Letter of Responses

Reply to anonymous referee 1's comments (C4524)

We thank the reviewer (Anonymous Referee #2) for their helpful comments and suggestions which will help improving the original paper. Below are our itemized responses.

General comments: The experimental work of NH3 measuring is very seriously and well described. This results are very interesting and are very usefully e.g. for modellers to evaluate their results and so on. There are some problems, however, with the manifold attempts to declare the experimental results. These explanations are often not very good reasoned. Because the complex relations between emissions (biogenic and anthropogenic), transport, transformation (especially gas to particle conversion), deposition etc. for gaseous compounds (here first of all ammonia) and particulate matter, these relations can not explained by knowledge of some concentrations and some meteorological aspects. To this, simulations are necessary with a state of the art atmospheric-chemical-transport-model. A special problem of the paper is first of all, that only two short episodes are investigated, one in summer and one in winter. So we have no statistically significant and robust results for discussion. One can accept the author's conclusion: 1) The NH3 concentrations showed regular seasonal variations, having significantly higher summertime concentrations. The seasonal trends seemed to be largely dominated by air temperature. The following conclusions are valid but their explanations are not well reasoned by the experimental results: 2) The NH3 concentrations didn't show any diurnal variation in both winter and summer seasons. 3) The effects of wind direction and of the atmospheric mixing on the NH3 concentrations were the two most significant meteorological parameters. The NH3 concentrations were slightly affected by wind speed. 4) Moderate correlations were obtained between NH3 and gas pollutants, such as NOx and CO, indicating an influence by traffic emissions. Before publication these conclusions must be better reasoned (if possible?) or the paper should be concentrated on the experimental results and only make a few educated guesses.

Reply:

As also replied to comments by referee #1, we followed your suggestions for point 1 in general comments discussing more detailed our experimental results. However, in this paper we cited all available references for ammonia measurements and the majority of them use two sampling periods (one winter and one summer period) to determine seasonal variations of NH_3 at Beijing. The ammonia concentration in northern cities, as Beijing, is relatively high during the spring and summer farming period, while in southern cities no obvious seasonal variation occurs because the farmland is worked during all four seasons. Other studies have carried out that NH_3 concentrations showed distinct seasonal variations, with highest concentrations in summer and lowest concentrations in winter. Source strength and removal efficiency can explain the seasonal variations of NH_3 concentrations. In summer, high temperatures will favor ammonia volatilization from urea and/or ammonium bicarbonate applied to crops. High temperatures in summer will also favor NH_3 emission from other sources, such as animal housing, landfill, laystalls and farmers' toilets, animal manure, natural and fertilized soils, and vegetation. Therefore, atmospheric ammonia concentrations were highest in summer at Beijing site. In winter, no fertilizer was applied and the temperature was very low at Beijing site. So less ammonia volatilized and hence the atmospheric NH_3 concentrations were low. Yet, if the references cited and discussed in this paper don't provide support for our measurements or don't demonstrate this seasonality for NH_3 although they also refer to only two periods, we will agree to replace the sentence (p.14216, 3.1, 9/11) "NH3 exhibited a distinct and significant ($p < 0.001$) seasonal variation with higher concentrations in summer than in winter (Fig. 1)" with "NH_3 exhibited a distinct and significant ($p < 0.001$) temporal variation with higher concentrations in summer than in winter (Fig. 1)". Thus, we will replace the words "seasonality" or "seasonal" with "temporal variation". Thus, we will modify the section 3.1 (after line 5) as follows:

"The temporal 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 ($p < 0.001$) variation with higher concentrations in summer than in winter (Fig. 1). This difference in NH_3 concentrations 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. The characteristics of these sources determine the temporal and spatial NH_3 distribution. Source strength and removal efficiency can explain the seasonal variations of NH_3 concentrations. In summer, high temperatures will favor ammonia volatilization from urea and/or ammonium bicarbonate applied to crops. High temperatures in summer will also favor NH_3 emission from other sources, such as animal housing, landfill, laystalls and farmers' toilets, animal manure, natural and fertilized soils, and vegetation. Therefore, atmospheric ammonia concentrations were highest in summer at Beijing site. 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 at Beijing."

As also replied to comments by referee #1, we followed your suggestions for points 2 and 3 in general comments discussing more detailed our experimental results. Thus, we will modify and add relevant sentences in sections 3.2.1 and 3.2.2 such that the conclusions on the NH_3 diurnal pattern are better supported by analysis of our data. Thus, we will modify section 3.2.1 and 3.2.2 as follows:

Section 3.2.1 (after the sentence p. 14218, 3.2.1, 4/6)

"However, a weak but significant linear correlation ($R^2 = 0.32$, $p = 0.01$) can be obtained between NH_3 and air temperature considering ammonia concentrations measured from 12:00 on 9 February, when the air temperature reached maxima values (12:00 – 16:00 on two days), to the end of intensive measurements on 10 February. This weak temperature dependence of NH_3 reflect the small influence of the emission sources from agricultural activity which increase as the temperature rises. Ammonia emissions from animal manure, natural and fertilized soils, and vegetation will increase with temperature owing to the temperature dependency of aqueous-phase partitioning between NH_3 and NH_4^+ in these systems, as well as the atmospheric equilibrium between NH_3 with volatile ammonium nitrate. In fact, during this period the winds came principally from northwest direction (73%) (Fig. 2b) coinciding with the direction of agricultural areas such as Xibeiwang and Changping District which are located at the northwest suburb of sampling site (Shen et al., 2009; Zhang et al., 2010). The temperature dependence of NH_3 disappeared from 00:00 to 12:00 on 9 February with prevailing winds from southeast and southwest (60%) (Fig. 2b) and lower temperatures. This different behaviour may be explained from prevalence of local sources, such as traffic emissions, in determining the atmospheric NH_3 concentrations during this period.

