

Characteristics of atmospheric ammonia over Beijing, China

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Abstract. Continuous measurements of atmospheric ammonia (NH_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_4^+ 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_3 conducted at the urban site assures the quality and accuracy of the measurements. The concentrations of NH_3 at the urban site ranged from 0.7 to 85.1 ppb, with the annual average of 18.5 ± 13.8 and 23.5 ± 18.0 ppb in 2008 and 2009, respectively. The NH_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 ± 4.6 , 6.6 ± 7.0 and 7.1 ± 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_3 concentrations in winter in urban areas of Beijing. This was illustrated by the strong correlations of NH_3 with the traffic related pollutants (NO_x and CO) and also by the bimodal diurnal cycle of NH_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_4^+ concentrations ranged from 0.10 to $36.53 \mu\text{g m}^{-3}$, with an average of $7.03 \mu\text{g m}^{-3}$ from June 2008 to December 2009. Monthly NH_3 were significantly correlated with NH_4^+ concentrations. Average monthly $\text{NH}_3/\text{NH}_4^+$ ratios varied from 0.13 to 2.28, with an average of 0.73. NH_4^+ in $\text{PM}_{2.5}$ was primarily associated with SO_4^{2-} at the rural site.

1 Introduction

Atmospheric ammonia (NH_3) is one of the primary air pollutants, influencing acidic deposition along with sulfur dioxide (SO_2) and nitrogen oxides (NO_x). NH_3 can react with acidic species to form ammonium sulfate $[(\text{NH}_4)_2\text{SO}_4]$, ammonium bisulfate (NH_4HSO_4), ammonium nitrate (NH_4NO_3), and ammonium chloride (NH_4Cl), etc., or deposit onto the Earth's surface. These NH_4^+ aerosols contribute significantly to fine particle mass ($\text{PM}_{2.5}$) 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_3 is emitted primarily from livestock wastes (39%), natural sources (19%), volatilization of NH_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_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;



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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 megacities 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, $39^\circ 56' \text{ N}$, $116^\circ 24' \text{ E}$, 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, $40^\circ 39' \text{ N}$, $117^\circ 07' \text{ E}$, 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 italica, 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 airtight 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

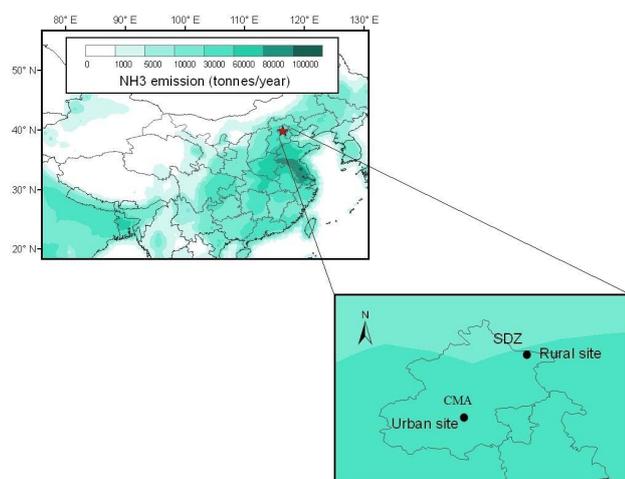


Fig. 1. The sampling locations in Beijing, China with emissions distributions reported by Streets et al. (2003).

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 $25\text{ }^{\circ}\text{C}$ is $15.5\text{ cm}^3\text{ min}^{-1}$ for each filter sampler, and is $31.1\text{ cm}^3\text{ min}^{-1}$ 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 glass ware were cleaned using ul-

