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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 rural site during 2008–2009. The field comparison between the Ogawa passive samplers and an active analyzer for NH_3 conducted at an urban site assures the quality and accuracy of the measurements. The concentrations of NH_3 at 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. The NH_3 concentrations at 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 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. These patterns were not observed during the summer, suggesting other sources became more important. At rural site, the daily NH_4^+ concentrations ranged from 0.10 to 36.53 μg/m^3, with an average of 6.94 μg/m^3 from June 2008 to December 2009. 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.

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 [$(NH_4)_2SO_4$], ammonium nitrate (NH_4NO_3), or ammonium chloride (NH_4Cl), or deposit onto the Earth's surface. These NH_4^+ aerosols contribute significantly to fine particle mass ($PM_{2.5}$) and have implications for human

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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; Bouwman, et al., 1997; Dentener, et al., 1994; Galloway, et al., 2008; 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%). 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 (Chou and Wang, 2007; 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). Clarisse et al. (2009) have used infrared spectra, obtained by the IASI/MetOp satellite, to map global ammonia concentrations from space in 2008. They have identified several ammonia hotspots in middle-low latitudes across the globe and the largest columns are observed from May to August.

Only few studies on ammonia emissions in China are available. Along with the rapid growth of the economy in China, the anthropogenic emissions of SO_2, NO_x and NH_3 contribute 59%, 43% and 49%, respectively, of the total emissions in Asia in 2000. For 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

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ten background and rural sites in China during 2007–2008 and found that the spatial variability of the NH_3 concentration was large in China, with higher level in North, Southwest and East China. Cao et al. (2009) reported the variation of ammonia concentrations in Xi'an, northwest China during 2006–2007. The annual average concentrations of NH_3 were 18.5 and 20.2 ppb, at the urban and suburban sites in Xi'an between April 2006 and April 2007, respectively.

Beijing with 17.55 million inhabitants in 2009 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. Recent the 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. Long-term observations of NH_3 in Beijing are currently unknown. In this paper, we present the measurements of NH_3 from February 2008 to July 2010 at an urban site and from January 2007 to July 2010 at a rural site in Beijing, China, characterize the levels and variations of ammonia in urban and rural areas over Beijing, and investigate the contribution of traffic to ammonia levels in 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

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in the courtyard of China Meteorological Administration (CMA, 39°56′ N, 116°24′ E) 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, 50 m above ground level.

The rural site, Shangdianzi (SDZ, 40°39′ N, 117°07′ E, 293.3 m a.s.l.), is located in the northeast of Beijing, with a distance about 150 km to urban area of Beijing. About 55 km southwest of SDZ is the nearest township, Miyun town with a population of about 0.426 millions. Within 30 km of the site, there are only small villages in mountainous areas with sparse population and thus insignificant anthropogenic emission sources. SDZ is one of the WMO/GAW regional background stations in China. More information of SDZ can be found in Lin et al. (2008) and Meng et al. (2009).

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, each sampler was exposed about 7 days from February 2008 to July 2010. At SDZ, each sampler was exposed about 10 days and samples were collected once per month from January 2007 to August 2009 and three per month from September 2009 to July 2010. A total of 219 samples were collected at both sites. Field blanks were taken by placing the loaded and sealed samplers beside the real samples.

The concentrations of NH_3 were parallel measured by a NO_x/NH_3 analyzer (EC9842, Ecotech, Australia) for inter-comparison with passive sampler from June 2009 to May 2010 at top of Building (50 m) of CMA Training Center, 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) and a gas filter correlation analyzer (TEI, model 48C) at top of Building of CMA Training Center.

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Daily aerosol $PM_{2.5}$ samples were collected using a MiniVol portable samplers (Airmetrics, Oregon, USA) operating at flow rates of 5 L/min 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° is 15.5 $cm^3\,min^{-1}$ for each filter of the 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 and ammonium in the solution was determined using ion chromatography (DX-3000, Dionex, US).

