | 141.78±68.38 |
| NO\(_3^-\) (\(\mu\text{g} \text{m}^{-3}\)) | 19.23±18.98 | 16.26±19.28 | 16.01±15.95 | 18.09±15.13 |
| SO\(_4^{2-}\) (\(\mu\text{g} \text{m}^{-3}\)) | 18.61±17.92 | 15.21±14.80 | 20.08±16.06 | 24.52±14.66 |
| NH\(_4^+\) (\(\mu\text{g} \text{m}^{-3}\)) | 10.78±10.26 | 9.67±9.54 | 10.49±8.31 | 12.25±7.02 |
| Cl\(^-\) (\(\mu\text{g} \text{m}^{-3}\)) | 3.74±4.82 | 2.28±2.70 | 3.52±4.36 | 2.42±2.81 |
| Ca\(^{2+}\) (\(\mu\text{g} \text{m}^{-3}\)) | 2.64±1.98 | 1.82±1.72 | 1.60±1.59 | 1.25±1.06 |
| Na\(^+\) (\(\mu\text{g} \text{m}^{-3}\)) | 0.93±0.87 | 0.84±0.73 | 0.71±0.69 | 0.70±0.69 |
| K\(^+\) (\(\mu\text{g} \text{m}^{-3}\)) | 1.32±1.24 | 1.21±1.16 | 1.73±1.24 | 2.04±1.43 |
| Mg\(^{2+}\) (\(\mu\text{g} \text{m}^{-3}\)) | 0.32±0.27 | 0.26±0.18 | 0.23±0.23 | 0.24±0.26 |
| F\(^-\) (\(\mu\text{g} \text{m}^{-3}\)) | 0.26±0.26 | 0.18±0.19 | 0.21±0.24 | 0.27±0.26 |
| Sum of ionic species (\(\mu\text{g} \text{m}^{-3}\)) | 58.84±48.88 | 47.73±43.78 | 55.31±41.95 | 61.97±35.63 |
| Secondary inorganic aerosol (\(\mu\text{g} \text{m}^{-3}\)) | 48.6±44.99 | 41.2±40.88 | 46.6±37.2 | 54.9±33.1 |
| WSII (%)\(^a\) | 0.35±0.18 | 0.34±0.17 | 0.35±0.15 | 0.44±0.15 |
| SIA (%)\(^b\) | 0.29±0.17 | 0.29±0.16 | 0.30±0.14 | 0.39±0.15 |

\(^a\)Proportion of water-soluble inorganic ions in PM\(_{2.5}\)
\(^b\)Proportion of secondary inorganic ions in PM\(_{2.5}\)
et al. 2012; Tao et al. 2014), but acidic aerosol has also been widely observed in different areas worldwide (Shon et al. 2012), who suggested that seasonal variation in PM2.5 acidity (He et al. 2012). Fully neutralized aerosol have been widely observed in different areas worldwide (Shon et al. 2012; Tao et al. 2014), but acidic aerosol has also been reported by many previous studies (Wang et al. 2006; Zhang et al. 2011; He et al. 2012). The seasonal anion/cation ratios of PM2.5 observed at the four sites, i.e., the slopes of linear regressions for the seasonally stratified data, were found to vary moderately (Fig. 6). This characteristic is consistent with the findings of Shon et al. (2012), who suggested that seasonal variation in ratio of anion/cation was caused by unmeasured cations such as ferric and non-ferric components.

### Secondary inorganic aerosol

Ammonia in the atmosphere can react with H₂SO₄ to form ammonium sulfate ((NH₄)₂SO₄) and ammonium bisulfate (NH₄HSO₄) and react with HNO₃ and HCl to form ammonium nitrate (NH₄NO₃) and ammonium chloride (NH₄Cl) (Ianniello et al. 2010). These compounds are referred to as “secondary inorganic aerosol (SIA)” in this paper. The 4Pearson correlation coefficients between the molar concentrations of NO₃⁻, SO₄²⁻, and Cl⁻ in PM2.5 are presented in Table S5. At the four sites, the correlation coefficients (CCs) between NH₄⁺, SO₄²⁻, and NO₃⁻ were comparable, but both of them were higher than CCs between NH₄⁺ and Cl⁻. Moreover, the CCs between NH₄⁺ and the sum of NO₃⁻ and SO₄²⁻ at all sites (except SZ) were higher than those between NH₄⁺ and the sum of NO₃⁻, SO₄²⁻, and Cl⁻. These results mean NH₄⁺ was probably mainly combined with NO₃⁻ and SO₄²⁻. In order to further understand the neutralization processes between them, we calculated the molar concentrations of positive electric charges of NH₄⁺ (PEC=NH₄⁺/18) and negative electric charges of NO₃⁻ and SO₄²⁻ (NEC=NO₃⁻/96 × SO₄²⁻/96). If all sulfate was assumed to be in the form of HSO₄⁻, then NEC=(NO₃⁻/62+SO₄²⁻/96) (Louie et al. 2005; Zhao et al. 2013). The seasonal average PEC and NEC are shown in Fig. 7. At all sites, we found that NH₄⁺ was enough to match NO₃⁻ and SO₄²⁻ to form NH₄HSO₄ in all four seasons and not sufficient to meet the complete neutralization of SO₄²⁻ and NO₃⁻ for formation of (NH₄)₂SO₄ aerosol in most seasons. This indicates acid-rich conditions at the study sites. Interestingly, our findings at CAU differ from results for urban sites in Beijing and its surrounding provinces during 2009–2010 when NH₄⁺ concentrations were far from enough to match NO₃⁻ and SO₄²⁻ throughout the year (Zhao et al. 2013). We can infer the enhanced alkalization of the atmosphere in Beijing and/or its surrounding areas because the levels of NO₃⁻ and SO₄²⁻ were closely comparable between