While agriculture is the main source of atmospheric ammonia in Beijing, 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 influencinf ammonia concentrations at urban locations and near roads (Sutton et al., 2000; Kean et al., 2000, Heeb et al., 2008). Also Beijing city is configured such that it is served by several ring roads with heavy traffic (Fig. 3b). Fig. 3a and 3b show Beijing city, measurement site and surrounding regions, where are the major NH_3 emission sources. 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 nitrogen oxides (NO_x) and carbon monoxide (CO), throughout this winter period. The time series of NH_3, NO_x, CO, wind direction, wind speed, temperature and relative hunidity are shown in Figure 3. Both CO and NO_x are commonly used as traffic emission indicators (He et al., 2002; Meng et al., 2008, Chak and Yao, 2008). 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 NOx emissions, respectively. They found that 74% of the ground NOx was due to vehicular emissions while power plants and industrial sources only contributed 2% and 13%, respectively. In addition, in Beijing and Guangzhou, automobile pollution contribution in terms of CO was estimated to be more than 80% with two peak vehicle pollution levels occurring during each day, one from about 8:00–10:00 and the other from 15:00–17:00 during the rush hours (Hao et al., 2000).

NO_x peaks were observed between 08:00 and 12:00 on 9 February (Fig. 4). Wind from the southeast and southwest was dominant at the sampling site on 9 February, while wind from the northwest dominated on 10 February. Wind speeds on 9 and 10 February ranged from 0.02 to 8.85 m/s and from 0.06 to 4.10 m/s, respectively. However, on 9 February the overall NO_x level was significantly higher (from 11.60 to 243.55 ppb) than that on 10 February (from 5.85 to 73.40 ppb). The locations of the major NO_x sources, including local roads (motor vehicles), expressways, and power plants, which are six and principally coal-fired in Beijing, are located from the east to the southwest of the sampling site (Lee et al., 2009). Thus, the weak wind speeds between 00:00 and 12:00 (0.02 – 1.53 m/s) and southeasterly and southwesterly wind directions on 9 February, in combination with the locations of the sources of NOx emissions, resulted in higher NO_x concentrations between 08:00 and 12:00 due to emissions from Friday traffic during this daytime. Instead, the high wind speeds (0.30 – 3.83 m/s) and northwesterly wind direction on 10 February resulted in lower NO_x concentrations at the sampling site. In fact, NO_x concentration was about 31.55 ppb at 08:00 on 10 February, which is about eight times lower than that recorded at the same time of day on 9 February (243.55 ppb). These differences in NO_x concentrations between two days might reflect the characteristic of Friday traffic (on 9 February) and the wind contitions, which were marked by low winds and prevailing wind direction from the center of Beijing toward the sampling site (60% from southeast and southwest). The scatter plot of NH_3 concentration vs. NO_x concentrations during this two days (Fig. 5) showed a good and significant (at the 99.9% confidence level, $p < 0.001$) linear correlation of the two data sets ($R^2 = 0.65$), supporting the hypothesis that the traffic is also an important source of NH_3 in this season within the city. However, for the NH_3 and NO_x data, the best correlation ($R^2 = 0.80$, $p < 0.001$) was obtained considering concentrations measured on 9 February during the formation of the highest peaks of ammonia and nitrogen oxides due to rush-hour traffic. However, the amount of scatter about these regression lines indicates that other ammonia sources not linked to NOx are also significant. In a city centre location, these will largely be human sources (Whitehead et al., 2007). In contrast, the correlation between NH_3 and NO_x did not occur considering concentrations measured only on 10 February during high wind speeds and northwesterly wind direction from where no major sources of NOx are located. These results, in combination with weak temperature dipendence of NH_3 during on 10 February, as said above, suggest that NH_3 concentrations were influenced mainly by non traffic-sources such as agricultural emissions.

In addition, the same findings were also observed comparing the ammonia concentrations with those of CO (Fig. 4). CO peaks were observed between 08:00 and 10:00 on 9 February. However, on 9 February the overall CO level was significantly higher (from 0.16 to 6.17 ppm) than that on 10 February (from 0.05 to 1.62 ppm) due to time period and wind conditions, as said above for NOx. The scatter plot of NH_3 concentration vs. CO concentrations during this two days (Fig. 6) showed a good and significant (at the 99.9% confidence level, $p < 0.001$) linear correlation of the two data sets ($R^2 = 0.67$), supporting the hypothesis that the traffic is also an important source of NH_3 in this season within the city. However, for the NH_3 and NO_x data, the best correlation ($R^2 = 0.84$, $p < 0.001$) was obtained considering concentrations measured on 9 February during the formation of the highest peaks of ammonia and carbon monoxide due to rush-hour traffic. In contrast, the correlation between NH_3 and CO did not occur considering concentrations measured only on 10 February during high wind speeds and northwesterly wind direction. These results, in combination with weak temperature dipendence of NH_3 during on 10 February, further show that NH_3 concentrations were influenced mainly by non traffic-sources such as agricultural emissions.

Thus, the presence of local sources, such as traffic emissions, on 9 February and non-traffic sources on 10 February probably explains why the temperature didn't determine NH_3 concentrations in Beijing and why a diurnal cycle of NH_3 has not been observed because it showed high variability due to variation in emissions during two days of winter intensive measurements.

To help interpret further in general terms the source regions affecting the sampled ammonia and, thus, to identify the origin and transport pathway of large-scale air masses, 24-h backward trajectories arriving at the sampling site were calculated for two days of winter intensive measurements (Fig. 7). The trajectories at 100 m arrival height above ground level were computed every 2 h (from 01:00 on 9 February to 23:00 on 10 February, local time) using the NOAA ARL HYSPLIT trajectory model (htpp://ready.arl.noaa.gov./HYSPLIT.php). The Fig. 7 shows dominant transport of air masses from northwest (83%) of Beijing coinciding with the direction of Inner Mongolia and agricultural areas such as Hebei province, which completely surrounds Beijing and Tianjin municipalities. Actually, intensive agriculture is concentrated in the North China Plain which includes five provinces (Hebei, Henan, Shangdong, Jiangsu and Anhui) and two municipalities (Beijing and Tianjin). Of the total agricultural ammonia emissions in the North China Plain, the Hebei, Henan and Shandong provinces take the larger part (Zhang et al., 2010). Contributions of NH_3 emissions from livestock and fertilizer activities were also found in Inner Mongolia (Klimont, 2001; Ju et al., 2004). Beijing is downwind of Shanxi, which is one of the largest coal mining and coal-fired power generation provinces in China, which can emit large amounts of NH_3 (Meng et al., 2010). In addition, these air masses passing the northwestern regions arrived faster (8.17 – 15.70 m/s) and, thus, they had less time to accumulate ammonia. Instead, as said above, on 9 February local wind speeds, especially between 00:00 and 12:00, coming principally from southeast and southwest of Beijing arrived slower and, thus, local air masses had much time to accumulate pollutants. This suggests that NH_3 received the largest impacts from local emissions in the city of Beijing, where morning peaks of NH_3, which correlated with morning traffic emissions, were observed.