$PM_{2.5}$ filters were extracted with ultrapure water. The concentrations of NH_4^+ in $PM_{2.5}$ were determined by using ion chromatography (DX-3000, Dionex, US).

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 wares were cleaned using ultra pure water before reuse. Clean dispensable polyethylene gloves were used to avoid bare hand contact with sampling components. The samplers were assembled and dissembled 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 calibration drift. The multi-point calibrations were performed at approximately 1-month interval.

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The comparison between the Ogawa passive samplers and a continuous active analyzers EC9842 for NH_3 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 periods as the passive samplings. Figure 2 presents the comparisons of NH_3 concentrations measured by passive samplers and an active monitor. Observed results showed a good correlation between the two methods of measurements of NH_3. Figure 2 presents the comparison results ($N = 42$, slope = 0.95, $R = 0.78$). 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.

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 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 CMA 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.

Table 2 lists NH_3 levels at different urban and suburban sites in the world. The average concentrations of NH_3 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.

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At SDZ, the 2007–2010 values are obviously higher than the 1999–2000 ones reported by Carmichael et al. (2003). Such differences may indicate an increase of the NH_3 levels in North China plain. As illustrated, the NH_3 level at CMA in Beijing was higher than that reported in Xi'an (18.6 ppb) (Cao et al., 2009), at same time, NH_3 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 NH_3 level at CMA in Beijing was also higher than that reported in Salzburg, Austria (3.9–40.3 ppb) (Loflund et al., 2002), Rome, Italy (5.5–65.6 ppb) (Perrion et al., 2002), Northern Adriatic and Croatia (17.3–28.8 ppb) (Alebic-Juretic, 2008). NH_3 level at Beijing was 2-5 times higher than that reported at Munich, Germany (3.5–15.8 ppb) (Loflund et al., 2002), New York, USA (5.1 ppb) (Bari et al. 2003), Clinton, USA (7.7 ppb), Kinston, USA (3.5 ppb), Morehead City, USA (0.8 ppb) (Walker et al., 2004), and Hong Kong (3.0 ppb) (Yao et al., 2006).

The NH_3 level at CMA in Beijing was lower than that reported in Lahore, Pakistan (30.3–116.9 ppb) (Biswas et al., 2008) and Munster, Germany (50.1 ppb) (Gietl et al., 2008). NH_3 concentrations at SDZ in Beijing was lower than those in Agra, India (14.7 ppb) (Singh et al., 2001) and Northern Adriatic area, Croatia (8.6–40.3 ppb) (Alebic-Juretic, 2008).

The above comparisons suggested that there exist complex NH_3 patterns in the Beijing region. Meng et al. (2007, 2008, 2009) found that the air masses from the North China Plain region and the air masses traveling over the coal mining and power generation regions west of Beijing contain the high concentrations of air pollutants. Therefore, transport of air masses from these regions is responsible for the high concentrations of the gaseous ammonia in Beijing. More research efforts are needed to quantify the contribution of local versus regional sources to the atmospheric ammonia variations in Beijing.

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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 winter at both sites. At CMA, 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). NH_3 concentrations and ambient temperatures in July reached maximum values (Fig. 3b). The lowest NH_3 value was in February 2009 at CMA, which was attributable to the very cold temperatures, moderate snowfall and less human activity in Beijing urban city for a lot of people going back their hometown during Spring Festival. NH_3 concentrations decreased dramatically in June and August, reflecting the important role wet removal plays in influencing the temporal variation in ambient NH_3 levels. Low 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.

At SDZ, the peak NH_3 value was 42.9 ppb on 11–21 July 2010 and the lowest concentrations of NH_3 (0.8 ppb) appeared on 19–29 December 2008 for over three-year period 2007–2010.