tra pure 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

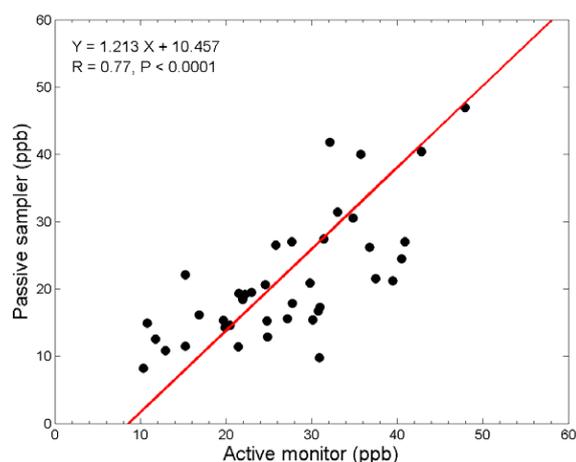
3.1 Overall results

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 NH₃ at urban and rural site in Beijing, in ppb.

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

**Fig. 2.** Comparison of results obtained with the Ogawa passive sampler and an active monitor at CMA from June 2009 to May 2010.

from 0.8 to 42.9 ppb, with the annual average concentrations of 4.5 ± 4.6 , 6.6 ± 7.0 and 7.1 ± 3.5 ppb in 2007, 2008 and 2009, respectively.

Table 2 lists NH₃ levels at different urban and suburban sites in the world. The average concentrations of NH₃ found at CMA in this study were higher than those obtained in 2001, 2002 and 2003 at Peking University site (PKU) in Beijing reported by Yao et al. (2003) and Wu et al. (2009), and were comparable to those reported by Ianniello et al. (2010) for winter and summer 2007 at PKU site. NH₃ concentrations at CMA are higher than the 2001–2003 PKU observations as a result of the substantial increase in vehicle traffic in urban centre of Beijing.

At SDZ, the values during 2007–2010 are obviously higher than that during 1999–2000 reported by Carmichael et al. (2003). Such differences may indicate an increase of NH₃ levels in North China Plain. As illustrated, the NH₃ level at urban site in Beijing was higher than that reported in Xi'an (18.6 ppb) (Cao et al., 2009), at same time, NH₃ concentrations at SDZ in Beijing was lower than those in Xi'an suburban site (20.3 ppb), which was consistent with the lower emission data in SDZ regional background station in China.

The NH₃ 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. NH₃ 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 NH₃ level at CMA in Beijing was lower than that reported in Lahore, Pakistan. NH₃ concentrations at SDZ in Beijing were lower than those at the suburban site in Croatia near the North Adriatic.

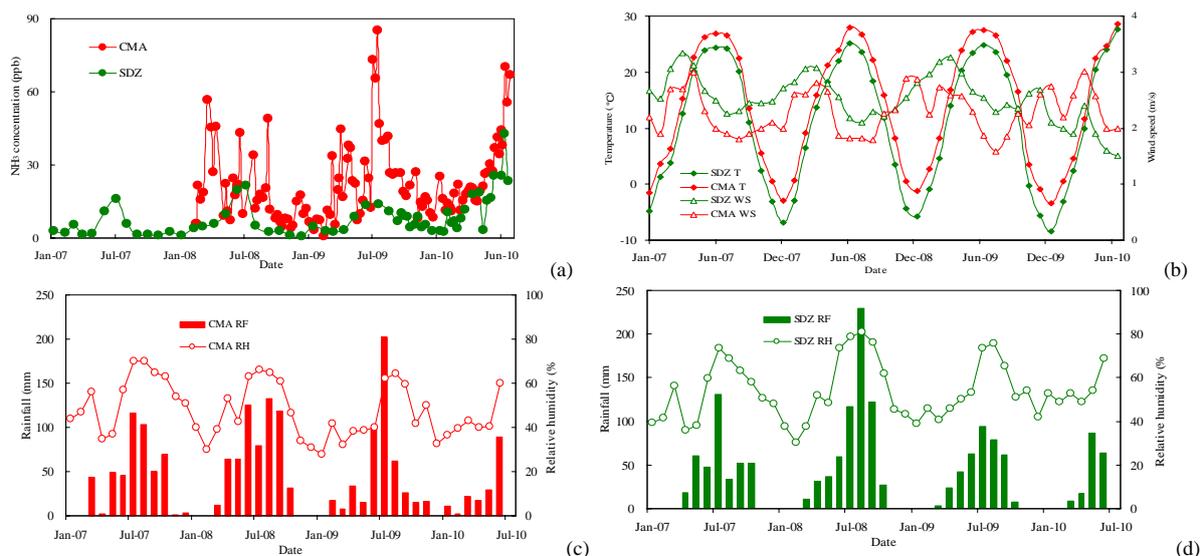
The above comparisons suggested that there exist complex NH₃ patterns in the Beijing region. More research efforts are needed to quantify the contribution of local versus regional sources to the atmospheric ammonia variations in Beijing.