In contrast, on 10 February local high wind speeds from the northwest dominated in Beijing, where the correlation between NH_3 and both CO and NO_x did not occur, in combination with temperature dipendence of NH_3. This suggests a possible and further contribution of regional and agricultural sources, located to the northwest of Beijing, to the ammonia concentrations observed in Beijing during on 10 February.

These results reveal that during the winter NH_3 concentrations are influenced by meteorological conditions (wind direction, wind speed and, sometimes, temperature), local and regional sources in the winter 2008 in Beijing. Further modeling studies are needed to quantify the contribution of local versus regional sources to the atmospheric ammonia variations.”

Section 3.2.2 ((after the sentence p. 14219, 3.2.2, 18/21)

“The highest ammonia concentrations were principally observed when the wind was from the northwest during low wind conditions (Fig. 8), reflecting the large contribution due to agricultural activity and fertilizer use. 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).

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. The temperature dependence of NH_3 can be examined further by filtering all the data by hours of day and for only particular hours during all days of intensive summer measurements (from 06:00 to 12:00 on 17 August, from 00:00 to 10:00 on 18 August, from 02:00 to 10:00 on 19 August, from 02:00 to 12:00 on 20 August, from 02:00 to 06:00 on 21 August) there is a weak but significant correlation between temperature and NH_3 concentration (at the 99.9% confidence level, $R^2 = 0.22$, $p = 0.03$) with prevailing winds from northwest. As said for winter period, this weak temperature dependence of NH_3 reflect the influence of the emission sources from agricultural activity coming from northwest suburb of Beijing (Shen et al., 2009; Zhang et al., 2010). The temperature dependence of NH_3 disappeared for the other hours of every day with prevailing winds from south and southwest. This different behaviour may be explained from prevalence of local sources, such as traffic emissions, in determining the atmospheric NH_3 concentrations during this summer period.

The data of Fig. 8 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 ($R^2 = 0.18$, $p < 0.001$) (Figure 6) for all sampling period (17-21 August 2007). For the NH_3 and NO_x data, this correlation did not occur (Figure 5). However, for the CO data, the best relationships with correlation coefficients of 0.73 ($p < 0.001$), 0.69 ($p = 0.03$) and 0.33 ($p = 0.03$) were obtained considering concentrations measured only on 18, 19 and 20-21 August 2007, respectively, during the formation of the higher peaks of NH_3 and CO supporting the hypothesis that the traffic is also a important mobile source of NH_3. In addition, for the NO_x data, the best relationships with correlation coefficients of 0.39 ($p < 0.001$), 0.32 ($p = 0.03$) and 0.70 ($p = 0.001$) were also obtained considering concentrations measured for the same days, respectively, in correspondence with the highest concentrations of NH_3 and NO_x. NO_x and CO peaks were observed between 06:00 and 10:00 during all days, in combination with northwesterly wind direction and low wind speeds (0.3 – 1.2 m/s). Winds from the south were dominant at the sampling site for the other hours of day, in combination with the locations of the sources of NOx and CO emissions. However, the amount of scatter about these regression lines indicates that other ammonia sources not linked to NOx and CO are also significant. In addition, the correlations between NH_3 and both NO_x and CO were 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 these gases.

The same findings were also observed comparing the ammonia concentrations with those of $PM_{2.5}$ which accounts for 90% of total PM emissions from on-road vehicles in Beijing (Zheng et al., 2005). $PM_{2.5}$ peaks were observed between 08:00 and 10:00 during all days (Fig. 8). A weak but significant linear correlation occurred between NH_3 and $PM_{2.5}$ ($R^2 = 0.17$, $p = 0.004$) (Fig. 9) for all sampling period. However, for the $PM_{2.5}$ data, the best relationships with correlation coefficients of 0.80 ($p < 0.001$), 0.60 ($p = 0.009$) and 0.30 ($p = 0.03$) were obtained considering concentrations measured only on 18, 19 and 20-21 August 2007, respectively, during the formation of the higher peaks of NH_3 and $PM_{2.5}$ supporting the hypothesis that the traffic is also a important mobile source of NH_3.

The highest ammonia values during the day can be also attributed to stable atmosphere conditions. The analysis of the temporal pattern of natural radioactivity (Fig. 8) 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 6:00 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 $\mu g/m^3$ (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 $\mu g/m^3$ (Figure 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).

In some studies, increased NH_3 concentrations have also been attributed to the dissociation of particulate ammonium nitrate (Langford et al., 1992; Lee H. S. 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^-) nitrate 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^+ leads 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 and 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, 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. 10 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 the ammonia is in balance on back-up filters (Fig. 10). 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.

As in winter, to help interpret further in general terms the source regions affecting the sampled ammonia and, thus, to identify the origin and transport pathway of large-scale air masses, 24-h backward trajectories arriving at the sampling site were also calculated for five days of summer intensive measurements (Fig. 11). The trajectories were computed every 2 h (from 07:00 on 17 August 2007 to 05:00 on 21 August, local time). The Figure 11 shows dominant and regional transport of air masses from south (53%) and southeast (15%) of Beijing, which are the most frequent in summer time, coinciding with the direction of Hebei province and Tianjin municipalities, which are not only agricultural areas but also quite polluted by industrial, vehicular, coal mining and power generation, and biomass burning emissions (Xia et al., 2007; Street et al., 2007; Chen et al., 2009; Meng et al., 2009; Zhang 2010). In addition, these air masses passing the southern regions were relatively slow (1.63 – 3.85 m/s) and, thus, they had much time to accumulate ammonia in the Beijing area, contributing greatly to the air pollution. The urban area itself is a major source for traffic emissions. This suggests that the atmosphere of Beijing received transported polluted air on locally produced NH_3.

Thus, the presence of local and regional sources during summer intensive measurements probably explains why the temperature didn't determine NH_3 concentrations and a diurnal cycle of this gas in Beijing was not observed due to variation in emissions.