The significant linear correlations ($R = 0.47$ for CMA and $R = 0.62$ for SDZ) were found between NH_3 and air temperature. 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 NH_3 in this rural area. Ambient NH_3 concentrations showed a positive correlation with temperature may be attributable to the increased NH_3 sources by enhancing volatilization of NH_3 and decreased the stability of NH_4NO_3 aerosols. Various studies have shown strong correlations between air temperature and ammonia concentration, suggesting that temperature is an important variable in influencing NH_3 volatilization from animal waste (Aneja et al., 2000).

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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. NH_3 levels correlated negatively ($R = -0.36$ for CMA and $R = -0.21$ for SDZ) with wind speed at both sites. Previous studies have reported an inverse relationship between ground-level concentrations of trace gases, such as ammonia, and wind speed (Robarge et al., 2002).

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.

3.2 Seasonal variations

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. 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 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

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activities can also increase ambient NH_3 concentrations during the summer months. Low NH_3 concentrations in winter were probably due to reduced NH_3 volatilization when the air temperature was frequently below freezing and there were snows.

3.3 Relationship with NO_x and CO in different season 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. They found that 74% of the ground NO_x was due to vehicular emissions while power plants and industrial sources only contributed 2% and 13%, 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. 5 and 6. The correlation coefficients (R) of NH_3 versus NO_x were 0.33, 0.13, 0.29 and 0.79 in spring, summer, autumn and winter, respectively. The correlation coefficients (R) of NH_3 versus CO were 0.46, 0.34, 0.37 and 0.72 in spring, summer, autumn and winter, respectively.

It was noted that the NH_3 versus NO_x and NH_3 versus CO were significantly correlated in winter but less significantly correlated in summer implies that the winter and summer variations of these species are driven by different dominant processes. In the

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winter, NH_3 levels were found to be highly correlated with NO_x ($R = 0.79$, $P < 0.0001$), with the slope of 0.28. Positive correlations were observed also between NH_3 and CO ($R = 0.72$, $P < 0.0001$), with the slope of 0.008. 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 the amount of scatter about these regression lines indicated that other ammonia sources not linked to NO_x and CO were also important. In a city centre location, these will largely be human sources and solvent use (Whitehead et al., 2007).

In other seasons, especially summer, less 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.

3.4 Diurnal variations in different season at urban site

The average diurnal variations of NH_3 concentrations were calculated from the hourly mean values obtained by a Nitrogen Oxides/Ammonia Analyzer during June 2009 to May 2010 at CMA. The average diurnal variations of NH_3 in different seasons are shown in Fig. 7a. Ammonia gas showed a significant diurnal variation in summer. The concentration of NH_3 increased slightly, with 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 were likely the result of accumulation and inefficient vertical mixing within a relatively shallow boundary layer.

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As described above, good relationships of NH_3 versus NO_x and NH_3 versus CO correlations indicated that they were emitted from a predominant source in winter. Figure 7b compared diurnal variations of NH_3 with that of NO_x and CO, the traffic related pollutants in winter. Figure 6b 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 level (1952 ppb) at 24:00 BST. The peak NH_3 occurred during the morning rushing hour like 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. Any bimodal pattern due to traffic cycles is too weak to be seen in summer, which implies that traffic is not the dominant source of NH_3 during the summer. Greater emission from other sources combined with greater volatilization from the aerosol phase appeared to dominate (Whitehead et al., 2007).

3.5 Relationship between NH_3 and NH_4^+ in $PM_{2.5}$ 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, 2011; Galloway et al., 2003). To understand the transformation of NH_3 and NH_4^+, the data of NH_4^+ 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 NH_4^+ concentrations ranged from 0.10 to 36.53 $\mu g/m^3$, with an average of 6.94 $\mu g/m^3$. Figure 8 illustrates the temporal variations of monthly concentrations for NH_3 and NH_4^+ in $PM_{2.5}$. Seasonal average concentrations of NH_4^+ were 7.4 ± 4.7,

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9.0 ± 9.3, 5.8 ± 7.5 and 4.7 ± 5.1 μg/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. The peak NH_4^+ value was found in summer may be due to transport of air pollutants from Beijing urban city and North China Plain (Meng et al., 2009). When the urban plume of Beijing is advected to the southwest, the interaction of the plume's SO_2 and NO_x with freshly emitted NH_3 may lead to substantial particle formation. 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).

