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Occurrence of gas phase ammonia in the area of Beijing (China)

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Abstract

The atmospheric concentrations of gaseous ammonia have been measured during two field campaigns in the winter and in the summer of 2007 at Beijing (China). These measurements were carried out by means of diffusion annular denuders coated with phosphorous acid. The results were discussed from the standpoint of seasonal and diurnal variations and meteorological effects. The daily average NH_3 concentrations were in the range of 0.20–44.38 µg/m^3 and showed regular seasonal variations with higher concentrations during summer and with lower during winter. The seasonal trends seemed to be largely affected by air temperature because of agricultural sources. No diurnal variability was observed for gaseous NH_3 levels in both winter and summer seasons. The highest ammonia value of 105.67 µg/m^3 was measured in the early morning during the summer period when stable atmospheric conditions occurred. The diurnal winter and summer trends of ammonia were nearly independent on the air temperatures but they were affected by wind direction suggesting a strong local source influences. Ammonia was also correlated with the atmospheric mixing in the boundary layer, and, with NO_x and CO air concentrations supporting the hypothesis that the traffic may be also an important source of ammonia in Beijing.

1 Introduction

Gaseous ammonia (NH_3) is the third most abundant nitrogen containing compound and is the primary alkaline trace gas in the atmosphere. The importance of ammonia in urban area is related to its role as a precursor for secondary aerosols (Erisman and Schaap, 2004). It neutralizes atmospheric acids such as nitric acid (HNO_3), hydrochloric acid (HCl) and sulphuric acid (H_2SO_4), formed by oxidation of nitrogen oxides (NO_x) and sulphur dioxide (SO_2), respectively (Krupa, 2003), thereby affecting the acidity of cloud water and aerosols (Heeb et al., 2006; Roelle and Aneja, 2002). The reaction rates for NH_3 depend on the acid concentration, humidity and temperature. The

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main chemical sink for ammonia in the atmosphere is the reaction with H_2SO_4, yielding ammonium sulphate [$(NH_4)_2SO_4$] and ammonium bisulphate [NH_4HSO_4] salts. Reactions with HNO_3 and HCl yield ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) salts in particulate phase. These NH_4^+ aerosols contribute significantly to fine particle mass (size <2.5 µm) and have implications for human health (Brunekreef and Holgate, 2002). They limit atmospheric visibility and global radiation budgets (Horvat, 1992; Sutton et al., 1994).

The most recent consideration for NH_3 emissions on the global scale is concerning with the climate change. NH_3 has a relatively short residence time of about 1 to 5 d. When airborne, it is either readily converted to ammonium aerosols, due to their extended lifetime (about 1–15 d), these particles may be transported far from the pollutant sources (Aneja et al., 2001) causing consequences to remote sensitive ecosystems as well as transboundary air pollution (Krupa, 2003). In fact, after deposition, NH_4^+ aerosols can contribute to acidification and eutrophication of sensitive habitats, with consequent changes in soil, plant and animal communities (Sutton et al., 1993; Fangmeier et al., 1994). Thus, since NH_3 is either readily converted to NH_4^+ or subjected to dry deposition, high concentrations are expected only close to the surface and near to emission sources (Ferm, 1998). Although the main source of atmospheric ammonia is agriculture, other sources include industries, landfills, household products, biomass burning, motor vehicles, and wild animals.

Only few studies on ammonia emissions in China are available. The total NH_3 emission from China exceeds that from Europe by at least 27% (Zhao and Wang, 1994). About 80% of NH_3 emission in China is from agriculture. This is the distinguishing feature which is different from developed countries. In China, the biggest contributors are livestock (which contributes about 30%–60%) and the application of nitrogenous fertilizer (which contributes about 17%–47%), followed by 20% for energy, 1% for poultry and 2.5% for human beings (Zhao and Wang, 1994; Oliver et al., 1998; Streets et al., 2003; He et al., 2007). However, estimations of NH_3 emissions have only been started relatively recently and still contain many uncertainties (Bouwman et al., 1997; Battye et

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al., 2003; Goebes et al., 2003). The characteristics of agricultural sources determine the temporal and spatial NH_3 distribution in many locations. The ammonia concentration in northern cities of China is relatively high during the spring and summer period due to farming, while in southern cities no obvious seasonal variation occurs because farmland is extended during all four seasons.

In addition to NH_3, the relative humidity, the temperature, and the insolation are also important factors influencing the formation, temporal and spatial distribution of secondary particles. But the interactions between these factors are so complex that no uniform result is forthcoming. According to studies of the ammonia level in China, in Beijing, some research has shown that the concentration of secondary particles are higher in the winter probably due to the high SO_2 emissions and low wind speed, which aid the formation of SO_4^{2-}. Another study has shown that summer has the highest secondary particle concentration, because of the large NH_3 emissions and sufficient temperature and humidity to ensure the oxidation of SO_2 to SO_4^{2-} (He et al., 2001, 2002).

The contribution of vehicles to non-agricultural NH_3 emissions has been considered to be negligible up to 1995 (Sutton et al., 1995). Recent studies, however, show that ammonia concentration in urban environments has also increased due to over-reduction of nitrogen oxide compounds in catalytic converters in automobiles exhaust and industrial and power station control systems (Sutton et al., 2000). From measurements in a roadway tunnel, Fraser and Cass (1998) concluded that the contribution of motor vehicle emissions had risen from 2% to 15% of the total ammonia emission in the Los Angeles area since the introduction of catalysts. Road side measurements in the UK, in the USA and Europe have shown strong links between ammonia emissions and traffic (Kean et al., 2000; Kirchner et al., 2002; Perrino et al., 2002; Cape et al., 2004). Perrino et al. (2002) found a close link between ammonia and CO emissions in a series of experiments conducted in Rome. These results indicated that petrol-engine vehicles constitute a major source of urban ammonia.