3.1.2 Temporal variations

Figure 3 shows the temporal variation of NH₃, temperature and wind speed at the two observation sites. NH₃ exhibited a distinct and significant temporal variation with higher concentrations in summer than in other season, especially in winter at both sites. At CMA, NH₃ increased gradually from April and reached the highest values on July, and then decreased until the following March. NH₃ values had a small peak in April as the temperature increase suddenly caused the accumulated emission of NH₃ from natural and fertilized soils, vegetation, and human sources in the city centre in winter. The peak NH₃ value was 85.1 ppb on 20–24 July 2009 and the lowest concentrations of NH₃ (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 NH₃ concentration is consistent with the highest ambient temperature in July. The lowest NH₃ 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.

Location	Type	Period	Concentration	measurement techniques	Reference
Beijing, China	Urban	2008.02–2010.07	22.8 ± 16.3	Passive sampler	This study
	Rural	2007.01–2010.07	10.2 ± 10.8		
Beijing, China	Urban	28 July–3 August 2001	16.8–42.2	Annular denuder	Yao et al. (2003)
Beijing, China	Urban	Summer 2002–2003	23.9	Annular denuder	Wu et al. (2009)
Beijing, China	Urban	Winter and Summer 2007	0.29–63.8	Annular denuder	Ianniello et al. (2010)
Beijing, China	Rural	1999.09–2000.05	3.0	Passive sampler	Carmichael et al. (2003)
Xi'an, China	Urban	2006.04–2007.04	18.6	Passive sampler	Cao et al. (2009)
	Suburban		20.3		
Rome, Italy	Urban	2001.05–2002.03	5.5–65.6	Annular denuder	Perrino et al. (2002)
New York, USA	Urban	1999.07–2000.06	5.1	Annular denuder	Bari et al. (2003)
Clinton, Carolina, USA	Urban	2000.01–2000.12	7.7	Annular denuder	Walker et al. (2004)
Kinston, Carolina, USA	Urban	2000.05–2000.12	3.5		
Morehead, Carolina, USA	Urban	2000.01–2000.12	0.8		
Hong Kong	Urban	Autumn 2000	3.0	Autoanalyser	Yao et al. (2006)
Northern Adriatic	Urban	1998–2005	17.3–28.8	Spectrophotometrically by Nesslerization	Alebic-Juretic, (2008)
area, Croatia	Suburban		8.6–40.3		
Lahore, Pakistan	Urban	2005.12–2006.02	30.3–116.9	Annular denuder	Biswas et al. (2008)

**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

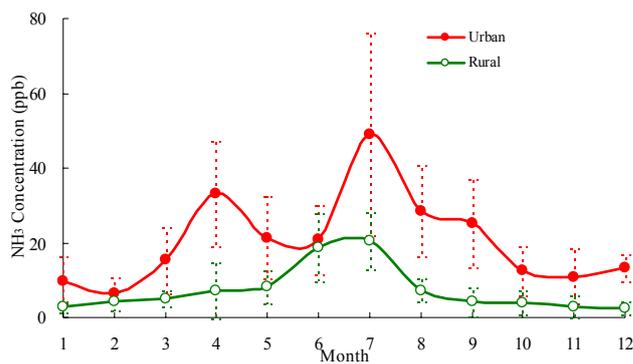


Fig. 4. The statistics of monthly mean concentrations of NH_3 during the sampling period at the two observation sites in Beijing.

