Characteristics of atmospheric ammonia over Beijing, China

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Abstract. Continuous measurements of atmospheric ammonia (NH\textsubscript{3}) were conducted using Ogawa passive samplers from February 2008 to July 2010 at an urban site and from January 2007 to July 2010 at a rural site in Beijing, China. NH\textsubscript{3} in fine particles was also collected at the rural site during 2008–2009. The field comparison between the Ogawa passive samplers and an active analyzer for NH\textsubscript{3} conducted at the urban site assures the quality and accuracy of the measurements. The concentrations of NH\textsubscript{3} at the urban site ranged from 0.7 to 85.1 ppb, with the annual average of 18.5 \(\pm\) 4.6 ppb in 2008 and 2009, respectively. The NH\textsubscript{3} concentrations at the rural site were lower than those at urban site, and varied from 0.8 to 42.9 ppb, with the annual average of 4.5 \(\pm\) 4.6, 6.6 \(\pm\) 7.0 and 7.1 \(\pm\) 3.5 ppb in 2007, 2008 and 2009, respectively. The data showed marked seasonal variations at both sites. The results emphasized traffic to be a significant source of NH\textsubscript{3} concentrations in winter in urban areas of Beijing. This was illustrated by the strong correlations of NH\textsubscript{3} with the traffic related pollutants (NO\textsubscript{x} and CO) and also by the bi-modal diurnal cycle of NH\textsubscript{3} concentrations that was synchronized with traffic. Similar patterns were not observed during the summer, suggesting other non-traffic sources became more important. At the rural site, the daily NH\textsubscript{3} concentrations ranged from 0.10 to 36.53 \(\mu g\) m\textsuperscript{-3}, with an average of 7.03 \(\mu g\) m\textsuperscript{-3} from June 2008 to December 2009. Monthly NH\textsubscript{3} were significantly correlated with NH\textsubscript{4}\textsuperscript{+} concentrations. Average monthly NH\textsubscript{3}/NH\textsubscript{4}\textsuperscript{+} ratios varied from 0.13 to 2.28, with an average of 0.73. NH\textsubscript{4}\textsuperscript{+} in PM\textsubscript{2.5} was primarily associated with SO\textsubscript{4}\textsuperscript{2-} at the rural site.

1 Introduction

Atmospheric ammonia (NH\textsubscript{3}) is one of the primary air pollutants, influencing acidic deposition along with sulfur dioxide (SO\textsubscript{2}) and nitrogen oxides (NO\textsubscript{x}). NH\textsubscript{3} can react with acidic species to form ammonium sulfate [(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}], ammonium bisulfate (NH\textsubscript{4}HSO\textsubscript{4}), ammonium nitrate (NH\textsubscript{4}NO\textsubscript{3}), and ammonium chloride (NH\textsubscript{4}Cl), etc., or deposit onto the Earth’s surface. These NH\textsubscript{4}\textsuperscript{+} aerosols contribute significantly to fine particle mass (PM\textsubscript{2.5}) and have implications for human health (Brunekreef and Holgate, 2002). They limit atmospheric visibility and alter global radiation budgets (Clarisse et al., 2009; Horvath, 1992; Sutton et al., 1994).

Global ammonia emissions have more than doubled since pre-industrial times, largely owing to agricultural intensification and widespread fertilizer use (Galloway et al., 2003). Despite its ecological significance, there are large uncertainties in the magnitude of ammonia emissions, mainly owing to a paucity of ground-based observations and a virtual absence of atmospheric measurements (Asman et al., 1998; Galloway et al., 2008; Dentener et al., 1994; Bouwman et al., 1997, Matthews et al., 1994). Atmospheric NH\textsubscript{3} is emitted primarily from livestock wastes (39%), natural sources (19%), volatilization of NH\textsubscript{3}-based fertilizers (17%), biomass burning (13%), crops (7%) and emissions from humans, pets and waste water (5%) (Clarisse et al., 2009). Recent evidence suggests that people and traffic may have a greater impact in the non-agricultural regions, where ambient levels of ammonia were found to be higher in more densely populated areas (Suh et al., 1995).

There have been a number of studies of NH\textsubscript{3} levels reported from various remote, rural, urban and suburban sites in the world (Galloway et al., 1987; Khemani et al., 1987; Kulshrestha et al., 1996; Lenhard and Gravenhorst, 1980;
Likens et al., 1987; Possanzini et al., 1988; Tuncel and Ungor, 1996; Chou and Wang, 2007). Clarisse et al. (2009) have retrieved the infrared spectra obtained by the IASI/MetOp satellite to map global ammonia concentrations from space in 2008. They have identified several ammonia hotspots with column above 0.5 mg m\(^{-2}\) in middle-low latitudes across the globe.

Few studies on ammonia emissions in China are available. Along with the rapid growth of the economy in China, the total NH\(_3\) emission in 2000 was estimated to be 13.6 Tg, of which 50% comes from fertilizer application and another 38% from the other agricultural sources (Streets et al., 2003). In spite of this, measurements of NH\(_3\) in China are currently sparse. Meng et al. (2010) carried out atmospheric NH\(_3\) measurements in ten background or rural sites in China during 2007–2008 and found that the spatial variability of the NH\(_3\) concentration was large in China, with higher levels in North, Southwest and East China. Cao et al. (2009) reported the variation of ammonia concentrations in Xi’an. It was found that the average concentrations of NH\(_3\) were 18.5 and 20.2 ppb at the urban and suburban sites in Xi’an from April 2006 to April 2007.