There have been a number of studies of urban ammonia concentrations in recent

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years. Long-term measurements have shown strong daily and seasonal variations in ammonia concentrations which depend mainly on temperature, relative humidity (RH), rainfall, and winds (Yamamoto et al., 1988, 1995; Lee D. S. et al., 1999; Bari et al., 2003; Vogt et al., 2005). Bimodal diurnal variations in NH_3 concentrations with peaks occurring during periods of peak traffic have been observed in some studies (Kirchner et al., 2002; Perrino et al., 2002; Li et al., 2006), confirming vehicles as a significant source of NH_3. Data about ammonia concentrations in the urban areas of China, especially of Beijing, are very rare. Median ammonia concentrations ranged from 20 to 1 ppb on a monthly basis according to measurements carried out in Asia (Carmichael et al., 2003). Yao et al. (2003) measured NH_3 concentrations in Beijing in summer 2001 and spring 2002. The concentrations were found from 4.6 to 42.4 $\mu g/m^3$ with the highest concentration detected in July. Recent real-time measurements of ammonia were conducted in the Pearl River Delta, China, from 4 October to 4 November 2004 (Hu et al., 2008). During this study the average concentration of NH_3 was 7.3 $\mu g/m^3$.

With increasing concern over the potential environmental damage caused by atmospheric transport and subsequent deposition of NH_3, it is very important to have reliable methods to accurately monitor its pollution level and emission pattern. Such information may then be used effectively to develop potential abatement strategies for NH_3.

Sampling of NH_3 is difficult because it is easily adsorbed on surfaces and is difficult to separate and discriminate from volatile ammonium salts. Annular denuder techniques are considered to be able to overcome these critical sources of error. In general, such systems are designed with a vertically positioned denuder tube to eliminate the sedimentation of particles (Possanzini et al., 1983; Allegrini et al., 1987, 1999; Febo et al., 1989; Perrino et al., 1990). This sampling technique is able to accurately determine gaseous ammonia and particulate ammonium without disturbing the partition existing in the atmosphere at the time of the sampling and without mutual interferent (Perrino et al., 1999, 2002).

We report in this paper the results of some measurements of ammonia concen-

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trations carried out during 2007 in Beijing, China, by using annular denuder based methods. The data are analyzed and presented here to investigate the daily and seasonal variations in ammonia concentrations and also to examine the contribution of traffic to ammonia levels in Beijing. The study is a part of a Sino-Italian collaboration project (Blue Sky of Beijing: Research on Regional Air Pollution Project) and also part of the international collaborative research CAREBEIJING (Campaigns of Air Quality Research in Beijing and Surrounding Region).

2 Experimental

Measurements were carried out in the campus of Peking University, located at North of Beijing (39°59′23″ N, 116°18′19″ E), not very far from Olympic sites in winter, from 23 January to 14 February 2007, and in summer, from 2 to 31 August 2007. The atmospheric ammonia concentrations were determined by means annular diffusion denuders coated with a solution of 1% phosphorous acid in 1:9 water and ethanol (Perrino and Gherardi, 1999) on a 24-h basis starting at midnight. The air samples on a 2-h basis (intensive measurements) were also carried out on 9 and 10 February during the winter period and on 13–15 and 17–21 August and during the summer period. Problems occurred on 9 February between 10:00 and 12:00 in the morning and on 19 August between 22:00 and 00:00, thus data from these events were not considered. The annular denuder sampling method and the analytical procedures were described in several past works (Possanzini et al., 1983; Allegrini et al., 1987, 1999; Febo et al., 1989; Perrino et al., 1990, 2001a; Beine et al., 2001; Ianniello et al., 2002).

After collection, the denuders and filters were extracted and samples were analyzed within 24-h by using Ion Chromatography (IC) (Dionex DX 120 connected with autosampler DX AS50 for anions and DX ICS90 connected with autosampler DX AS40 for cations).

The individual annular denuders placed at PKU site are made of Pyrex glass, 21 cm in length, 3.0 and 3.3 cm in annulus diameter. The sampling flow rate was 15 l/min. The

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sampling volume was about 23.10 m^3 for a 24-h sampling period. In these operative conditions the collection efficiency for ammonia was higher than 99% and the detection limit, based on three times the standard deviations of field blanks, was 0.06 $\mu g/m^3$ for a sampling time of 24 h. Precision of these measurements was 1.22%.

Although this paper was focused on atmospheric ammonia, the denuder system also sampled other gaseous as well as particulate species. In fact, the denuder line consisted of two sodium fluoride coated denuders for the simultaneous collection of HCl and HNO_3, followed by two sodium carbonate coated denuders for the collection of HONO and SO_2. A fifth denuder in the line is coated with phosphorous acid for the collection of NH_3. Downstream of the denuder train a cyclone collects coarse particles (>2.5 µm of cut size at flow rate of 15 l/min), while fine particles (<2.5 µm at flow rate of 15 l/min) are collected on a filter pack set in series. The filter pack consisted of one Teflon, one Nylon filter, and one paper filter impregnated with phosphorous acid. The last two back-up filters were used to measure the volatile ammonium salts indicated with term of evolved salts. The particulate chloride, nitrate, sulphate, sodium, ammonium, potassium, magnesium and calcium coarse and fine fractions were measured and analyzed.