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### Table

| Season | CAU | SZ | QZ | YC |
|--------|-----|----|----|----|
| Winter | 1.09 | 0.94 | 0.97 | 1.22 |
| Autumn | 0.94 | 1.14 | 0.93 | 1.22 |
| Summer | 0.83 | 1.17 | 0.98 | 1.22 |
| Spring | 1.04 | 1.23 | 1.02 | 1.16 |

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### Figures

- **Fig. 6** The molar inorganic ion balance in PM₂.₅ at the four sites: a CAU, b SZ, c QZ, and d YC.
the two studies. The average molar ratio of \( \text{NH}_4^+ \) to \( \text{SO}_4^{2-} \) were 3.07±2.08 at CAU, 3.96±2.53 at SZ, 2.84±1.23 at QZ, and 2.85±0.97 at YC, suggesting the main form of \((\text{NH}_4\text{)}_2\text{SO}_4\). According to Guo et al. (2014), reductions in emissions of the aerosol precursor gases from transportation and industry are essential to mediate severe haze pollution in China. Based on our findings, we suggest that a feasible and ideal pathway to control PM\(_{2.5}\) pollution in the NCP should target ammonia and acid gases together.

The average SIA concentrations (the sum of \( \text{NO}_3^- \), \( \text{SO}_4^{2-} \), and \( \text{NH}_4^+ \)) were 48.6±44.9, 41.2±40.8, 46.6±37.2, and 54.9±33.1 \( \mu \text{g m}^{-3} \) at CAU, SZ, QZ, and YC, respectively (Table 3). All averages exceeded the Chinese ambient air quality standard for annual average value of PM\(_{2.5}\) (grade II, 35 \( \mu \text{g m}^{-3} \) (MEPC 2012), suggesting serious SIA pollution at all sites. The SIA concentrations in the present study were much higher than those reported in many European countries, the USA, and other developed countries (Shen et al. 2013), as well as many other cities in China (Zhang et al. 2011a). SIA concentrations at CAU were comparable to values in urban Beijing reported by a recent study (Zhao et al. 2013) but were obviously higher than 2001–2003 observations at five urban sites in Beijing (average 35.9 \( \mu \text{g m}^{-3} \), Wang et al. 2005). This reflects enhanced emissions of the gaseous precursors (i.e., \( \text{NH}_3 \), \( \text{SO}_2 \), and \( \text{NO}_x \)) as a result of substantial increase in vehicle traffic, coal consumption, etc.

Seasonal concentrations of SIA at the four sites are shown in Fig. 8. At all sites except YC, the seasonal pattern of SIA is similar to that of PM\(_{2.5}\) (Fig. 5), consistent with the findings of Yin et al. (2014). The \( \text{SO}_4^{2-} \) concentrations at the urban and suburban sites (CAU and SZ) exhibited a consistent seasonal variation, with the order ranked by winter>spring>summer>autumn (Fig. 8). It should be noted that the average \( \text{SO}_4^{2-} \) concentration in winter (22.7 \( \mu \text{g m}^{-3} \)) at CAU was slightly higher than the concentration (19.1 \( \mu \text{g m}^{-3} \)) observed in Beijing for winter in 2009 (Zhao et al. 2013). The similar level of sulfate loading suggests that the effect of gas desulfurization in power plants might be greatly offset by the increasing coal consumption. In contrast, the seasonal \( \text{SO}_4^{2-} \) concentrations at the rural sites were ranked in different orders: spring, autumn>winter>summer at QZ and summer, winter>autumn>spring at YC. We observed relatively high \( \text{SO}_4^{2-} \) concentrations in summer at each site. However, \( \text{SO}_2 \) concentrations were usually lowest in summer (Table S6) not only because of lower coal combustion but also owing to the increased photochemical oxidation activity, which was one of the important factors for the enhanced sulfate level in summer (Husain and Dutkiewicz 1990). At all sites, \( \text{NO}_3^- \) concentrations were distinctly lower in summer than in the other three seasons (Fig. 8). Nitrate is more sensitive to temperature, and higher temperature in summer does not favor the formation of nitrate. Moreover, a large portion of ammonium nitrate \((\text{NH}_4\text{NO}_3)\) could evaporate from the filters, especially in...
summer (Ianniello et al. 2011). In contrast, low temperature and high emissions of NO\textsubscript{x} were favorable for formation of NO\textsubscript{3}\textsuperscript{−} aerosol and the reaction with NH\textsubscript{4}\textsuperscript{+} (Mariani and Mello 2007). As already discussed in “Seasonal variation of gaseous NH\textsubscript{3}, NO\textsubscript{2}, and HNO\textsubscript{3},” NO\textsubscript{3} emissions increase between mid-September and mid-March which, in combination with winter heating under relatively low temperature during that period (Fig. S1a), lead to high NO\textsubscript{3}− concentrations. NH\textsubscript{4}\textsuperscript{+} concentrations at the four sites were higher in autumn and winter than in spring and summer. The formation of NH\textsubscript{4}\textsuperscript{+} depends on air concentrations of acid gases, temperature, water availability (Khoder 2002), as well as flux rates of NH\textsubscript{3} (Nemitz et al. 2001). Compared with spring and summer, the lower temperature and higher SO\textsubscript{2} and NO\textsubscript{2} emissions in winter and autumn, especially in winter, favor the gas-to-particle phase conversion and result in higher NH\textsubscript{4}\textsuperscript{+} aerosol concentration. Previous studies also showed higher NH\textsubscript{4}\textsuperscript{+} in winter compared with higher NH\textsubscript{3} in summer (Shen et al. 2009; Zhang et al. 2011a; Li et al. 2012).