Beijing with 19.61 million inhabitants in 2010 is one of megalaticies in the world (Beijing Municipal Bureau of Statistics, http://www.bjstats.gov.cn). Very rapid economic growth and the urbanization aggravate air pollution problems in Beijing and present a great challenge for both scientific research and management of urban and regional air quality. Yao et al. (2003) measured NH\(_3\) concentrations in Beijing in summer 2001 and spring 2002, with the concentrations in the range of 6.6–60.9 ppb. Wu et al. (2009) reported the measurement of acidic gases and ammonia during the summers of 2002 and 2003 at a site in Beijing. Recently, measurements of ammonia were conducted in winter and summer of 2007 at an urban site in Beijing and the daily average NH\(_3\) concentrations were in the range of 0.3–63.7 ppb (Ianniello et al., 2010). However, these studies were of short duration. There have been no long-term observations of NH\(_3\) in Beijing. In this paper, we present for the first time NH\(_3\) measurements from February 2008 to July 2010 at an urban site and from January 2007 to July 2010 at a rural site in Beijing, China, characterizing the levels and variations of ammonia in urban and rural areas over Beijing. In addition, we investigate the impact of surface wind and long-range transport on the NH\(_3\) concentrations and the contribution of traffic to ammonia levels in the urban area.

2 Description of experiment

2.1 Measurement sites

Measurements were conducted at an urban site and a rural site in Beijing. The field descriptions are as follows and the location of the sites are shown in Fig. 1, with the emission data of NH\(_3\) for the year 2000 from Streets et al. (2003). The urban site is located in the courtyard of China Meteorological Administration (CMA, 39°56’N, 116°24’E, 50 m a.s.l.) which is situated in the northwestern urban area of Beijing. Passive samplers were installed on the rooftop of the Chinese Academy of Meteorological Sciences (CAMS) building.

The rural site, Shangdianzi (SDZ, 40°39’N, 117°07’E, 293.3 m a.s.l.), is located to the northeast of Beijing, about 150 km away from the urban center of Beijing. About 55 km southwest of SDZ is the nearest township, Miyun town with a population of about 0.46 million. SDZ is also one of the WMO/GAW regional background stations in China. The site is on the gentle slope of a small hill. The geography surrounding the station is characterized by rolling hills with farmland, orchard and forests. On the foot of the hill about 2 km south is the Shangdianzi village with about 1200 inhabitants. The main agricultural products include corn, setaria italicata, vegetables and fruit. Ammonium dibasic phosphate and urea are used as fertilizers in the region.

2.2 Sampling and analysis

Ammonia samples were collected using Ogawa passive samplers (Ogawa USA, Pompano Beach, Florida). The Ogawa sampler, with two reactive glass-filters impregnated with citric acid, was used to trap and determine ambient NH\(_3\) concentrations. At CMA, the sampler was prepared in the laboratory and exposed about 7 days on top of the CAMS building from February 2008 to July 2010. The laboratory blank remained frozen in a refrigerator in the laboratory until analyzed. The prepared samplers were sealed in individual air-tight storage vials in the laboratory and shipped in a cooling box to SDZ site. The samplers were deployed by trained SDZ station operators in the thermometer screen (1.5 m above the ground), which protects the samplers from rain and direct sunshine. At SDZ, each sampler was exposed about 10 days and samples were collected once per month from January 2007 to August 2009 and three times per month from September 2009 to July 2010. A total of 219 samples were collected at both sites. Field blank measurements were made each month at the SDZ site. The field blank was a loaded sampler taken to and from the field with the other samplers but never removed from its air-tight vial. Both the laboratory and field blanks were prepared and processed at the same time and in the same way as the deployed samplers to determine if contamination occurred during the sampler loading, transport, or analysis.

The concentrations of NH\(_3\) were measured in parallel by a NO\(_x\)/NH\(_3\) analyzer (EC9842, Ecotech, Australia) for inter-comparison with passive sampler from June 2009 to May 2010 at the top of the CMA Training Center building (50 m), 200 m away from the CAMS building. Trace gases (such as NO\(_x\) and CO) were simultaneously determined by a chemiluminescence analyzer (TEI, model 42CTL) for NO\(_x\) and a
gas filter correlation analyzer (TEI, model 48C) for CO on top of the CMA Training Center building.

Daily aerosol PM$_{2.5}$ samples were collected using the MiniVol portable sampler (Airmetrics, Oregon, USA) operating at flow rates of 5 L min$^{-1}$ from June 2008 to December 2009 at SDZ. PM$_{2.5}$ samples were collected on 47 mm Whatman quartz microfiber filters (QM/A).

In the laboratory, samples were analyzed following the manufacturer’s protocols (Ogawa, http://www.ogawausa.com). The two filters of sample can be analyzed independently for the purpose of replication, but in this study both were combined for a single analysis. The mass transfer coefficient at 25 °C is 15.5 cm$^3$ min$^{-1}$ for each filter sampler, and is 31.1 cm$^3$ min$^{-1}$ for both filters. The NH$_3$ collection filters were put into 25-ml glass vials containing 8 ml ultrapure water for 30 min with occasional shaking. The ammonium extract was analyzed using Dionex ICS-3000 Ion Chromatography ( Dionex, USA) with a CG12A 4 mm guard column and a CS12A 4 mm analytical column. The CSRS (cation self-regenerating suppressor) was set at 50 mV. The detector used was a CD conductivity detector. The eluent was methanesulfonic acid (MSA).

PM$_{2.5}$ filters were extracted with ultrapure water. The concentrations of NH$_4^+$, NO$_3^-$, SO$_4^{2-}$ and Cl$^-$ in PM$_{2.5}$ were also determined by using Dionex ICS-3000.