Information about the mixing properties of the lower boundary layer were obtained by means of a Stability Monitor (OPSIS SM200) during the summer period. This instrument collects atmospheric particles and determines their short life radioactivity due to Radon decay products, providing 1-h interval radioactivity data. From the study of the temporal trend of natural radioactivity and of its time derivative one can gather important information about the mixing properties of the lower atmosphere and about its ability to dilute atmospheric pollutants (Perrino et al., 2001b).

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3 Results and discussion

3.1 Seasonal variation

The temporal patterns of gaseous ammonia determined by means of the diffusion lines in the winter and summer periods are reported in Fig. 1. Table 1 shows summary statistics for NH_3 concentrations ($\mu g/m^3$) and air temperature (T) values (°C) measured during the two sampling periods in Beijing.

The seasonal variations are evaluated applying the paired t-test to determine the significance at the 0.05 level ($p \leq 0.05$) of differences among the mean of components by examining the amount of variation between the samples. NH_3 exhibited a distinct and significant ($p < 0.001$) seasonal variation with higher concentrations in summer than in winter (Fig. 1). This seasonality has also been observed by other papers and is in agreement with the temperature dependence of NH_3 emissions from animal waste, natural and fertilized soils, and vegetations (Langford and Fehsenfeld, 1992; Langford et al., 1992; Yamamoto et al., 1995, Asman et al., 1998; Lefer et al., 1999; Aneja et al., 2000; Robarge et al., 2002; Pryor et al., 2001), which are at low values during winter. NH_3 temporal patterns, with higher values during warm conditions and lower values during the cold months, confirm that the air temperature is one key parameters determining seasonal cycle in ammonia concentrations in Beijing. Thus, in agreement with past studies, higher ammonia emissions occurred when air temperature increased, suggesting intense local sources for NH_3 during the summer season.

3.2 Diurnall variation

3.2.1 Winter

During the intensive measurements at PKU in Beijing, the wind speed reached a maximum value of 8.8 m/s on 9 February at 14:00 and the wind blew mainly from north-west (53%) (Fig. 2). The air temperature increased at 08:00 reaching maxima values be-

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tween 12:00 and 14:00 of about 13.98 °C. In addition, the solar radiation also reached higher values of about 13 W/m^2 on 9–10 February at 13:00 while the relative humidity decreased during all the intensive measurements starting on 9 February at 06:00 in the morning.

The mean level of ammonia within ± one standard deviation for the entire data ($N = 23$) was 5.22±3.75 µg/m^3. Ammonia hardly showed any diurnal variation in winter period (Fig. 3), in agreement with past studies (Lefer et al., 1999; Danalatos and Glavas, 1999; Walker et al., 2004). Data were grouped into day (between 06:00 and 18:00) and night (between 18:00 and 06:00) periods. Day and night hours were based on sunrise and sunset times within each sampling period. On applying t test to day and night samples, diurnal variation was not found to be statistically significant ($p = 0.18$). Having a short lifetime of about one day, ammonia would be expected to peak in the middle of the day as higher emissions are expected in that part of the day. This occurred on 9 and 10 February between 08:00 and 10:00 but higher ammonia emissions occurred also in other periods of the day, as measured after sunset and night, during the intensive measurements. Night time high ammonia levels can be attributed to stable atmosphere during the night time (Cadle et al., 1982; Perrino et al., 2002) while the higher mixing height in the middle of the day balanced the higher ammonia emissions resulting in little diurnal variation (Singh et al., 2001).

The source of NH_3 is at ground level, thus NH_3 concentrations might be generally lower at higher wind speeds because of turbulent diffusion. Previous studies have reported an inverse relationship between ground-level concentrations of trace gases, such as ammonia, and wind speed (Katsoulis, 1996; D. S. Lee et al., 1999; Robarge et al., 2002). This inverse relationship between natural-log transformed NH_3 concentrations and wind speeds (Robarge et al., 2002) did not occur at significant level ($R^2 = 0.18$, $p < 0.001$) considering concentrations measured only on 9 February 2007. In addition, highest NH_3 concentrations were also associated with low wind speeds during this day.

Besides, the diurnal pattern of ammonia did not show a clear and well-defined tem-

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perature and humidity dependence during the winter field campaign, as observed elsewhere (Langford and Fehsenfeld, 1992; Yamamoto et al., 1995; Burkhardt et al., 1998; Horvath and Sutton, 1998; Pryor et al., 2001; Olszyna et al., 2005; Vogt et al., 2005). This may reflect the influence of other factors, such as local sources and wind direction, in determining ambient concentrations of NH_3 (Burkhardt et al., 1998; Huber and Kreutzer, 2002; Vogt et al., 2005). Figure 3 shows also that most of the time, NH_3 was coming nearly from northwest direction (85%). Highest NH_3 concentrations were also associated with these predominant northwest winds, reflecting the large contribution due to agricultural activity and fertilizer use. Thus, wind direction and speed influenced the variability of atmospheric NH_3 concentrations during the winter season in Beijing.