Summary and conclusions

This study provides insights into the characteristics of variations in atmospheric pollutants over three typical land-use types in the North China Plain during China’s 12th FYP (2011–2015) period, which targeted the reduction of national NO\textsubscript{x} emissions, as well as SO\textsubscript{2} and primary particles. The major results and conclusions are as follows:

1. Atmospheric NH\textsubscript{3} concentrations showed clear spatial variation among the five sites. However, it was found that the difference in annual NH\textsubscript{3} concentrations was not significant across all sites. High NH\textsubscript{3} concentration observed at the urban site was probably due to high emissions from biological sources (e.g., sewage systems and garbage containers) and vehicles in the urban area, as well as agricultural activity in the suburban area. Annual average NH\textsubscript{3} concentrations showed consistent increasing trends at the five sites, reflecting the elevated NH\textsubscript{3} emission intensities from transportation, agriculture, and livestock husbandry.

2. Annual average NO\textsubscript{2} concentrations exhibited obvious spatial difference, showing significantly higher concentrations at the urban site than at the suburban and rural sites. An overall decreasing trend of annual NO\textsubscript{2} concentrations was observed at all sites, likely related to implementation of the national controls on NO\textsubscript{x} emissions. All annual averages, however, exceeded (or were close to) the Chinese annual NO\textsubscript{2} exposure limit for humans, indicating serious atmospheric NO\textsubscript{2} pollution not only at the urban site but also at suburban and rural sites resulting from local emission sources and atmospheric transport.

3. Unlike for NH\textsubscript{3} and NO\textsubscript{2}, annual average HNO\textsubscript{3} concentrations were relatively low and showed small spatial and annual variations.

4. The PM\textsubscript{2.5} pollution was severe in the NCP, with more than 70% of sampling days across the sites exceeding the Chinese Grade II standard for daily PM\textsubscript{2.5} concentration. Ion balance calculations indicated that PM\textsubscript{2.5} was neutral at the urban and suburban sites and acidic at the rural sites.

5. NO\textsubscript{3}−, SO\textsubscript{4}\textsuperscript{2−}, and NH\textsubscript{4}\textsuperscript{+} were the dominant ionic particulate species at the four sites and accounted for 29–39% of the PM\textsubscript{2.5} mass. NH\textsubscript{4}\textsuperscript{+} was the dominant cation at all sites, whereas NO\textsubscript{3}− and SO\textsubscript{4}\textsuperscript{2−} were the dominant anions at the non-rural and rural sites, respectively. NH\textsubscript{4}\textsuperscript{+} was insufficient to fully neutralize SO\textsubscript{4}\textsuperscript{2−} and NO\textsubscript{3}− at all sites, indicating an acid-rich condition. The seasonal variation of SIA was similar to that of PM\textsubscript{2.5}, implying that a reduction of the concentrations of SIA is a feasible way to control PM\textsubscript{2.5} pollution in the NCP, by directly targeting ammonia or acid gases. Compared with observations of the three dominant ions in Beijing in previous studies, enhanced alkalinization of the atmosphere was found.

6. Similar seasonal variations were observed for concentrations of NH\textsubscript{3}, NO\textsubscript{2}, and aerosols NO\textsubscript{3}− and NH\textsubscript{4}\textsuperscript{+} over the three land-use types, whereas seasonal variation of PM\textsubscript{2.5} and HNO\textsubscript{3} concentrations showed different spatial characteristics. All above seasonal patterns were affected by meteorological condition and pollution sources.

Acknowledgments The study was supported by the China National Fund for Distinguished Young Scientists (Grant 40425007) and the innovative group grant of NSFC (Grant 31421092). We thank Ms. Lu Li and Zhao Jingxian for their help in collecting and analyzing samples.

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