These results reveal that during the summer NH_3 concentrations are influenced by meteorological conditions (wind direction, wind speed and, sometimes, temperature), atmospheric mixing, local and regional sources in the winter 2008 in Beijing. Further modeling studies are needed to quantify the contribution of local versus regional sources to the atmospheric ammonia variations."

Thus, we will also modify old Figures and add new Figures, which will become Fig. 10. They will be showed to the end, as also replied to comments by referee #1.

It is indeed very difficult to isolate the effects of local emission, regional sources and changes in meteorology. In fact, NH_3 is typically considered, but large uncertainties remain in emission inventories, chemistry, deposition, and dynamic treatments. Thus, quantifying the interactions of NH_3 necessary to interpret temporal trends also requires improved mechanistic understanding and modelling. There are major uncertainties in dry deposition which still need to be built into atmospheric transport models and require further process and experimental studies to allow generalizations to be developed. Work is also required to advance the regional-temporal modelling of NH3 emissions in relation to environmental conditions. Our measurement data clearly illustrate the impact and the importance of meteorology and regional sources. We agree with the referee that more quantitative analysis will be needed (as we have indicated in manuscript), thus, we modified relevant sentences such that the conclusions are directly/better supported by the analysis of our data.

As also replied to comments by referee #1 and as said above, we followed your suggestions for point 4 in general comments discussing more detailed our experimental results about correlations between NH_3, NO_x, and also CO and $PM_{2.5}$. Indeed, we added new data on the concentrations of CO in the winter and $PM_{2.5}$ in the summer, which support further our interpretations regarding NH_3

emission sources. During the winter $PM_{2.5}$ data were not good and significant because there were instrumental troubles.

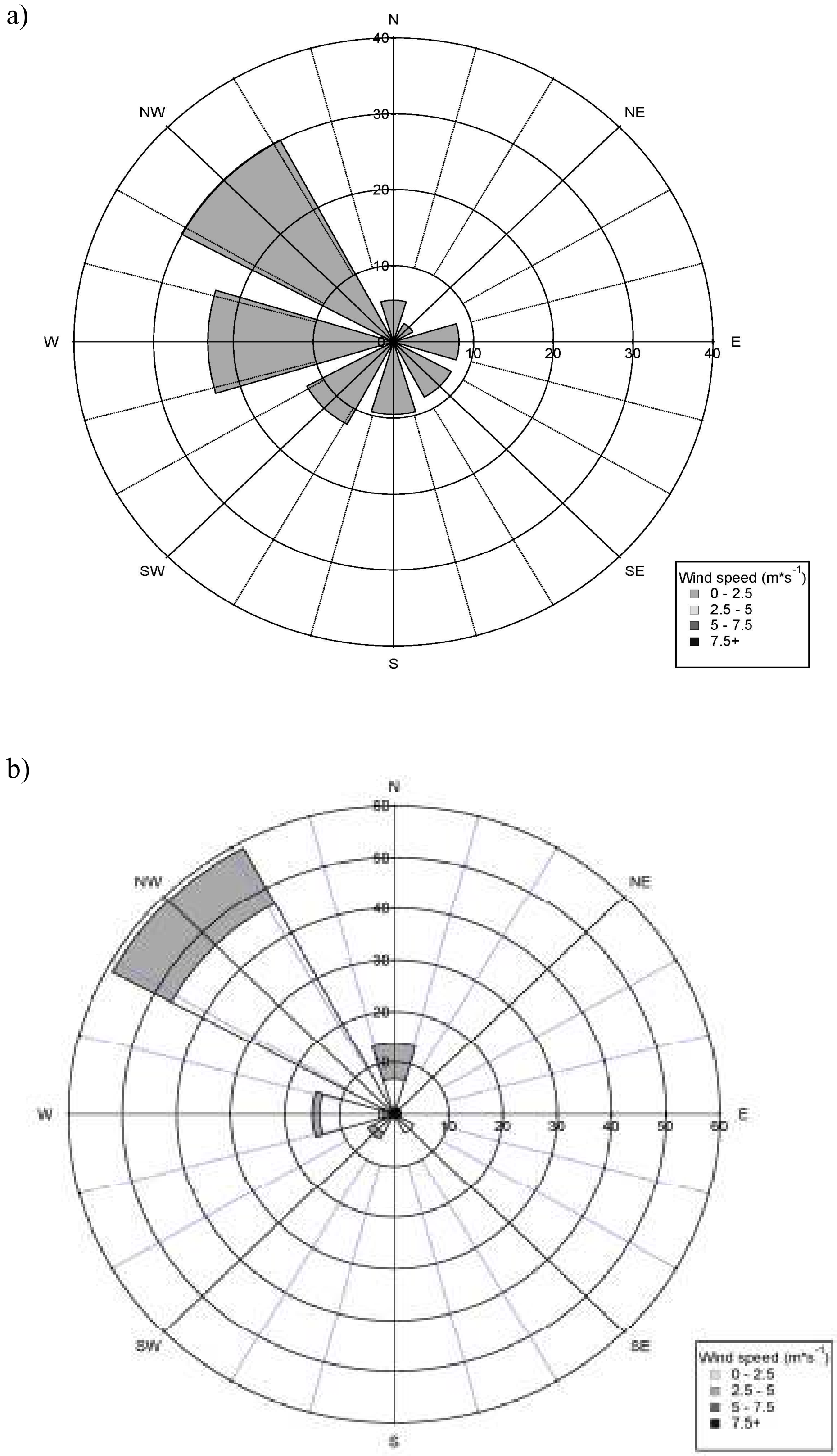

Fig. 2. Wind plots showing the frequency distributions of wind directions and speeds (grey scale) of the intensive winter measurements for two days: on 9 February (a) and 10 February (b). The radius axis represents the occurrence from 0% to 40% and from 0% to 60%, respectively.