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

4 Conclusions

Continuous measurements of atmospheric ammonia 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 rural site during 2008–2009. The measurements of NH_3 by passive sampling method showed high correlation with that by the active analyzer at urban site, which assure 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 ppb and 23.5 ± 18.0 ppb in 2008 and 2009. The NH_3 concentrations at the rural site 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 highest during summer at both sites, with summer to winter

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concentration ratios of 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 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. Other sources of NH_3 are indicated by the large amount of scatter in these correlations. 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 $\mu g/m^3$, with an average of 6.94 $\mu g/m^3$ from June 2008 to December 2009 at SDZ. Seasonal average concentrations of NH_4^+ were 7.4 ± 4.7, 9.0 ± 9.3, 5.8 ± 7.5 and 4.7 ± 5.1 $\mu g/m^3$ 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.

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Table 1. Annual summary statistics of weekly and monthly average concentration of NH_3 at urban and rural site in Beijing, in ppb.

Site	Period	Mean	Standard Deviation	Minimum	25th percentile	75th percentile	Median	Maximum
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

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Table 2. Comparison of NH_3 at Beijing with other areas, in ppb.

Location	Type	Period	Concentration	Reference
Beijing, China	Urban Rural	2008.02–2010.07 2007.01–2010.07	22.8±16.3 10.2±10.8	This study
Beijing, China	Urban	28 July–3 August 2001	16.8–42.2	Yao et al. (2003)
Beijing, China	Urban	Summer 2002–2003	23.9	Wu et al. (2009)
Beijing, China	Urban	Winter and Summer 2007	0.29–63.8	Ianniello et al. (2010)
Beijing, China	Rural	1999.09–2000.05	3.0	Carmichael et al. (2003)
Xi'an, China	Urban Suburban	2006.04–2007.04	18.6 20.3	Cao et al. (2009)
Agra, India	Suburban	1997.07–09	14.7	Singh et al. (2001)
Salzburg, Austria	Urban	2000.08–2001.01	3.9–40.3	Loflund et al. (2002)
Munich, Germany			3.5–15.8	
Rome, Italy	Urban	2001.05–2002.03	5.5–65.6	Perrini et al. (2002)
New York, USA	Urban	1999.07–2000.06	5.1	Bari et al. (2003)
Clinton, USA	Urban	2000.01-2000.12	7.7	Walker et al. (2004)
Kinston, USA	Urban	2000.05–2000.12	3.5	
Morehead City, USA	Urban	2000.01–2000.12	0.8	
Hong Kong	Urban	Autumn 2000	3.0	Yao et al. (2006)
Northern Adriatic	Urban	1998–2005	17.3–28.8	Alebic-Juretic, (2008)
area, Croatia	Suburban		8.6–40.3	
Lahore, Pakistan	Urban	2005.12–2006.02	30.3–116.9	Biswas et al. (2008)
Munster,Germany	Urban	2006.01	<50.1	Gietl et al. (2008)