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).

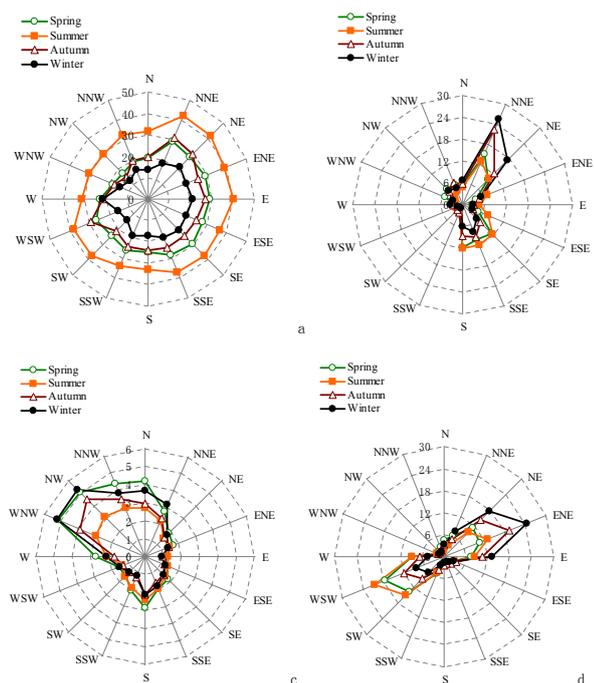


Fig. 5. Seasonal average NH₃ concentrations at CMA (a), wind frequency at CMA (b), wind speed at CMA (c) and wind frequency at SDZ (d) distributions in different wind direction sectors during 2009–2010.

The NH₃ concentrations at CMA were highly correlated with those at SDZ ($R = 0.71$, $P < 0.0001$). The high correlation of NH₃ at two typical sites may point to that NH₃ at both sites are affected by similar synoptic conditions.

3.3 The impact of long-rang air transport on the surface NH₃ 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

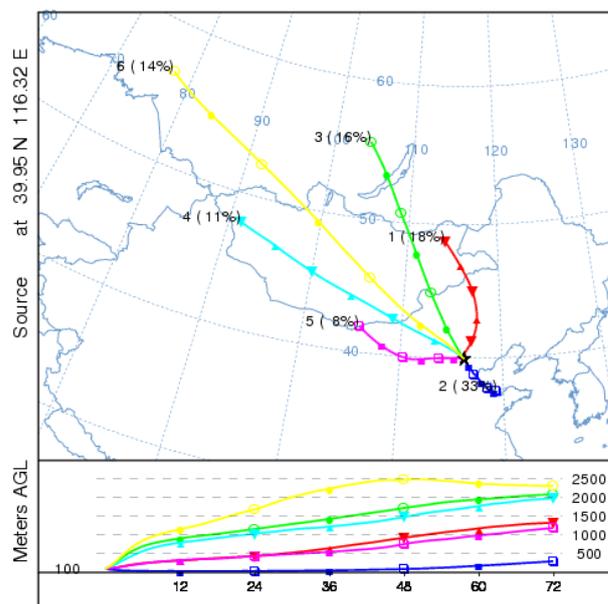


Fig. 6. 72-h backward trajectories for 100 m above ground level at CMA during July 2009 to June 2010.

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 NH₃ 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 NH₃ exist among the different clusters, with cluster 2 corresponding to the highest NH₃ levels (25.7 ppb), and cluster 5 corresponding to the second highest NH₃ levels (24.4 ppb). These two types of trajectories have the shortest transport distances and lowest transport heights, which help the accumulation of NH₃. 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 NH₃.