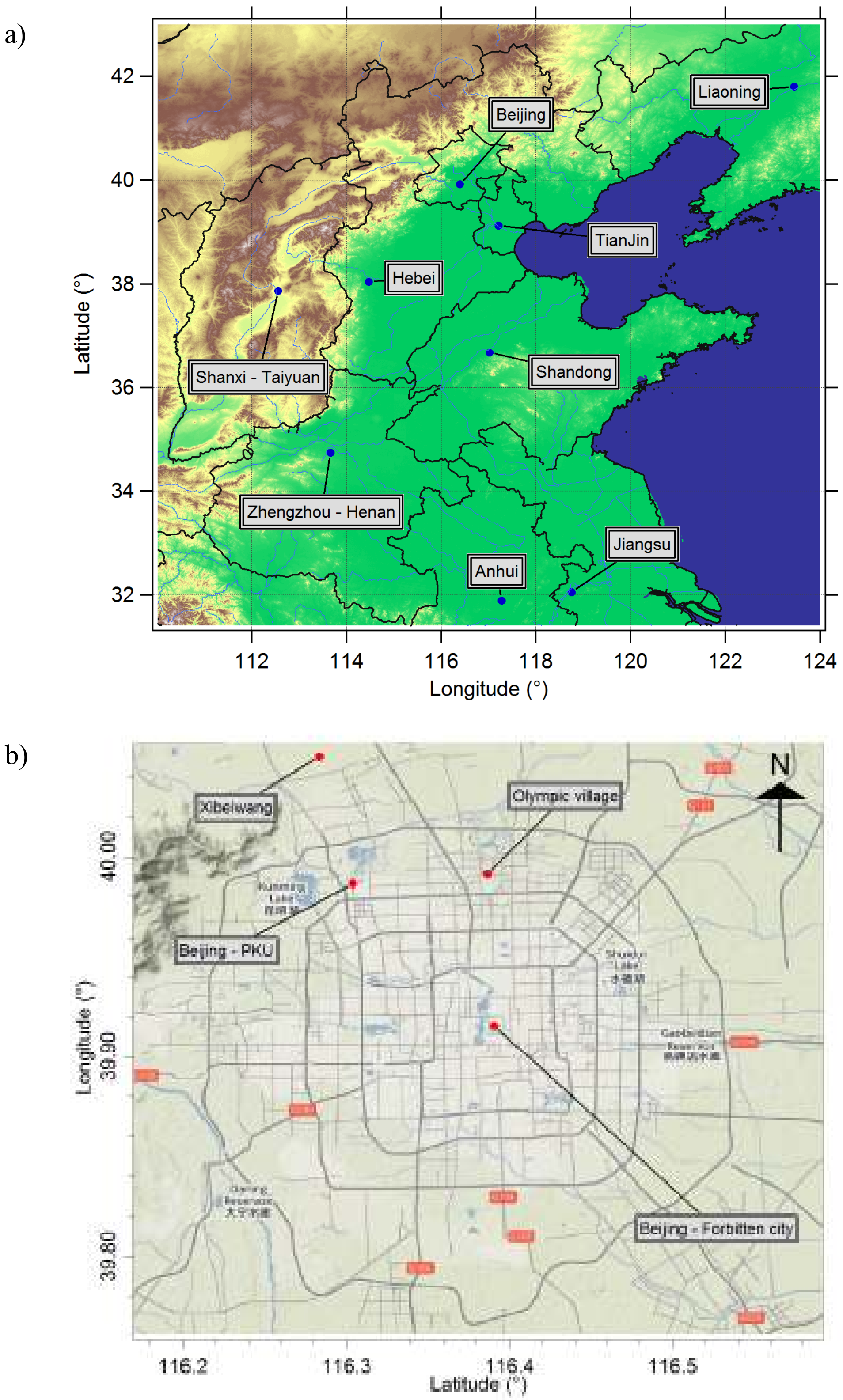

Fig. 3. Beijing city and measurement site (b) and surrounding regions (a).