Atmospheric equilibrium of NH_3, HNO_3 and HCl with aerosol containing NH_4NO_3 and NH_4Cl may increase NH_3 gaseous concentrations at higher temperatures, while surface-atmosphere exchange of NH_3 also tends toward emission in warm (and dry) conditions. In fact, the presence of local sources probably explains why the temperature did not determine NH_3 concentrations in Beijing.

While agriculture is the main source of atmospheric ammonia in Beijing, the contribution of vehicles, equipped with catalytic converters, to non-agricultural NH_3 emissions has recently been considered. 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 non-reactive pollutants mainly emitted by motor-vehicle exhausts (Perrino et al., 2002), such as carbon dioxide (CO) and nitrogen oxides (NO_x). CO data were not collected during the winter period, but we can consider the time trend of NO_x since it has been estimated that the transport sector is responsible for about 35–40% of NO_x emissions in Beijing (He et al., 2002; Meng et al., 2008, Chak and Yao, 2008). The scatter plot of NH_3 concentration vs. NO_x concentration during the intensive winter measurements is reported in Fig. 4. A good and significant (at the 99.9% confidence level, $p < 0.001$) linear correlation of the two data sets ($R^2 = 0.65$) can be seen, supporting the hypothesis that the traffic is also an important source of NH_3 in this season within the city. For the NH_3 and NO_x data, the best correlation ($R^2 = 0.80$, $p < 0.001$)

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was obtained considering concentrations measured on 9 February during the formation of the highest peaks of ammonia and nitrogen oxides (Fig. 4). However, the amount of scatter about these regression lines indicates that other ammonia sources not linked to NO_x are also significant. These are due to human and agricultural sources and solvent use.

These results confirm that NH_3 evolution is governed by at least three main parameters: wind direction, wind speed and traffic emissions.

3.2.2 Summer

During the intensive measurements the wind speed reached a maximum value of 3 m/s at 18:00 in the afternoon, the wind blew mainly from south (36%) and northwest (25%) (Fig. 5). In addition, the air temperature and relative humidity reached a value of about 35 °C and 90%, respectively.

The mean level of ammonia within ± one standard deviation for the entire data ($N = 47$) was 31.84±16.57 µg/m^3. As in winter, the diurnal variation of ammonia is not statistically significant ($p = 0.53$) in the summer (Fig. 6). Usually, broad peaks of NH_3 concentrations were observed in the morning (between 06:00, and 10:00), as higher ammonia emissions occurred in summer, with one exception of 19 August at 20:00 in the evening. As suggested by other studies, the transport of NH_3 from downwind sources was the cause of higher daytime concentrations, while dry deposition and conversion to aerosol may exceed the contribution from transport at night, resulting in higher concentrations during the day. However, the diurnal pattern of ammonia did not show a clear and well-defined temperature dependence during the summer field campaign, as it was in the winter.

In addition, ammonia concentrations showed a dependency of wind direction. The NH_3 concentrations from northwest, southwest and south sector were observed nearly 41%, 17% and 38%, respectively, of the sampling period. The highest ammonia concentrations were principally observed when the wind was from the northwest during low wind conditions (Fig. 6), reflecting the large contribution due to agricultural activ-

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ity and fertilizer use. In fact, a moderate but a significant linear correlation ($R^2 = 0.29$, $p < 0.001$) was detected between natural-log transformed ammonia concentrations and wind speeds (Robarge et al., 2002).

These higher ammonia values during the day can be also attributed to stable atmosphere conditions. The analysis of the temporal pattern of natural radioactivity (Fig. 6) shows that the convective mixing of the atmosphere occurs between the late morning (12:00–13:00 a.m.) of the previous day and the early morning of the subsequent day (03:00–04:00 a.m.). Subsequently, a rapid increase of natural radioactivity determines atmospheric stability with high values at 06:00 and at 08:00 in the morning. In these conditions, pollution events are generally favoured. This implies that most of the traffic emission is injected into a stagnant atmosphere causing the sharp increase in the concentration of ammonia, which reached the remarkable value of 105.67 µg/m^3 (18 August 2007), one of the highest values during the intensive measurements. During the same hours CO and NO_x concentrations reached the levels of 2.15 mg/m^3 and 112.6 µg/m^3 (Fig. 6), respectively, and this is an indication of a common origin of these pollutants, i.e., traffic emission (Perrino et al., 2002; Edgerton et al., 2007).

The data of Fig. 6 show that NH_3, CO and NO_x had similar temporal patterns, but the correlations between these species were not good. A weak but significant linear correlation occurred between NH_3 and CO ($R^2 = 0.18$, $p < 0.001$) (Fig. 7). For the NH_3 and NO_x data, the correlation did not occur (Fig. 8). However, for the CO and NO_x data, the best relationships, with a correlation coefficients of 0.72 (Fig. 7) and 0.39 (Fig. 8), respectively, were obtained considering concentrations measured only on 18 August 2007 during the formation of the higher peaks of ammonia and low winds supporting the hypothesis that the traffic is also a important mobile source of NH_3. However, the correlation between NH_3 and NO_x are weaker than that in the winter, suggesting that other, non-traffic sources, became significant. The higher temperatures in the summer will increase ammonia emission from agricultural sources, resulting in the breakdown in the relationship between the two gases.