2.3 Quality control and inter-comparison for passive samplers

To prevent the collection filters from deterioration, measures were taken to reduce the time in which the collection filters or the loaded samplers were exposed to warmer conditions. All collection filters were sealed and stored in the refrigerator before being loaded into the samplers. The sampler components, airtight vials, and glassware were cleaned using ultrapure water before reuse. Clean dispensable polyethylene gloves were used to avoid bare hand contact with sampling components. The samplers were assembled and disassembled in a clean laboratory room using clean forceps. Samplers were transported to and from the field in an ice box. Upon retrieval, the exposed samplers were frozen until analysis. The concentrations of NH$_3$ were corrected using field blanks.

For continuous active analyzers (such as NH$_3$, NO$_x$ and CO analyzers), zero and span checks were done every week to check for possible analyzer malfunction and zero drifts. The multi-point calibrations were performed at approximately 1-month interval.

The comparison between the Ogawa passive samplers and a continuous active NH$_3$ analyzer (EC9842, Australia) was carried out at CMA from June 2009 to May 2010. The average NH$_3$ concentrations measured by EC9842 were averaged over the same time period as the passive samplings. Figure 2 presents the comparisons of NH$_3$ concentrations measured by passive samplers and the active monitor. The 2-sided linear regression (reduced major axis technique) is performed for the regression statistics. As shown in Fig. 2, the observed results showed a good very significant correlation ($N = 42$, slope = 1.21, $R = 0.77$, $P < 0.0001$) between the two measurement methods. The low cost in long-term observations, low operating requirements and good agreement with active sampling techniques indicate that the Ogawa passive sampler is an excellent alternative to the other methods for determining NH$_3$ and could find wide application in environmental monitoring studies.

The quality not only depends on the sampler, but also on the analysis and the evaluation of results. The coefficient of variation is a statistical measure of precision based on the difference between duplicate samples. In this study, the coefficients of variation (COV) are defined as the median relative standard deviation, assuming a normal distribution of the deviation between parallel samples. The coefficients of variation of all duplicates were 9.9 % and 6.5 % for urban and rural site, which is acceptable for indicative monitoring.

3 Results and discussion

3.1 Overall results

3.1.1 Concentration levels and comparison with other areas

The statistics of concentrations of NH$_3$ during the sampling period at the two observation sites in Beijing are listed in the Table 1. It is obvious that ammonia concentrations varied greatly between two sites. The concentrations of NH$_3$ at CMA ranged from 0.7 to 85.1 ppb, with the annual average concentrations and one standard deviation of 18.5 ± 13.8 ppb in 2008 and 23.5 ± 18.0 ppb in 2009. The NH$_3$ concentrations at SDZ were lower than those at urban site and varied...
Table 1. Annual summary statistics of weekly and monthly average concentration of NH$_3$ at urban and rural site in Beijing, in ppb.

<table>
<thead>
<tr>
<th>Site</th>
<th>Period</th>
<th>Mean</th>
<th>Standard Deviation</th>
<th>Minimum</th>
<th>25th percentile</th>
<th>75th percentile</th>
<th>Median</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban Site</td>
<td>2008.02–2008.12</td>
<td>18.5</td>
<td>13.8</td>
<td>4.0</td>
<td>8.1</td>
<td>21.8</td>
<td>15.3</td>
<td>56.6</td>
</tr>
<tr>
<td>(CMA)</td>
<td>2009.01–2009.12</td>
<td>23.5</td>
<td>18.0</td>
<td>0.7</td>
<td>15.3</td>
<td>30.5</td>
<td>19.5</td>
<td>85.1</td>
</tr>
<tr>
<td></td>
<td>2010.01–2010.07</td>
<td>26.9</td>
<td>15.7</td>
<td>10.9</td>
<td>15.5</td>
<td>33.5</td>
<td>21.0</td>
<td>70.4</td>
</tr>
<tr>
<td>Rural Site</td>
<td>2007.01–2007.12</td>
<td>4.5</td>
<td>4.6</td>
<td>1.2</td>
<td>1.5</td>
<td>5.5</td>
<td>2.4</td>
<td>16.2</td>
</tr>
<tr>
<td>(SDZ)</td>
<td>2008.01–2008.12</td>
<td>6.6</td>
<td>7.0</td>
<td>0.8</td>
<td>2.1</td>
<td>7.0</td>
<td>4.5</td>
<td>21.6</td>
</tr>
<tr>
<td></td>
<td>2009.01–2009.12</td>
<td>7.1</td>
<td>3.5</td>
<td>2.6</td>
<td>4.4</td>
<td>9.0</td>
<td>6.3</td>
<td>13.8</td>
</tr>
<tr>
<td></td>
<td>2010.01–2010.07</td>
<td>14.2</td>
<td>10.8</td>
<td>2.6</td>
<td>6.3</td>
<td>18.6</td>
<td>11.5</td>
<td>42.9</td>
</tr>
</tbody>
</table>

The NH$_3$ level at CMA in Beijing was also higher than that reported in Rome, Italy, and at the urban site in Croatia near the North Adriatic. NH$_3$ level at Beijing was 2–5 times higher than that reported at New York, USA, Clinton, Kinston, Morehead City of North Carolina, USA and Hong Kong. The NH$_3$ level at CMA in Beijing was lower than that reported in Lahore, Pakistan. NH$_3$ concentrations at SDZ in Beijing were lower than those at the suburban site in Croatia near the North Adriatic.

The above comparisons suggested that there exist complex NH$_3$ patterns in the Beijing region. More research efforts are needed to quantify the contribution of local versus regional sources to the atmospheric ammonia variations in Beijing.