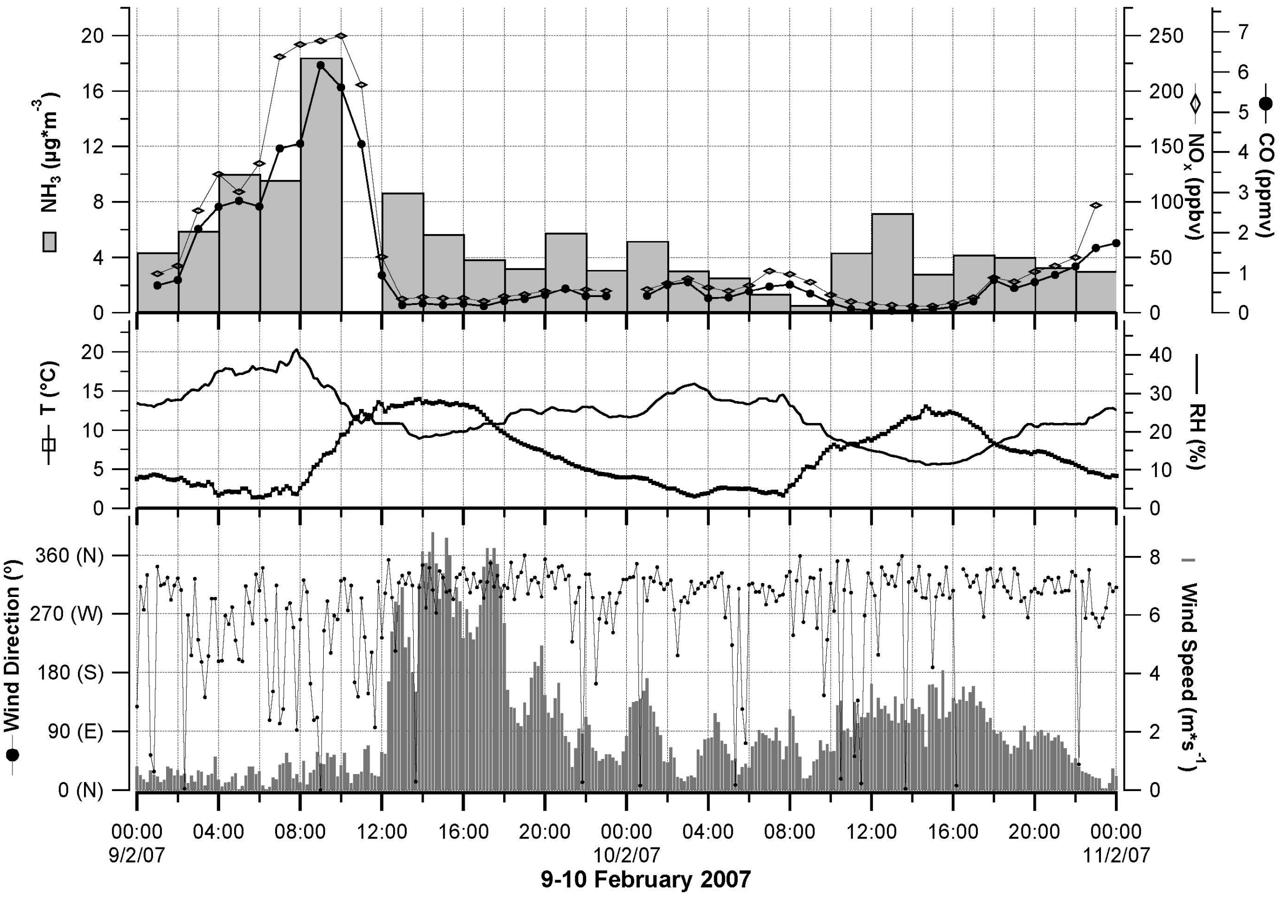

Fig. 4. Diurnal trends of NH_3, NOx, CO, temperature (T), relative humidity (RH), wind speed and direction during the intensive winter measurements.

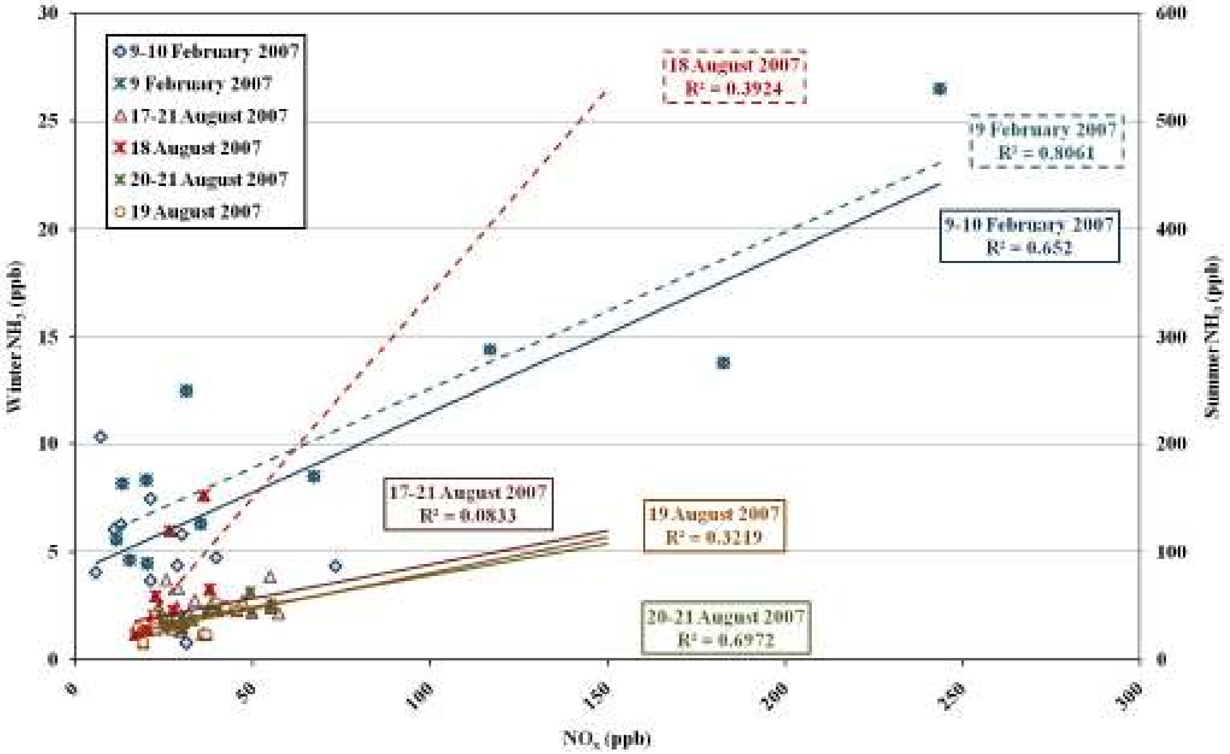

Fig. 5. Relationship between NH$_3$ and NOx during the intensive winter and summer measurements.