In some studies, increased NH_3 concentrations have also been attributed to the dis-

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sociation of particulate ammonium nitrate (Langford et al., 1992; H. S. Lee et al., 1999; Possanzini et al., 1999). Volatilization of NH_3 from the aerosol phase may be significant enough to dominate over traffic emissions during the summer (Whitehead et al., 2007) and mask any correlations with traffic related pollutants. It is known that volatile ammonium salts collected on the Teflon filter (NH_4Cl and NH_4NO_3) dissociate to HCl and HNO_3, a phenomenon which depends mainly upon meteorological conditions (air temperature and relative humidity), on the aerosol composition, and on the acidity of the particles. In this work the gases evolved from the front Teflon filters were recovered on the back-up Nylon and phosphorous acid-impregnated filters. Data from 2h sampling over the 17–21 August period showed that Teflon filters exhibited a nearly complete depletion of nitrate and chloride (>90%) which were recovered on Nylon filters. This indicated that nitrate and chloride were almost entirely associated to ammonium. Indeed, a comparison of µmol amount of NH_4^+ with µmol amounts of anions (NO_3^-+Cl^-) determined on the back-up filters showed a good correlation (R^2=0.80, $p < 0.001$). However, the diurnal variation in NH_3 concentrations had a similar trend as for NH_4^+, with one exception of 17 August. During this day, the formation of aerosol NH_4^+ lead to the decrease of NH_3 concentrations and vice versa. This behaviour could be explained with the displacement of the thermodynamic equilibrium between ammonium salts and their gaseous precursors. While for the other days (18–21 August), the fact that the NH_3 and NH_4^+ exhibited similar patterns is due to dissolution of a significant fraction of NH_3 in humid aerosols under high relative humidity conditions (Hesterberg et al., 1996; Krupa, 2003; Trebs et al., 2004, 2005; Hu et al., 2008). In fact, the concentrations of ammonia and ammonium reach the maximum values at the same time (between 06:00 and 10:00). Possible evaporation of NH_3 from wet surfaces due to temperature increase just after sunrise, when relative humidities were still high might have caused a significant fraction of gaseous NH_3 to dissolve in still deliquescent aerosols, therefore enhancing aerosol NH_4^+.

A more detailed study of the behaviour of ammonia and ammonium salts in the atmosphere may be carried out considering the mass balance on back-up filters. In fact,

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in principle we should find equimolecular amounts of anions ($Cl^- + NO_3^-$) and of evaporated ammonia (NH_{3ev}) determined on the back-up filters. On the contrary, the results reported in Fig. 9 show that during the intensive measurements in the summer period, ammonia frequently exceeded the sum of chloride and nitrate. This unbalance can be regarded as an additional phenomenon which adds ammonia to the dissociation of ammonium nitrate and chloride; a possible explanation is the presence of other anions (e.g. organic matter) or of gaseous ammonia adsorbed or dissolved in deliquescent aerosol (NH_{3ads}), as said before, which is desorbed from the collected fine particulate matter during the sampling and is then recovered on the back-up acid-coated filters, as already seen in previous studies (Perrino and Gherardi, 1999). This unbalanced amount of ammonia, ranged from 0.06 µmol/m^3 (1.15 µg/m^3) to 0.72 µmol/m^3 (13 µg/m^3) with an average value of about 0.26 µmol/m^3 (4.75 µg/m^3) during the summer sampling period. The value of 0 indicated that ammonia is in balance on back-up filters (Fig. 9). The unbalanced ammonia, clearly adsorbed on particles, can be a further source of atmospheric ammonia during specific meteorological conditions such as dry and warm and windy environments.

These results confirm that NH_3 evolution is governed in summer by at least four main parameters: wind direction, wind speed, atmospheric mixing and traffic emissions.

4 Conclusions

The atmospheric concentrations of NH_3 have been measured at an urban site (Peking University) in Beijing in the winter and summer of 2007. All data were analyzed to investigate temporal variations, meteorological effects and special features of the gas-particulate equilibrium. According to the results, the following conclusions were reached:

– The NH_3 concentrations showed regular seasonal variations, having significantly higher summertime concentrations. The seasonal trends seemed to be largely

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dominated by air temperature.

- The NH_3 concentrations didn't show any diurnal variation in both winter and summer seasons.
- The effects of wind direction and of the atmospheric mixing on the NH_3 concentrations were the two most significant meteorological parameters. The NH_3 concentrations were slightly affected by wind speed.

Moderate correlations were obtained between NH_3 and gas pollutants, such as NO_x and CO, indicating an influence by traffic emissions.

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Table 1. Statistics for NH_3 and T during the winter and summer campaign at PKU site.

	Winter		Summer	
	NH_3 (µg/m^3)	T (°C)	NH_3 (µg/m^3)	T (°C)
N of cases	23	23	30	30
Minimum	0.20	−0.71	14.87	22.19
Maximum	14.08	8.06	44.38	32.37
Median	5.12	3.05	24.33	28.80
Mean	5.47	3.51	25.39	28.27
Standard Dev	3.75	2.88	6.91	2.46