A detailed estimate of NH₃ emission in Beijing and the surrounding areas in 2005, carried out by Ianniello et al. (2010), has shown that the largest sector contributor to NH₃ emissions in the North China Plain (NCP) is agriculture, while mineral fertilizer use contributing 54 % to the total NH₃ 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).

Table 3. Occurrence frequency and mean values of NH₃ for each type of air masses arriving at CMA during July 2009 to June 2010.

Air mass	Spring	Summer	Autumn	Winter	Ratio	Height (m)	NH ₃ (ppb)
Cluster 1	92	49	56	66	18 %	722	18.1
Cluster 2	105	268	81	23	33 %	100	25.7
Cluster 3	66	14	83	69	16 %	1420	11.9
Cluster 4	37	11	54	63	11 %	1260	16.3
Cluster 5	13	22	47	28	8 %	629	24.4
Cluster 6	51	0	39	107	14 %	1913	12.0

Contributions of NH₃ 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 NH₃ 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 NH₃ levels corresponding to cluster 5. The cluster 1 has the third highest concentration of NH₃. The data in Table 3 suggest that the NH₃ 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 NH₃, 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 NH₃ 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 NH₃ 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 NH₃ 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 NH₃ versus NO_x and NH₃ 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 NH₃, 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 (NH₃, NO_x and CO) are considered. The slope value of 0.84 of NH₃/NO_x in summer indicates the comparable levels of NH₃ with NO_x (Fig. 7). In autumn and winter, the levels of NH₃ are about one third of the levels of NO_x. The intercepts ([NO_x] = 0; [CO] = 0) tell us the regional background of NH₃ (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 NH₃ in winter was less than 1 ppb which also indicates the similar source between NO_x, CO and NH₃ in winter Beijing.

The correlation coefficients (*R*) of NH₃ 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 NH₃ 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 NH₃ versus NO_x and NH₃ 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 NH₃ versus NO_x and NH₃ 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, less correlation of NH₃ versus NO_x and NH₃ 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 NH₃ from the aerosol phase may be significant enough to dominate over traffic emissions during summer in Beijing. In addition, as

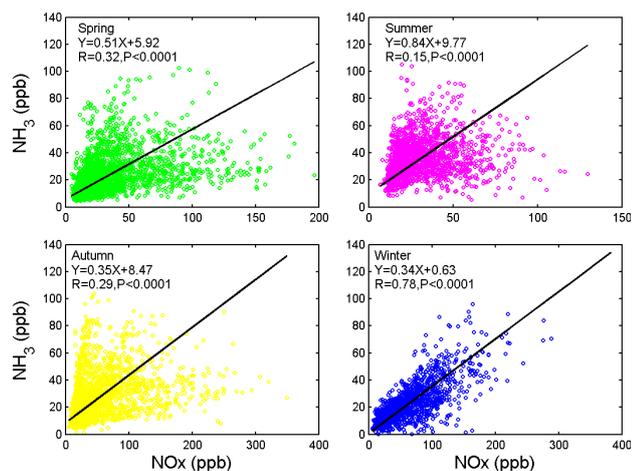


Fig. 7. The 2-sided regression of NH_3 versus NO_x at CMA in different seasons from June 2009 to May 2010.

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

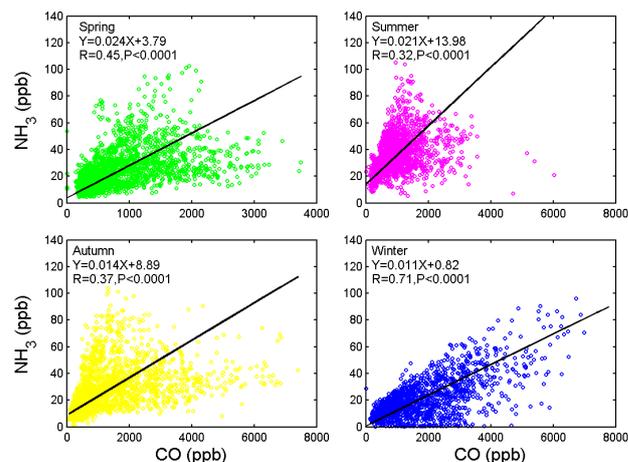


Fig. 8. The 2-sided regression of NH_3 versus CO at CMA in different seasons during June 2009 to May 2010.