3.1.2 Temporal variations

Figure 3 shows the temporal variation of NH$_3$, temperature and wind speed at the two observation sites. NH$_3$ exhibited a distinct and significant temporal variation with higher concentrations in summer than in other season, especially in winter at both sites. At CMA, NH$_3$ increased gradually from April and reached the highest values on July, and then decreased until the following March. NH$_3$ values had a small peak in April as the temperature increase suddenly caused the accumulated emission of NH$_3$ from natural and fertilized soils, vegetation, and human sources in the city centre in winter. The peak NH$_3$ value was 85.1 ppb on 20–24 July 2009 and the lowest concentrations of NH$_3$ (0.7 ppb) appeared on 18–24 February 2009 for over two-year period 2008–2010 (Fig. 3a). The annual average temperatures were 14.0 °C, 14.1 °C and 14.4 °C in 2007, 2008 and 2009, respectively, with the highest monthly temperature (28.6 °C) in July of 2010 and the lowest temperature (−3.5 °C) in January of 2010 at CMA (Fig. 3b). The maximum value of NH$_3$ concentration is consistent with the highest ambient temperature in July. The lowest NH$_3$ value was in February 2009 which might be attributable to the cold temperatures, moderate snowfall and less human activity because lots of mobile population moving back to their hometowns during the Chinese Spring Festival.
Table 2. Comparison of NH₃ concentrations in Beijing with other areas, in ppb.

<table>
<thead>
<tr>
<th>Location</th>
<th>Type</th>
<th>Period</th>
<th>Concentration</th>
<th>measurement techniques</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China</td>
<td>Urban</td>
<td>2008.02–2010.07</td>
<td>22.8 ± 16.3</td>
<td>Passive sampler</td>
<td>This study</td>
</tr>
<tr>
<td></td>
<td>Rural</td>
<td>2007.01–2010.07</td>
<td>10.2 ± 10.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Urban</td>
<td>28 July–3 August 2001</td>
<td>16.8–42.2</td>
<td>Annular denuder</td>
<td>Yao et al. (2003)</td>
</tr>
<tr>
<td>Beijing, China</td>
<td>Rural</td>
<td>Winter and Summer 2007</td>
<td>0.29–63.8</td>
<td>Annular denuder</td>
<td>Ianniello et al. (2010)</td>
</tr>
<tr>
<td>Xi’an, China</td>
<td>Suburban</td>
<td>2006.04–2007.04</td>
<td>18.6</td>
<td>Passive sampler</td>
<td>Cao et al. (2009)</td>
</tr>
<tr>
<td>Rome, Italy</td>
<td>Urban</td>
<td>2001.05–2002.03</td>
<td>5.5–65.6</td>
<td>Annular denuder</td>
<td>Perrino et al. (2002)</td>
</tr>
<tr>
<td>Kinmont, Carolina, USA</td>
<td>Urban</td>
<td>2000.05–2000.12</td>
<td>3.5</td>
<td>Annular denuder</td>
<td></td>
</tr>
<tr>
<td>Morehead, Carolina, USA</td>
<td>Urban</td>
<td>2000.01–2000.12</td>
<td>0.8</td>
<td>Annular denuder</td>
<td></td>
</tr>
<tr>
<td>Hong Kong</td>
<td>Urban</td>
<td>Autumn 2000</td>
<td>3.0</td>
<td>Autoanalyser</td>
<td>Yao et al. (2006)</td>
</tr>
</tbody>
</table>

Fig. 3. Temporal variations of NH₃, temperature (T), wind speed (WS), rainfall (RF) and relative humidity (RH) at CMA and SDZ sites in Beijing during 2007–2010.

At SDZ, the peak NH₃ value was 42.9 ppb on 11–21 July 2010 and the lowest concentrations of NH₃ (0.8 ppb) appeared on 19–29 December 2008 from January 2007 to July 2010. The annual average temperatures at SDZ site were 11.3 °C, 10.7 °C and 10.9 °C in 2007, 2008 and 2009, respectively, with the highest monthly temperature (27.7 °C) in July of 2010 and the lowest temperature (−8.4 °C) in January of 2010. In summer, high temperatures will favor ammonia volatilization from urea and ammonium dibasic phosphate applied to crops.

NH₃ and air temperature were found to be significantly correlated ($R = 0.47$ for CMA and $R = 0.62$ for SDZ). This phenomenon showed that the air temperature was one of the key parameters determining ammonia concentration in Beijing, especially at SDZ, because agriculture is the main source of NH₃ in this rural area. A positive correlation of NH₃ with temperature may be attributable to an increase in NH₃ sources via enhanced volatilization of NH₃ and/or decreased stability of the NH₄NO₃ aerosol. Various studies have shown strong correlations between air temperature and ammonia concentration, suggesting that temperature is an important variable in influencing NH₃ volatilization from fertilizer and animal waste (Aneja et al., 2000; Zhang et al., 2010).
In CMA, the highest annual rainfall (626.0 mm) was found in 2008 during observation period (Fig. 3c). In 2008, the monthly rainfalls were 125.3, 79.3 and 132.1 mm in June, July and August, respectively. NH$_3$ concentrations were 17.9, 26.5 and 19.9 ppb in June, July and August of 2008, respectively. Much lower NH$_3$ concentrations were observed (7.4 and 9.7 ppb, respectively) on 2–10 June 2008 and 1–8 June 2009, those were rainy days. The highest annual rainfall (633.9 mm) was also found in 2008 in SDZ during the observation period (Fig. 3d). In 2008, the monthly rainfalls were 104.7, 77.8 and 223.7 mm in June, July and August, respectively. NH$_3$ concentrations were 19.6, 21.6 and 5.2 ppb in June, July and August of 2008, respectively. The lower NH$_3$ levels were consistent with the heavier rain in summer months, reflecting the important role wet removal plays in influencing the temporal variation in ambient NH$_3$ levels.