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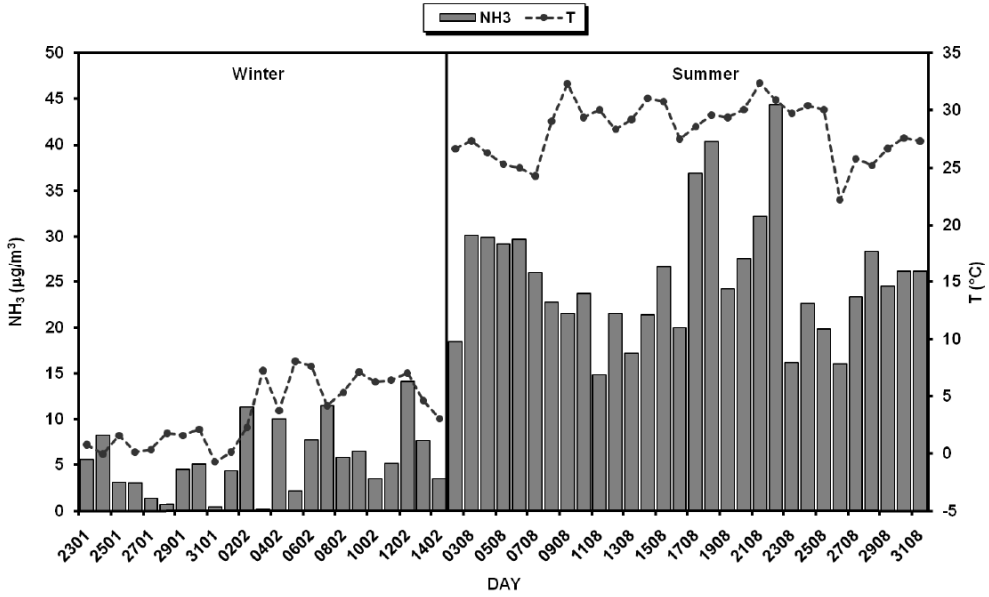

Fig. 1. Temporal trend of ammonia during the winter and summer campaigns in Beijing.

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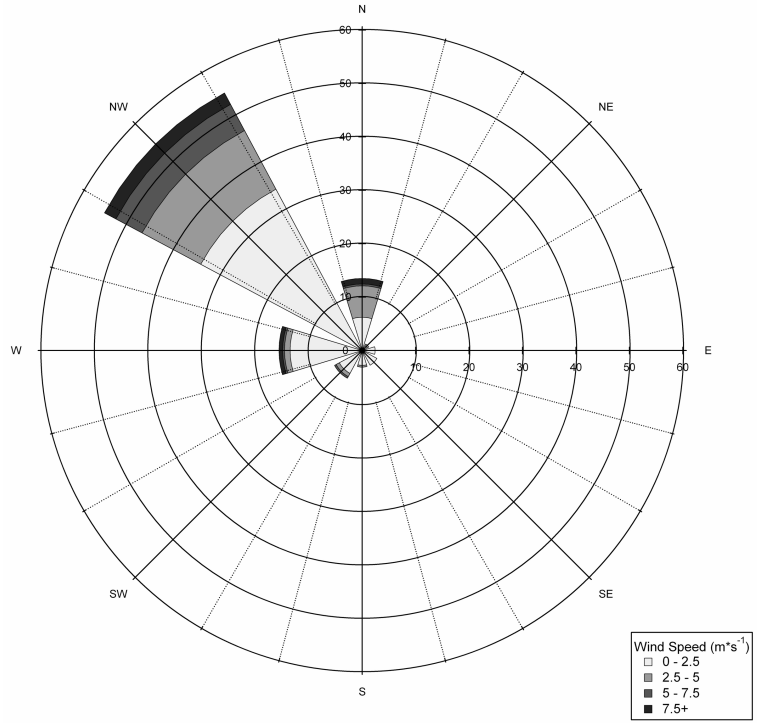

Fig. 2. Wind plot showing the frequency distribution of wind directions and speeds (grey scale) of the intensive winter measurements. The radius axis represents the occurrence from 0% to 60%.

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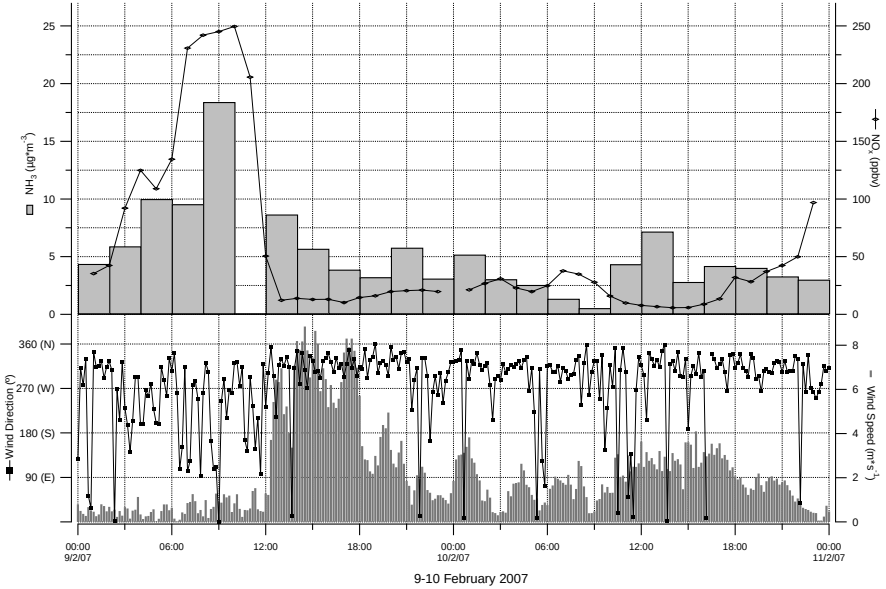

Fig. 3. Diurnal trends of NH_3, NO_x, wind speed and direction during the intensive winter measurements.