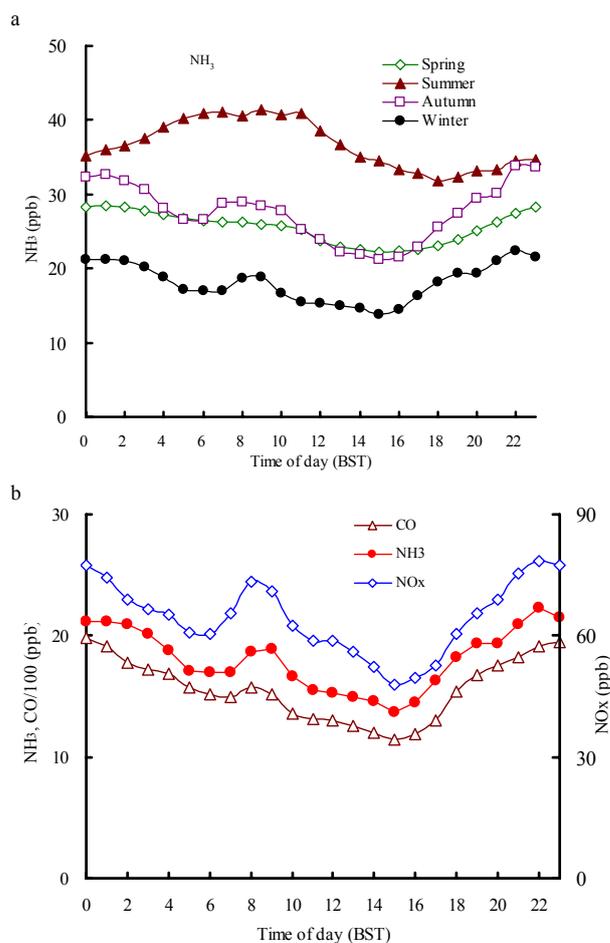


Fig. 9. Averaged diurnal variations of NH_3 at CMA in four seasons during June 2009 to May 2010 (a), and NO_x and CO in winter 2009 (b).

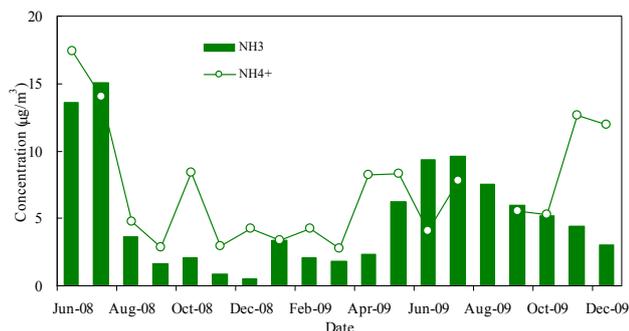


Fig. 10. Temporal variations of monthly concentrations for NH_3 and NH_4^+ in $\text{PM}_{2.5}$ at SDZ from June 2008 to December 2009.

level (1952 ppb) at 24:00 BST. The peak NH_3 occurred during the morning rush hour similar to NO_x and CO supports the hypothesis that the enhanced NH_3 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 NH_3 . Greater emission from other sources combined with greater volatilization from the aerosol phase appeared to dominate (Whitehead et al., 2007).

3.6 Relationship between NH_3 and NH_4^+ in $\text{PM}_{2.5}$ at rural site

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 (NH_4^+) has a longer atmospheric lifetime than NH_3 and can therefore be transported over relatively long distances. Deposition of NH_3 and NH_4^+ 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 NH_3 and NH_4^+ , the data of NH_4^+ in $\text{PM}_{2.5}$ were collected at SDZ. A total of 117 $\text{PM}_{2.5}$ samples were analyzed for the period from June 2008 to December 2009.