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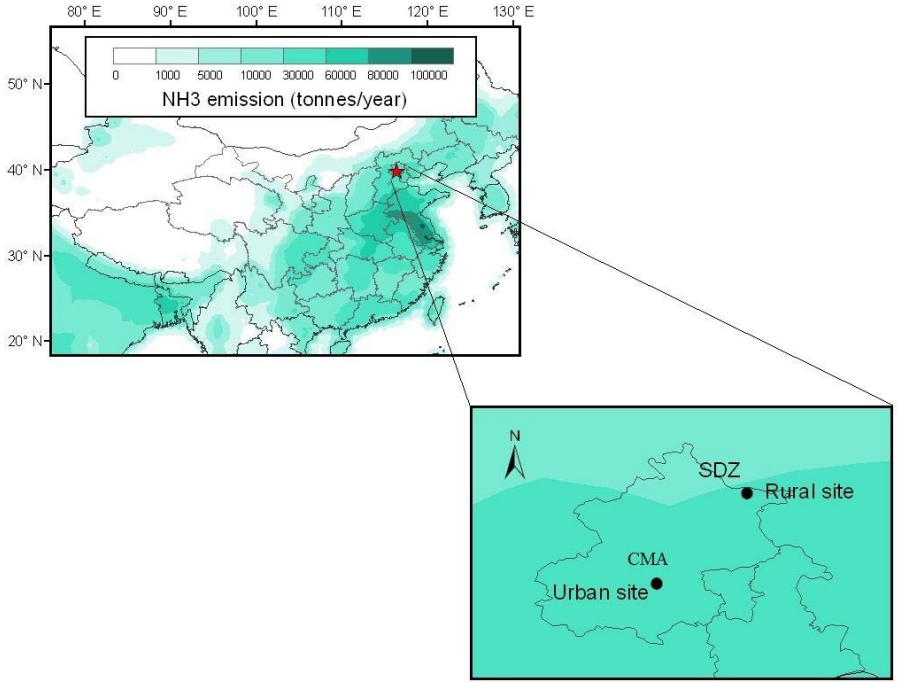

Fig. 1. The sampling locations in Beijing, China with emissions distributions.

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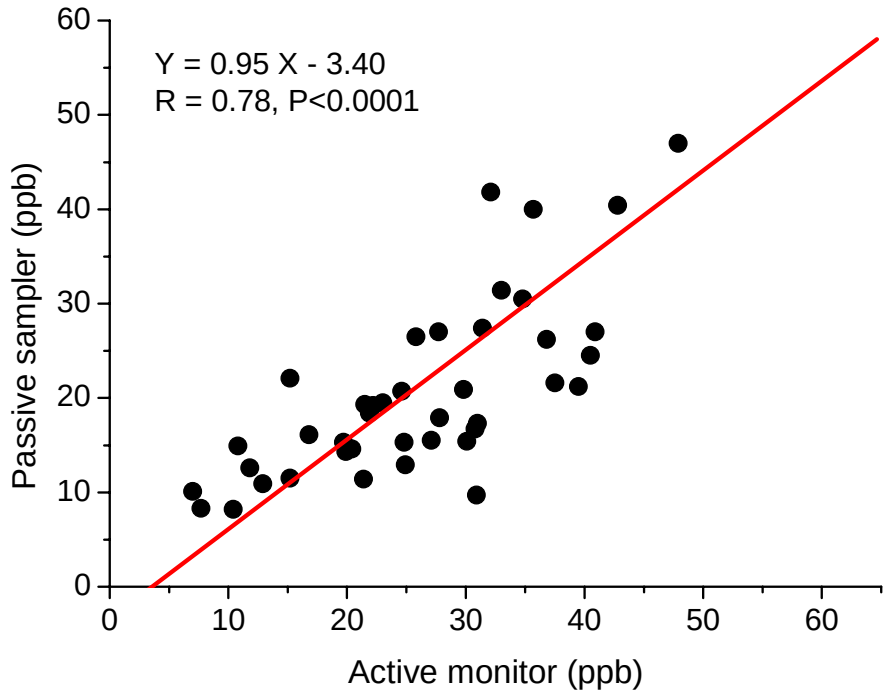

Fig. 2. Comparison of results obtained with the Ogawa passive sampler and an active monitor at CMA.