3.2 Seasonal variations

The seasonal concentration of ammonia is dependent on its source and meteorological conditions. Figure 4 displays the monthly statistics of NH$_3$ concentrations observed at both sites. NH$_3$ values were higher in April, especially at CMA, with the rapidly increase of air temperature after winter. The NH$_3$ emission from natural and fertilized soils, city garbage, and vegetation may be greatly enhanced by the abrupt increase of temperature as the end of winter time. The highest monthly mean NH$_3$ concentration was 48.9 ppb in July and the lowest one was 6.4 ppb in February at CMA. Seasonal average concentrations of NH$_3$ at CMA were 21.6 ± 9.9, 33.5 ± 15.5, 16.6 ± 8.5 and 10.3 ± 5.2 ppb in spring, summer, autumn and winter, respectively. The NH$_3$ mean concentrations ratio of summer to winter was 3.2.

As can be seen in Fig. 4, the peak monthly NH$_3$ level was 20.6 ppb in July, which was approximately 8 times higher than that (2.6 ppb) in December at SDZ. Seasonal average concentrations of NH$_3$ at SDZ were 6.9 ± 4.9, 16.3 ± 8.8, 3.7 ± 3.0 and 3.3 ± 2.0 ppb in spring, summer, autumn and winter, respectively. The summer to winter ratio for NH$_3$ concentrations was 4.9 at SDZ. The highly amplified seasonality at SDZ may result primarily from increased emission rates of local agricultural NH$_3$ sources during summer.

The ratio of summer to winter mean concentrations at CMA was lower than that at SDZ, which was consistent with the pattern observed by Walker et al. (2004) at non-agricultural city site. Higher NH$_3$ volatility from city garbage and animal husbandry activities can also increase ambient NH$_3$ concentrations during the summer months. Low NH$_3$ concentrations in winter were attributed to reduced NH$_3$ volatilization when the air temperature was frequently below freezing and there were snows.

Figure 5 shows the wind roses of hourly average NH$_3$ concentrations, wind direction frequencies and wind speeds in different seasons at CMA and SDZ. As shown in Fig. 5b, the dominant winds are from NNE-NE sectors and SE-SSE-S sectors. The highest and lowest average winds speeds occur under the WNW and WSW sectors, respectively (Fig. 5c). The concentrations of NH$_3$ in different seasons show similar patterns, with the highest values in summer (Fig. 5a). The higher NH$_3$ values were in northeast to southwest sectors and lower values in northwest to north sectors of the urban site. In summer, the average NH$_3$ concentrations in the NNE, NE, ENE, and E sectors were 42.3, 41.9, 39.1, and 40.2 ppb, respectively. They are about 10 ppb higher than that in W-N sectors, in which the wind speeds are much stronger. When winds come from northeast direction, the emissions of NH$_3$ from the agricultural areas such as Shunyi district which is located in the suburb northeast of the CMA site might contribute higher levels of NH$_3$. The higher average NH$_3$ concentrations in W and WSW sectors might be attributed to transport of industrial emission from Shijingshan district.

Since NH$_3$ is either readily converted to NH$_4^+$ or subjected to dry deposition, high concentrations are found only close to the surface and near to emission sources. Thus, NH$_3$ concentrations might be generally lower at higher wind speeds because of turbulent diffusion. The wind speeds were high more than 5 m s$^{-1}$ during spring and winter, with the higher values in summer and autumn in NW-WNW sectors (Fig. 5c). As can be seen in Fig. 5a, the lowest concentrations in four seasons were in these sectors. Previous studies have reported an inverse relationship between ground-level concentrations of trace gases, such as ammonia, and wind speed (Robarge et al., 2002; Lin et al., 2011).

At SDZ, the prevailing winds are northeasterly in autumn and winter and southwesterly in spring and summer (Fig. 5d). The wind direction distribution at SDZ is typical of the larger-scale situation in the North China Plain. Therefore, polluted air masses from urban areas and even those regions in south of Beijing at North China Plain, can be easily transported to SDZ under southwesterly winds, while relatively clean air masses are transported to the site with winds from other directions (Lin et al., 2008).
The NH$_3$ concentrations at CMA were highly correlated with those at SDZ ($R = 0.71$, $P < 0.0001$). The high correlation of NH$_3$ at two typical sites may point to that NH$_3$ at both sites are affected by similar synoptic conditions.

### 3.3 The impact of long-range air transport on the surface NH$_3$ levels

While the wind roses provide insight into the distribution of local emission sources around the monitoring site, trajectory analysis are further used to identify the impact of long-range air transport on the surface air pollutants levels (Meng et al., 2007, 2009). The 72-h backward trajectories were calculated using the HYSPLIT 4.9 model (http://www.arl.noaa.gov/ready/hysplit4.html). The trajectory calculations were done for four times of each day from July 2009 to June 2010, with the four time points of 00:00, 06:00, 12:00, and 18:00 UTC, respectively. The various back trajectories were grouped into 6 clusters. As can be seen in Fig. 6, Clusters 1, 2 and 5 represent relatively low and slow moving air parcels, with cluster 2 coming from southeast areas at the lowest transport height among the 6 clusters. The other three clusters represent air parcels mainly from the northwest. These clusters of trajectories originated from clean regions and travelled quickly from higher atmosphere to Beijing, which is expected to bring cleaner air masses into surface. The cluster 2 from the North China Plain region was most important for the Beijing urban site, contributing 33% of air masses.

To know the seasonal variations in the trajectories, the occurrence frequencies of each type of air masses arriving at CMA in different seasons were calculated and are shown in Table 3. The corresponding mean concentrations of NH$_3$ in different clusters of backward trajectories are also included in Table 3 in order to characterize the dependences of the pollutants concentrations on air masses. Based on this table, much more trajectories in cluster 2 occurred in summer months, more trajectories in cluster 6 occurred in winter, and more trajectories in cluster 1 occurs in spring.