The daily NH_4^+ concentrations ranged from 0.10 to $36.53 \mu\text{g m}^{-3}$, with an average concentration of $7.03 \mu\text{g m}^{-3}$. Figure 10 illustrates the temporal variations of monthly concentrations for NH_3 and NH_4^+ in $\text{PM}_{2.5}$. The average concentrations of NH_4^+ were 7.44, 9.04, 5.75 and $4.73 \mu\text{g m}^{-3}$ in spring, summer, autumn and winter, respectively. The summer to winter ratio for NH_4^+ concentrations was approximately 2.0. NH_3 concentrations were lower than NH_4^+ in spring, autumn and winter, but higher than NH_4^+ in summer. NH_3 may undergo conversion to NH_4^+ 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 NH_3 (Nemitz et al., 2001).

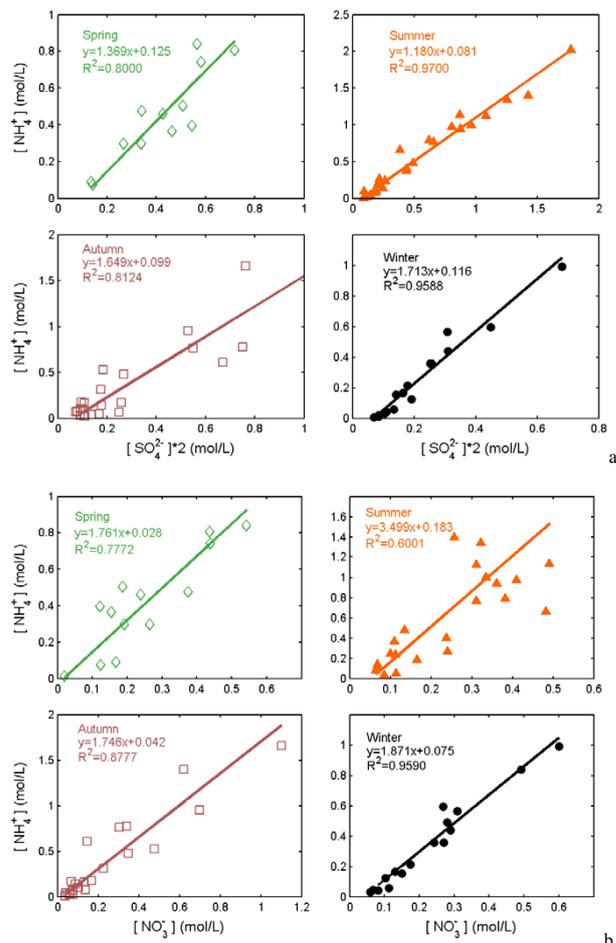


Fig. 11. The relationships of observed $[\text{NH}_4^+]$ concentrations vs. $2[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$ concentrations in different seasons. The reduced major axis regression is performed for the linear fit.

Monthly NH_3 concentrations were significantly correlated with NH_4^+ concentrations ($R = 0.64$, $P < 0.0001$). Average monthly $\text{NH}_3/\text{NH}_4^+$ ratios varied from 0.13 to 2.28, with an average of 0.73. The highest $\text{NH}_3/\text{NH}_4^+$ ratio was found in June 2009, implying that abundant NH_3 gas existed in the atmosphere in summer. The lowest $\text{NH}_3/\text{NH}_4^+$ ratio appeared in December 2008.

Table 4 summarizes the daily concentrations of inorganic ions in $\text{PM}_{2.5}$ from June 2008 to December 2009. The average concentrations of SO_4^{2-} , NO_3^- and Cl^- were 15.00, 11.57 and $1.33 \mu\text{g m}^{-3}$, respectively, and the total concentration of inorganic ions ($\text{NH}_4^+ + \text{NO}_3^- + \text{SO}_4^{2-} + \text{Cl}^-$) was $34.93 \mu\text{g m}^{-3}$.