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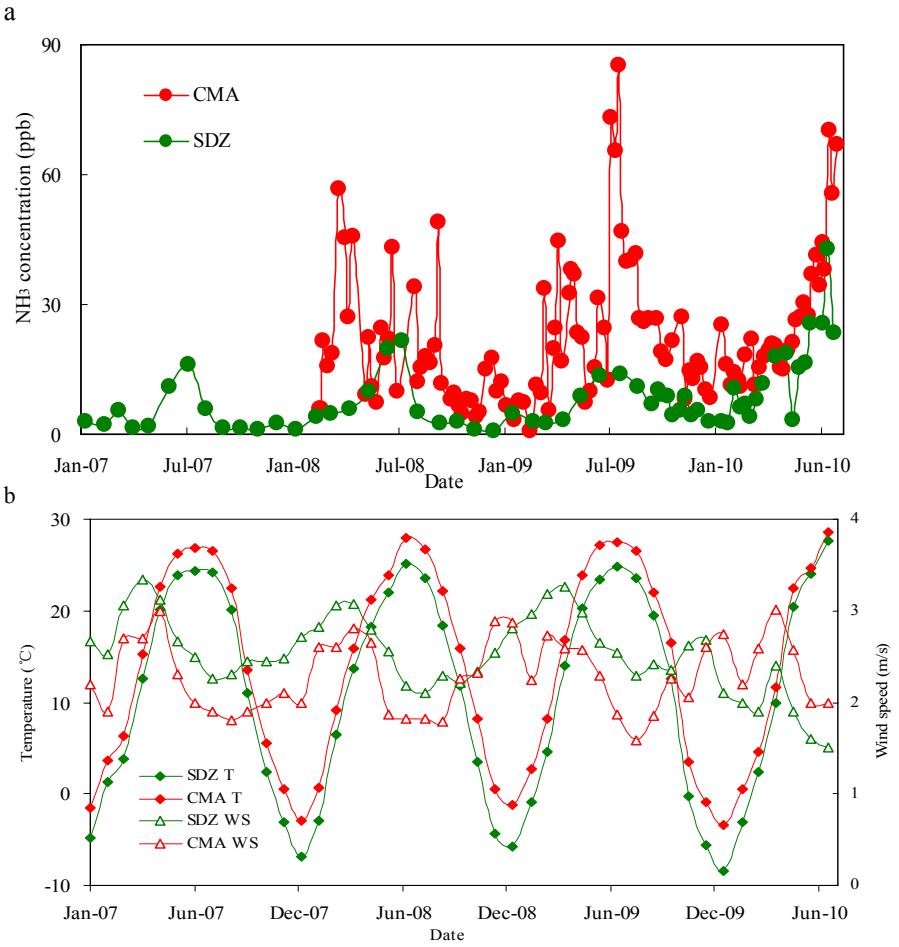

Fig. 3. Temporal variations of NH_3, temperature and wind speed at urban (CMA) and rural (SDZ) sites in Beijing during 2007–2010.

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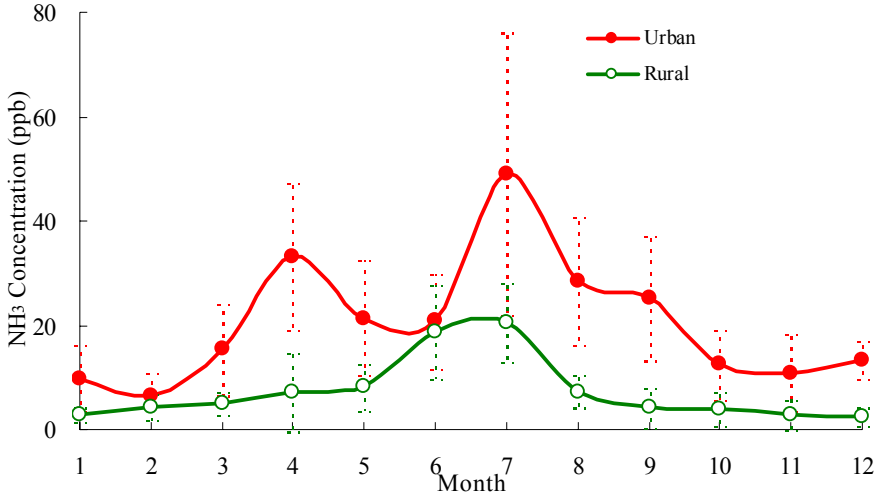

Fig. 4. The statistics of monthly mean concentrations of NH_3 during the sampling period at the two observation sites in Beijing.