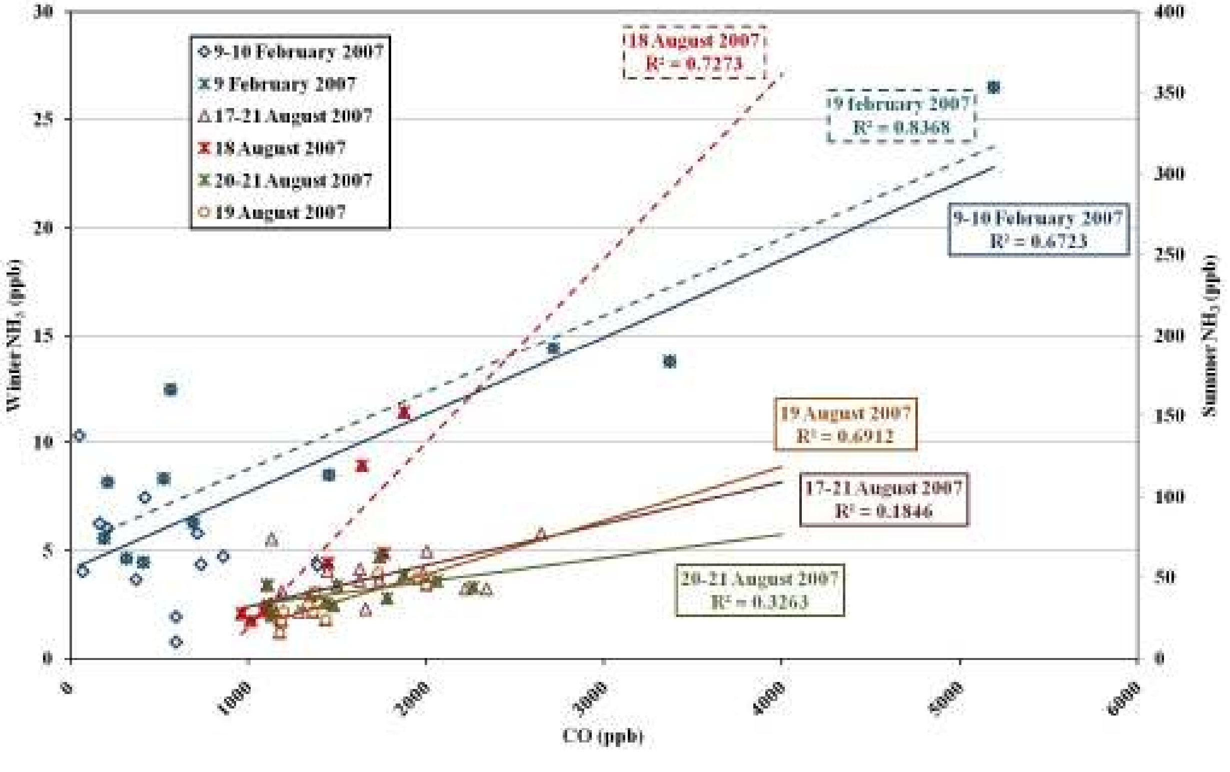

Fig. 6. Relationship between NH$_3$ and CO during the intensive winter and summer measurements.

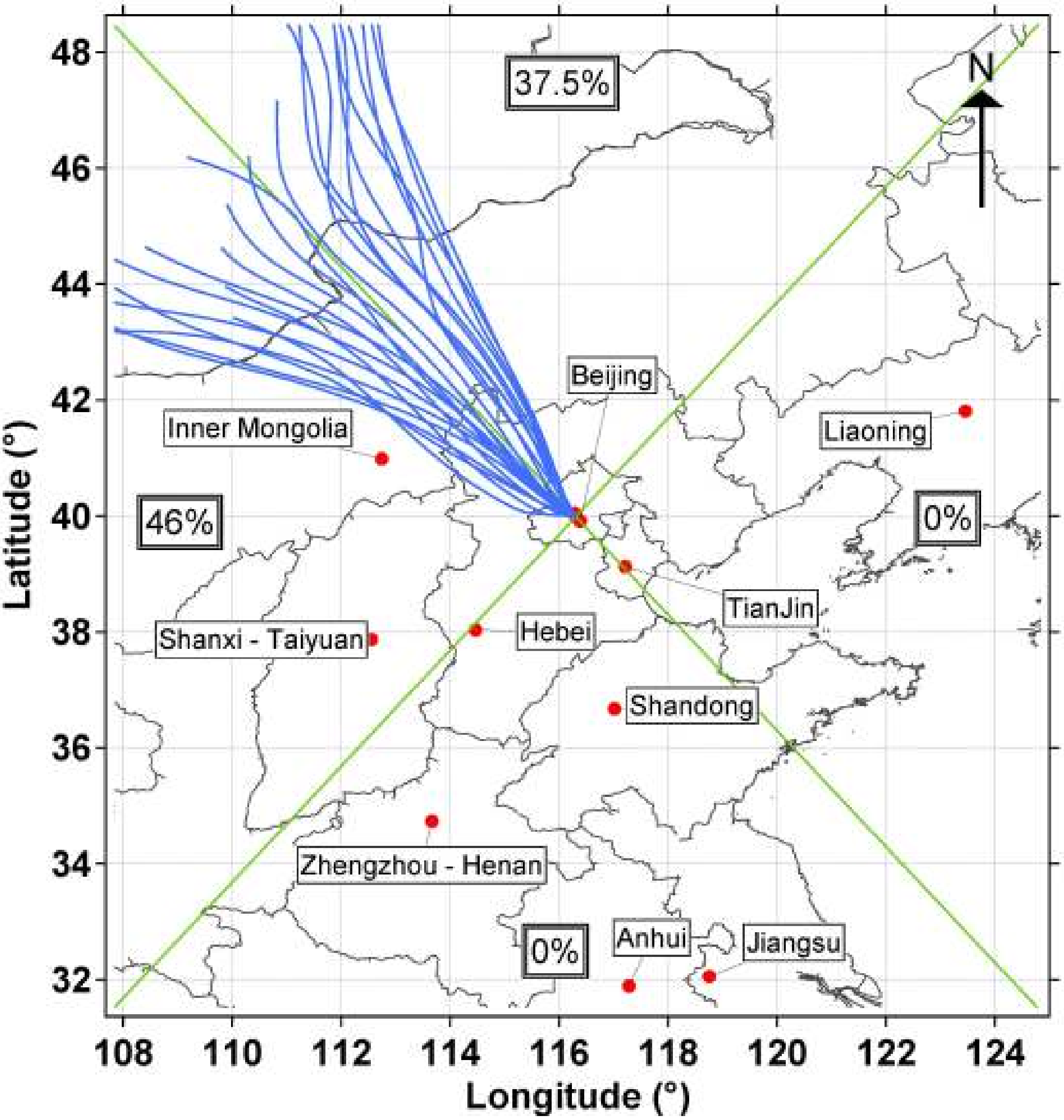

Fig. 7. Geographical map showing the 24-h backward trajectories arriving at Beijing during the intensive winter measurements, reconstructed using the NOAA ARL HYSPLIT trajectory model (htpp://ready.arl.noaa.gov./HYSPLIT.php).

.