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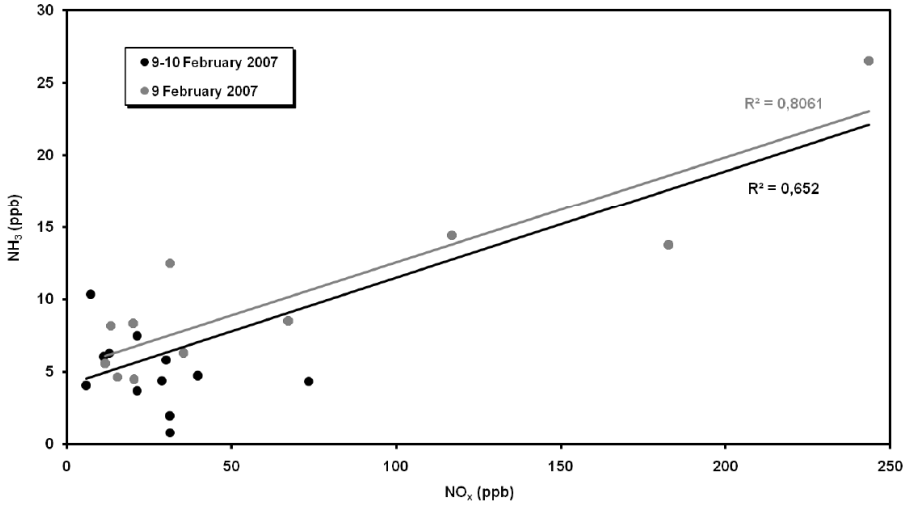

Fig. 4. Relationship between NH_3 and NO_x during the intensive winter measurements.

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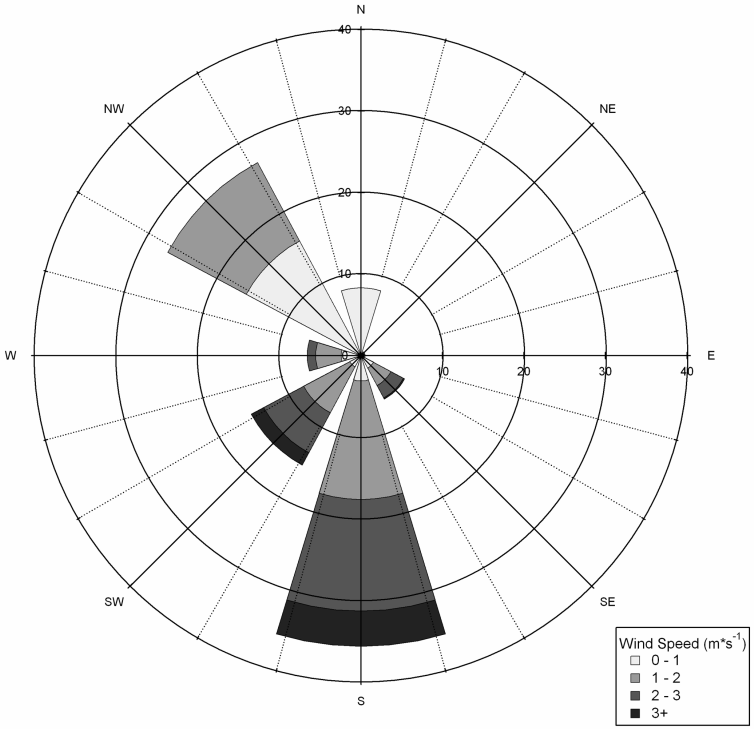

Fig. 5. Wind plot showing the frequency of wind directions and speeds (grey scale) of the intensive summer measurements. The radius axis represents the occurrence from 0% to 40%.

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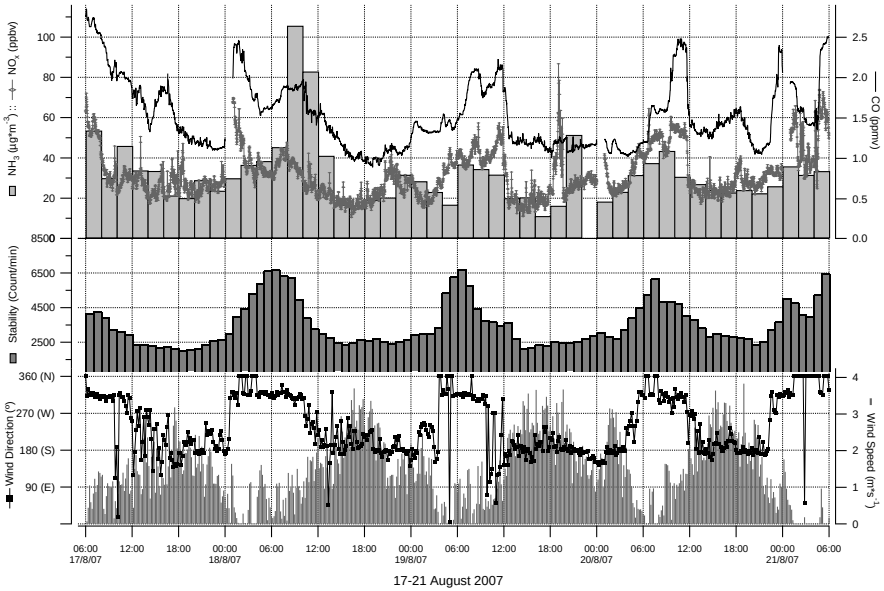

Fig. 6. Diurnal trends of NH_3, NO_x, CO, atmospheric stability, wind speed and direction during the intensive summer measurements.