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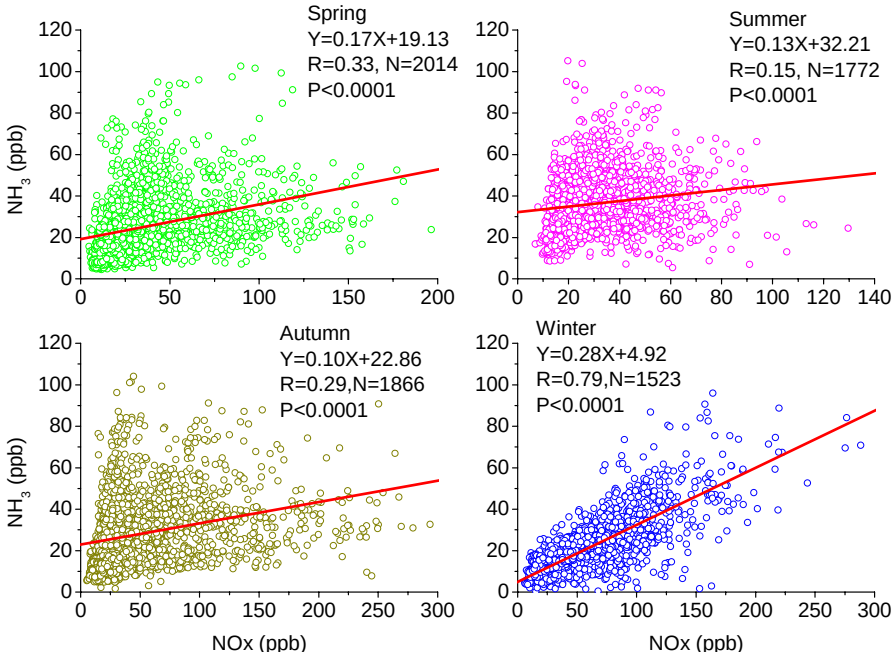

Fig. 5. The scatter plot of the concentration of NH_3 versus NO_x at CMA from June 2009 to May 2010.

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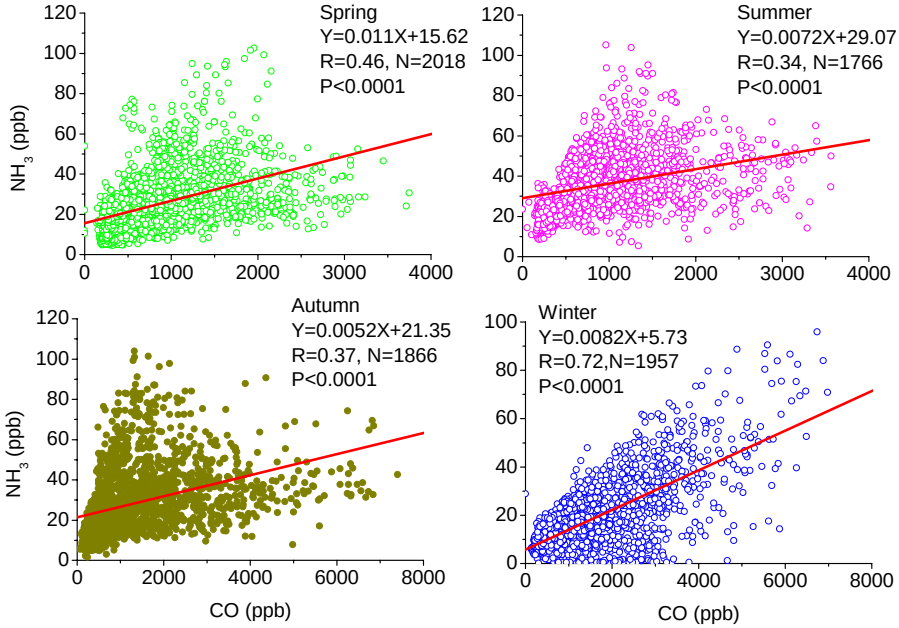