Large differences in the concentrations of NH$_3$ exist among the different clusters, with cluster 2 corresponding to the highest NH$_3$ levels (25.7 ppb), and cluster 5 corresponding to the second highest NH$_3$ levels (24.4 ppb). These two types of trajectories have the shortest transport distances and lowest transport heights, which help the accumulation of NH$_3$. In addition, the different source areas as the different types of trajectories originated or passed over will also give different contributions to surface levels of NH$_3$.

A detailed estimate of NH$_3$ emission in Beijing and the surrounding areas in 2005, carried out by Ianniello et al. (2010), has shown that the largest sector contributor to NH$_3$ emissions in the North China Plain (NCP) is agriculture, while mineral fertilizer use contributing 54% to the total NH$_3$ emission, and livestock sources contributing the remaining 46% in the NCP. Of the total agricultural ammonia emissions in the NCP, the Hebei, Henan and Shandong provinces take the larger part (Zhang et al., 2010).
Contributions of NH$_3$ emissions from livestock and fertilizer activities were also found in Inner Mongolia (Klimont, 2001; Ju et al., 2004).

Since cluster 2 represents air masses originating from NCP, it is not surprising that the highest NH$_3$ levels were observed in this cluster of air mass trajectories. Air masses in cluster 5 traveled over China’s key coal mining and power generation regions in Inner Mongolia, Shanxi Province, and Hebei Province (e.g., Datong, Zhangjiakou, etc.). This explains the second highest NH$_3$ levels corresponding to cluster 5. The cluster 1 has the third highest concentration of NH$_3$. The data in Table 3 suggest that the NH$_3$ concentrations corresponding to clusters 3, 4 and 6 are low. This is attributable to the less polluted air over the northwest sector and the higher traveling heights and speeds of air mass with good atmospheric mixing and dilution.

Overall, the air masses from the North China Plain region contain the highest concentration of NH$_3$, and the air masses traveling over the coal mining and power generation regions west of Beijing contain the second highest concentrations of ammonia. Therefore, transport of air masses from these regions is responsible for the high concentrations of NH$_3$ at urban site.

### 3.4 Relationship with NO$_x$ and CO in different seasons at urban site

Although agriculture is the main source of atmospheric ammonia for the whole Beijing area, the contribution of vehicles equipped with catalytic converters, especially since the introduction of three-way-catalysts, to non-agricultural NH$_3$ emissions has recently been considered and might be the most important factor influencing ammonia concentrations at urban locations and near roads (Sutton et al., 2000; Kean et al., 2000; Huai et al., 2005; Tanner, 2009; Heeb et al., 2008; Saylor et al., 2010). Since 2009 the total number of vehicles registered in Beijing city had increased to about 4.1 million and is still increasing by more than 10% per year (Wang et al., 2010). Therefore, in order to examine the contribution of traffic to NH$_3$ concentrations, it may be useful to compare the ammonia concentrations with those of primary pollutants mainly emitted by motor-vehicle exhausts, such as nitrogen oxides (NO$_x$) and carbon monoxide (CO). Hao et al. (2005) estimated that the emissions in Beijing from vehicles, power plants, and industries in 1999 accounted for 35%, 27% and 26% in the total local NO$_x$ emissions, respectively.

The scatter plots of the hourly concentration of NH$_3$ versus NO$_x$ and NH$_3$ versus CO obtained by continuous active analyzers at CMA from June 2009 to May 2010 are reported in Figs. 7 and 8. As the concentrations of NH$_3$, NO$_x$ and CO are independently measured, an alternative 2-sided linear regression (reduced major axis technique) is performed for the regression statistics. To do this, the errors come from all the variables (NH$_3$, NO$_x$ and CO) are considered. The slope value of 0.84 of NH$_3$/NO$_x$ in summer indicates the comparable levels of NH$_3$ with NO$_x$ (Fig. 7). In autumn and winter, the levels of NH$_3$ are about one third of the levels of NO$_x$. The intercepts ([NO$_x$] = 0; [CO] = 0) tell us the regional background of NH$_3$ (sources different with NO$_x$) in spring, summer, and autumn were within 4–14 ppb with the maximum one in summer. The regional background of NH$_3$ in winter was less than 1 ppb which also indicates the similar source between NO$_x$, CO and NH$_3$ in winter Beijing.

The correlation coefficients ($R$) of NH$_3$ versus NO$_x$ were 0.32, 0.15, 0.29 and 0.78 in spring, summer, autumn and winter, respectively. The correlation coefficients ($R$) of NH$_3$ versus CO were 0.45, 0.32, 0.37 and 0.71 in spring, summer, autumn and winter, respectively. The correlations are all in a very significant level ($P < 0.001$).

It was noted that the correlations of NH$_3$ versus NO$_x$ and NH$_3$ versus CO are the best in winter and poorest in summer, which implies that the variations of these species in winter and summer are driven by different dominant processes. The positive linear relationship observed between NH$_3$ versus NO$_x$ and NH$_3$ versus CO in winter emphasized that traffic is a significant source of ammonia in urban areas of Beijing. However, in other seasons, especially in summer, the correlation of NH$_3$ versus NO$_x$ and NH$_3$ versus CO, suggesting that other, non-traffic sources became more important. The higher temperatures in summer will increase emission from biological sources in the city such as humans, sewage treatment and landfill. The volatilization of NH$_3$ from the aerosol phase may be significant enough to dominate over traffic emissions during summer in Beijing. In addition, as

### Table 3. Occurrence frequency and mean values of NH$_3$ for each type of air masses arriving at CMA during July 2009 to June 2010.