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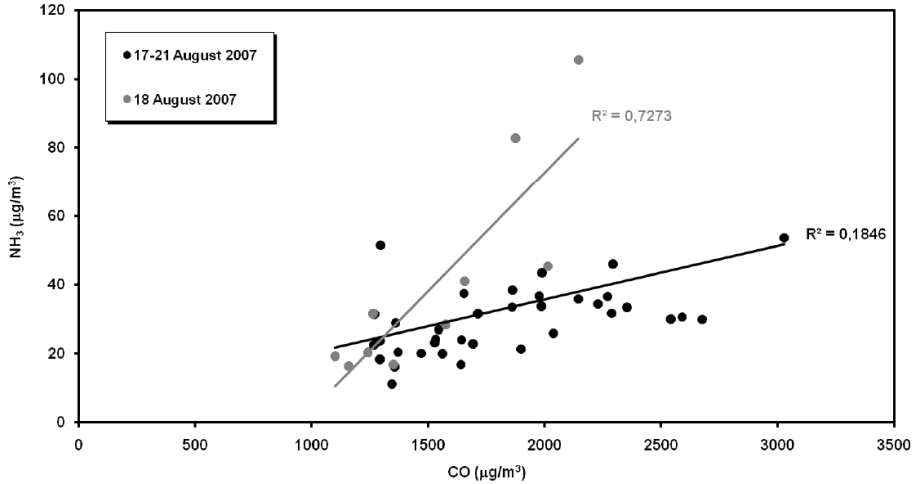

Fig. 7. Relationship between NH_3 and CO during the intensive summer measurements.

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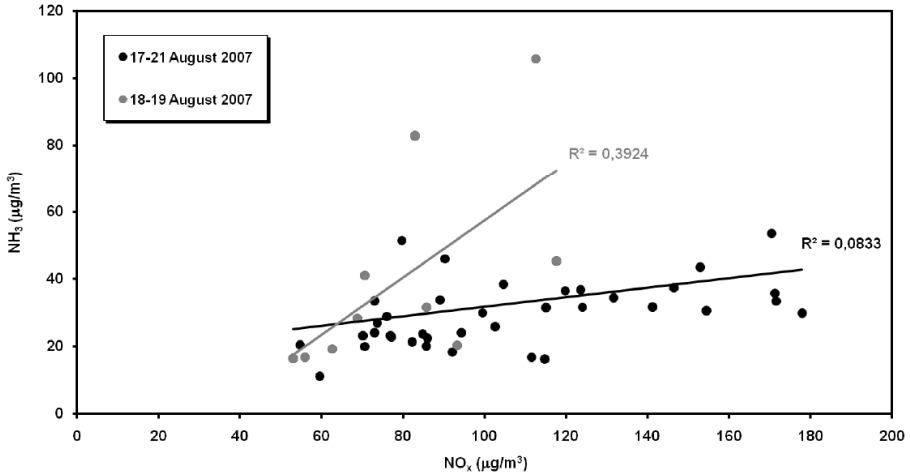

Fig. 8. Relationship between NH_3 and NO_x during the intensive summer measurements.

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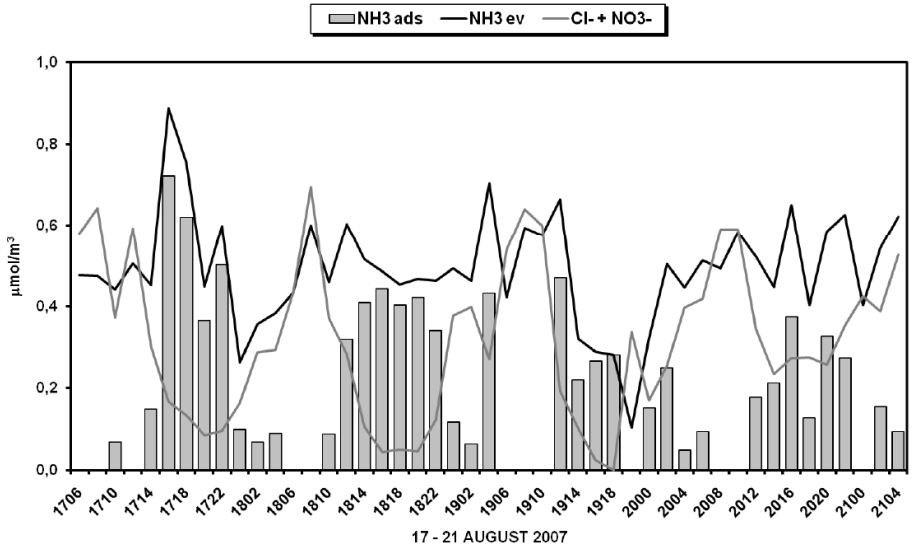

Fig. 9. Comparison between the amounts of evaporated ammonia (NH_{3ev}) and of its anions ($Cl^- + NO_3^-$) on the back-up filters and trend of unbalanced ammonia ($NH_{3ads\ on\ particulate}$) during the intensive summer measurements at PKU site.

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