With respect to percentage of the total mass, SO_4^{2-} was the most important species on average in $\text{PM}_{2.5}$ at SDZ. Nitrate contributes more significantly to total mass during colder months when SO_2 oxidation rates are reduced in response to lower concentrations of oxidants such as OH. The average

Table 4. Summary statistics of daily average concentration of inorganic ions in PM_{2.5} from June 2008 to December 2009 at SDZ, in $\mu\text{g m}^{-3}$.

Ions	Standard		Minimum	25th percentile	75th percentile	Median	Maximum
	Mean	Deviation					
NH ₄ ⁺	7.03	7.76	0.10	1.05	10.67	3.83	36.53
NO ₃ ⁻	11.57	11.40	1.14	3.32	17.15	7.10	68.24
SO ₄ ²⁻	15.00	15.68	0.58	4.48	21.23	8.56	85.31
Cl ⁻	1.33	1.29	0.01	0.55	1.57	0.96	8.60

molar ratios of NH₄⁺ to SO₄²⁻, NO₃⁻ to NH₄⁺ and Cl⁻ to NH₄⁺ were 1.8, 0.5 and 0.1, respectively.

Figure 11a shows the relationship of the molar concentrations between [NH₄⁺] and 2*[SO₄²⁻] in different seasons. According to 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 SO₄²⁻ and NH₄⁺ are the highest but the ratio of [NH₄⁺]/(2*[SO₄²⁻]) is the lowest among the 4 seasons. Figure 11b shows the relationship of the molar concentrations between [NH₄⁺] with [NO₃⁻] 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 [NH₄⁺] with [NO₃⁻] is less strong than that of [NH₄⁺] and 2*[SO₄²⁻] and the mean concentration of [NO₃⁻] is less than the mean concentration of 2*[SO₄²⁻], which indicate most of NH₄⁺ in aerosol in summer is present as (NH₄)₂SO₄. The considerable levels between [NO₃⁻] and 2*[SO₄²⁻] in winter and both strong correlations between [NH₄⁺] with 2*[SO₄²⁻] and [NH₄⁺] with [NO₃⁻] indicate the NH₄⁺ in aerosol exists as (NH₄)₂SO₄ and NH₃NO₃.

4 Conclusions

The concentrations of NH₃ 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 NH₃ 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. NH₃ 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 NH₃ sources in summer.

The NH₃ 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 NH₃ 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 NH₃ at Beijing urban areas.

The measurements showed significant positive correlations between hourly concentrations of NH₃ 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 NH₃. The contribution from vehicles is further supported by the observation of a bimodal diurnal cycle of NH₃ in winter, with peaks occurring roughly at times of high traffic density.

The daily NH₄⁺ concentrations ranged from 0.10 to 36.53 $\mu\text{g m}^{-3}$, with an average concentration of 7.03 $\mu\text{g m}^{-3}$ from June 2008 to December 2009 at the rural site. The average concentrations of NH₄⁺ were 7.4 ± 4.7, 9.0 ± 9.3, 5.8 ± 7.5 and 4.7 ± 5.1 $\mu\text{g m}^{-3}$ in spring, summer, autumn and winter, respectively. Monthly NH₃ were significantly correlated with NH₄⁺ concentrations. Average monthly NH₃/NH₄⁺ ratios varied from 0.13 to 2.28, with an average of 0.73. The average concentrations of SO₄²⁻, NO₃⁻ and Cl⁻ were 15.00, 11.57 and 1.33 $\mu\text{g m}^{-3}$, respectively, and the total concentration of inorganic ions (NH₄⁺+NO₃⁻+SO₄²⁻+Cl⁻) was 34.93 $\mu\text{g m}^{-3}$. In summer, most of NH₄⁺ in PM_{2.5} is present as (NH₄)₂SO₄.

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