<table>
<thead>
<tr>
<th>Air mass</th>
<th>Spring</th>
<th>Summer</th>
<th>Autumn</th>
<th>Winter</th>
<th>Ratio</th>
<th>Height (m)</th>
<th>NH$_3$ (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cluster 1</td>
<td>92</td>
<td>49</td>
<td>56</td>
<td>66</td>
<td>18%</td>
<td>722</td>
<td>18.1</td>
</tr>
<tr>
<td>Cluster 2</td>
<td>105</td>
<td>268</td>
<td>81</td>
<td>23</td>
<td>33%</td>
<td>100</td>
<td>25.7</td>
</tr>
<tr>
<td>Cluster 3</td>
<td>66</td>
<td>14</td>
<td>83</td>
<td>69</td>
<td>16%</td>
<td>1420</td>
<td>11.9</td>
</tr>
<tr>
<td>Cluster 4</td>
<td>37</td>
<td>11</td>
<td>54</td>
<td>63</td>
<td>11%</td>
<td>1260</td>
<td>16.3</td>
</tr>
<tr>
<td>Cluster 5</td>
<td>13</td>
<td>22</td>
<td>47</td>
<td>28</td>
<td>8%</td>
<td>629</td>
<td>24.4</td>
</tr>
<tr>
<td>Cluster 6</td>
<td>51</td>
<td>0</td>
<td>39</td>
<td>107</td>
<td>14%</td>
<td>1913</td>
<td>12.0</td>
</tr>
</tbody>
</table>
a site in urban city centre, other emission sources due to human activity, such as solvent use (Whitehead et al., 2007) and house concrete walls (Bai et al., 2006), can be also as NH$_3$ contributors.

### 3.5 Diurnal variations at urban site

The average diurnal variations of NH$_3$ in different seasons during June 2009 to May 2010 at CMA are shown in Fig. 9a. Ammonia gas showed a significant diurnal variation in summer. The concentration of NH$_3$ increased slightly, with a broad peak in the morning (between 07:00 and 11:00 Beijing Standard Time (BST)). The winter diurnal pattern of NH$_3$ is considerably different to that of summer. A bimodal diurnal cycle of NH$_3$ concentration was seen in winter, with higher values in the morning (18.9 ppb, 09:00 BST) and in the evening (22.4 ppb, 22:00 BST). There is no apparent difference between bimodal patterns of spring and autumn, with minima and maxima in the afternoon and evening, respectively. Higher concentrations at night in winter were likely the result of accumulation, stronger temperature inversion and low mixing depth.

As described above, the best relationships of NH$_3$ versus NO$_x$ and NH$_3$ versus CO correlations in winter indicated that these gases are mainly emitted from a predominant source in winter. Figure 9b compared diurnal variations of NH$_3$ with that of NO$_x$ and CO, the traffic related pollutants in winter. Figure 9b showed that NO$_x$ peaks during rush hour at 08:00 BST with 73.3 ppb, and then decreased with a minimum (47.8 ppb) at 15:00 BST. After 15:00 BST, NO$_x$ values began rising again as traffic volume picks up in late afternoon, leading to a second peak (78.3 ppb) at 22:00 BST. Similarly, CO values decreased gradually from early morning, but reached a higher value (1579 ppb) at 08:00 BST. After 16:00 BST, CO values began rising again with a highest
Ammonia is a very reactive gas, which plays a major role in the neutralization of atmospheric sulfuric and nitric acid to form ammonium salts. Particulate ammonium (NH₄⁺) has a longer atmospheric lifetime than NH₃ and can therefore be transported over relatively long distances. Deposition of NH₃ and NH₄⁺ to the Earth’s surface can fertilize nitrogen-limited ecosystems, and have detrimental effects such as eutrophication, soil acidification, and biodiversity loss in sensitive ecosystems (Ellis et al., 2010 and 2011; Galloway et al., 2003). To understand the transformation of NH₃ and NH₄⁺, the data of NH₃ and NH₄⁺ in PM_{2.5} were collected at SDZ. A total of 117 PM_{2.5} samples were analyzed for the period from June 2008 to December 2009.

The daily NH₄⁺ concentrations ranged from 0.10 to 36.53 µg m⁻³, with an average concentration of 7.03 µg m⁻³. Figure 10 illustrates the temporal variations of monthly concentrations for NH₃ and NH₄⁺ in PM_{2.5} at SDZ from June 2008 to December 2009. The peak NH₃ occurred during the morning rush hour similar to NOₓ and CO supports the hypothesis that the enhanced NH₃ level at this time was a direct contribution of the higher traffic volumes. No bimodal pattern is seen in summer, which implies that traffic is not the dominant source of NH₃. Greater emission from other sources combined with greater volatilization from the aerosol phase appeared to dominate (Whitehead et al., 2007).

3.6 Relationship between NH₃ and NH₄⁺ in PM_{2.5} at rural site

Figure 11 illustrates the temporal variations of monthly concentrations for NH₃ and NH₄⁺ in spring, summer, autumn and winter, respectively. The concentrations of NH₃ in spring, summer, autumn and winter, but higher than NH₄⁺ in summer. NH₃ concentrations were lower than NH₄⁺ in spring, autumn and winter, respectively. The summer to winter ratio for NH₄⁺ concentrations was approximately 2.0. NH₃ concentrations were lower than NH₄⁺ in spring, autumn and winter, and higher than NH₄⁺ in summer. NH₃ may undergo conversion to NH₄⁺ aerosol in the atmosphere, which depends on the concentration of acids in the atmosphere, temperature, and water availability (Kobara et al., 2007), as well as flux rates of NH₃ (Nemitz et al., 2001).