Fig. 6. The scatter plot of the concentration of NH_3 versus CO at CMA from June 2009 to May 2010.

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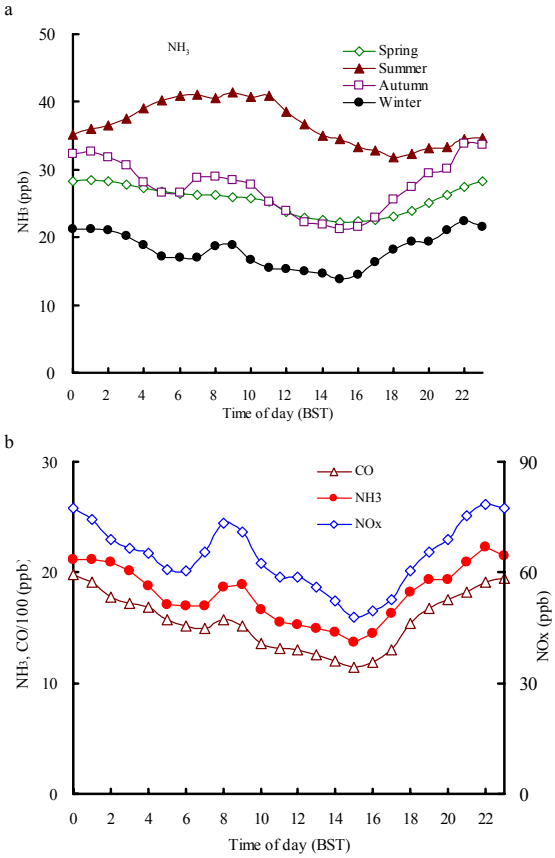

Fig. 7. Averaged diurnal variations of NH_3 at CMA in four seasons from June 2009 to May 2010 **(a)**, and NO_x and CO in winter 2009 **(b)**.

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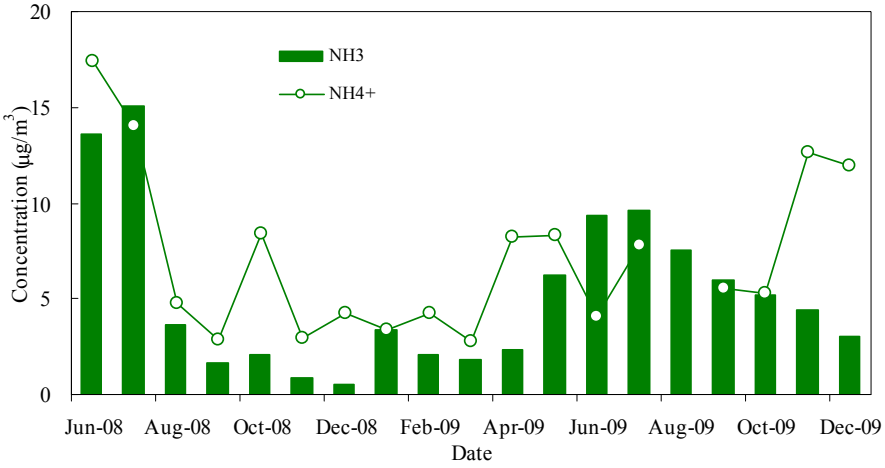

Fig. 8. Temporal variations of monthly concentrations for NH_3 and NH_4^+ in $PM_{2.5}$ at SDZ from June 2008 to December 2009.

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