Monthly NH₃ concentrations were significantly correlated with NH₄⁺ concentrations (R = 0.64, P < 0.0001). Average monthly NH₃/NH₄⁺ ratios varied from 0.13 to 2.28, with an average of 0.73. The highest NH₃/NH₄⁺ ratio was found in June 2009, implying that abundant NH₃ gas existed in the atmosphere in summer. The lowest NH₃/NH₄⁺ ratio appeared in December 2008.

Table 4 summarizes the daily concentrations of inorganic ions in PM_{2.5} from June 2008 to December 2009. The average concentrations of SO₄²⁻, NO₃⁻ and Cl⁻ were 15.00, 11.57 and 1.33 µg m⁻³, respectively, and the total concentration of inorganic ions (NH₄⁺ + NO₃⁻ + SO₄²⁻ + Cl⁻) was 34.93 µg m⁻³.

With respect to percentage of the total mass, SO₄²⁻ was the most important species on average in PM_{2.5} at SDZ. Nitrate contributes more significantly to total mass during colder months when SO₂ oxidation rates are reduced in response to lower concentrations of oxidants such as OH. The average...
molar ratios of NH$_4^+$ to SO$_4^{2-}$, NO$_3^-$ to NH$_4^+$ and Cl$^-$ to NH$_4^+$ were 1.8, 0.5 and 0.1, respectively.

Figure 11a shows the relationship of the molar concentrations between [NH$_4^+$] and 2*[SO$_4^{2-}$] in different seasons. According the values of the different slopes, the lowest value of 1.18 is found in summer and the highest one of 1.71 is found in winter. The slope in spring is a little higher than that in summer and the slope in autumn is close to that in winter. In summer, the mean concentration of SO$_4^{2-}$ and NH$_4^+$ are the highest but the ratio of [NH$_4^+$]/(2*[SO$_4^{2-}$]) is the lowest among the 4 seasons. Figure 11b shows the relationship of the molar concentrations between [NH$_4^+$] with [NO$_3^-$] in different seasons. The highest slope of 3.50 is found in summer and the similar values among the other three seasons. In summer, the relationship of [NH$_4^+$] with [NO$_3^-$] is less strong than that of [NH$_4^+$] and 2*[SO$_4^{2-}$] and the mean concentration of [NO$_3^-$] is less than the mean concentration of 2*[SO$_4^{2-}$], which indicate most of NH$_4^+$ in aerosol in summer is present as (NH$_4$)$_2$SO$_4$. The considerable levels between [NO$_3^-$] and 2*[SO$_4^{2-}$] in winter and both strong correlations between [NH$_4^+$] with 2*[SO$_4^{2-}$] and [NH$_4^+$] with [NO$_3^-$] indicate the NH$_4^+$ in aerosol exists as (NH$_4$)$_2$SO$_4$ and NH$_3$NO$_3$.

4 Conclusions

The concentrations of NH$_3$ at Beijing urban site ranged from 0.7 to 85.1 ppb, with the annual average concentrations of 18.5 ± 13.8 ppb and 23.5 ± 18.0 ppb in 2008 and 2009, respectively. The NH$_3$ concentrations at the rural site in Beijing were lower than those at the urban site, and varied from 0.8 ppb to 42.9 ppb, with the annual average of 4.5 ± 4.6, 6.6 ± 7.0 and 7.1 ± 3.5 ppb in 2007, 2008 and 2009, respectively. NH$_3$ concentrations were the highest in summer at both sites, and the summer to winter concentration ratios were 3.2 and 4.9 at urban and rural site, respectively. The highly amplified seasonality at the rural site may be primarily from the increased emission rates of local agricultural NH$_3$ sources in summer.

The NH$_3$ wind roses show that the higher values were in northeast to southwest sectors and lower values in northwest to north sectors of the Beijing urban site. The back trajectory analysis indicates that the air masses from the North China Plain region contain the highest concentration of NH$_3$ and the air masses traveling over the coal mining and power generation regions west of Beijing contain the second highest concentrations of ammonia. Therefore, transport of air masses from these regions is responsible for the high concentrations of NH$_3$ at Beijing urban areas.

The measurements showed significant positive correlations between hourly concentrations of NH$_3$ with NO$_x$ and CO in winter in urban areas of Beijing. Since NO$_x$ and CO are primarily traffic related pollutants, this result points to traffic as a significant source of NH$_3$. The contribution from vehicles is further supported by the observation of a bimodal diurnal cycle of NH$_3$ in winter, with peaks occurring roughly at times of high traffic density.

The daily NH$_4^+$ concentrations ranged from 0.10 to 36.53 µg m$^{-3}$, with an average concentration of 7.03 µg m$^{-3}$ from June 2008 to December 2009 at the rural site. The average concentrations of NH$_4^+$ were 7.4 ± 4.7, 9.0 ± 9.3, 5.8 ± 7.5 and 4.7 ± 5.1 µg m$^{-3}$ in spring, summer, autumn and winter, respectively. Monthly NH$_3$ were significantly correlated with NH$_4^+$ concentrations. Average monthly NH$_3$/NH$_4^+$ ratios varied from 0.13 to 2.28, with an average of 0.73. The average concentrations of SO$_4^{2-}$, NO$_3^-$ and Cl$^-$ were 15.00, 11.57 and 1.33 µg m$^{-3}$, respectively, and the total concentration of inorganic ions (NH$_4^+$+NO$_3^-$+SO$_4^{2-}$+Cl$^-$) was 34.93 µg m$^{-3}$. In summer, most of NH$_4^+$ in PM$_{2.5}$ is present as (NH$_4$)$_2$SO$_4$.

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