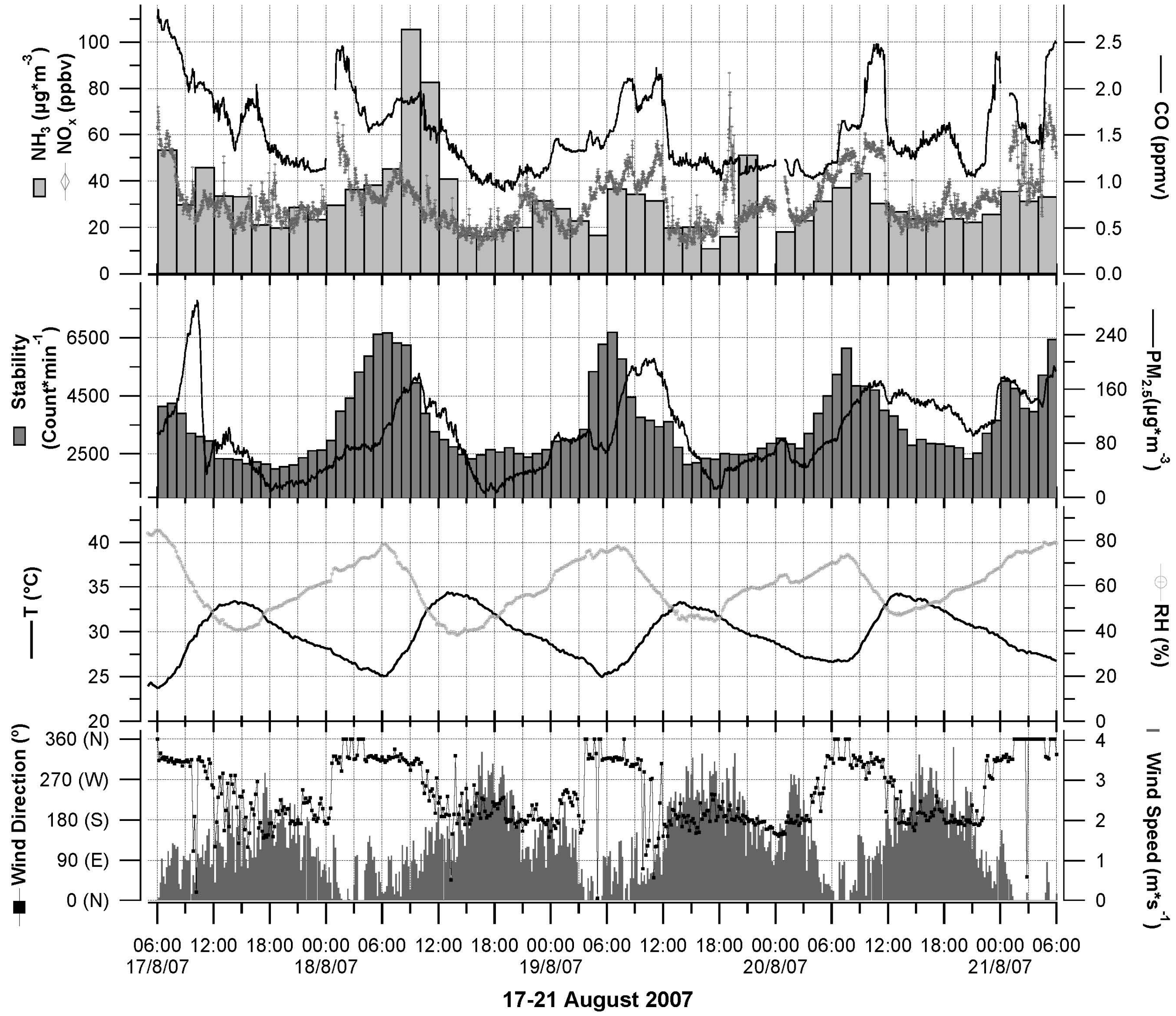

Fig. 8. Diurnal trends of NH_3, NOx, CO, $PM_{2.5}$, temperature (T), relative humidity (RH), wind speed and direction during the intensive summer measurements.

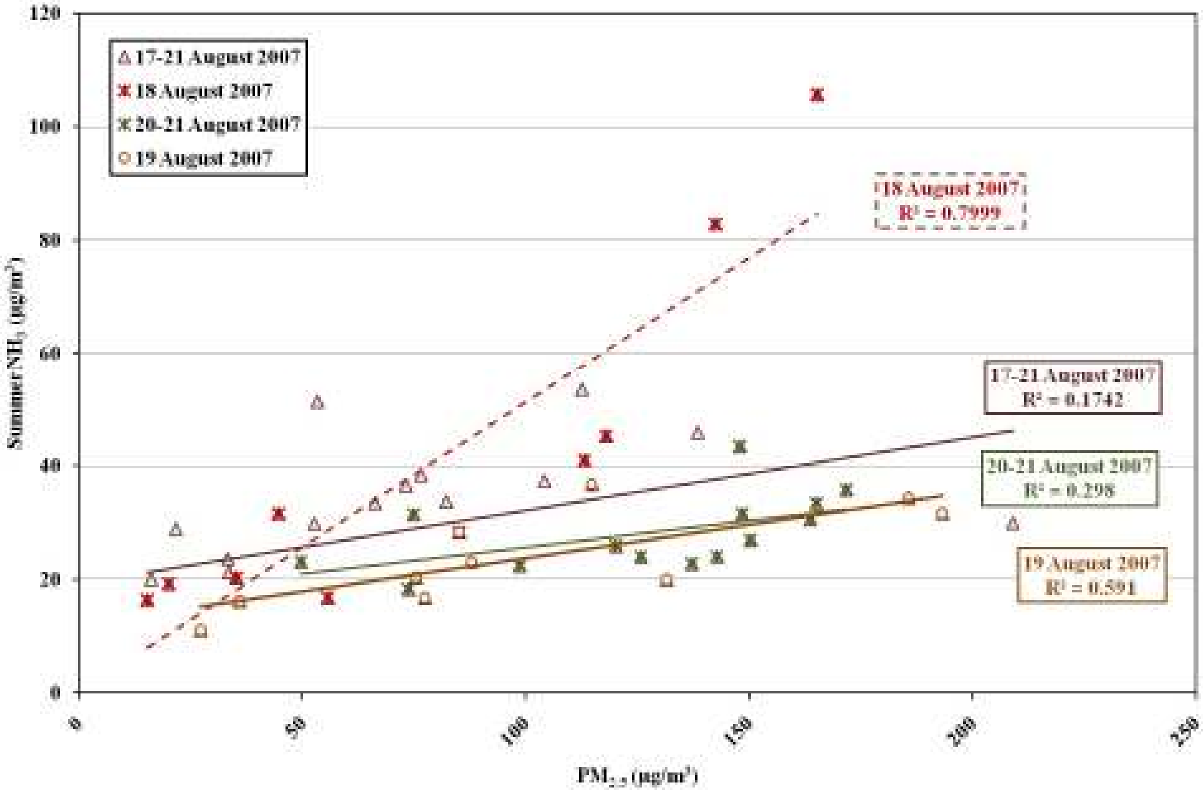

Fig. 9. Relationship between NH_3 and $PM_{2.5}$ during the intensive summer measurements.

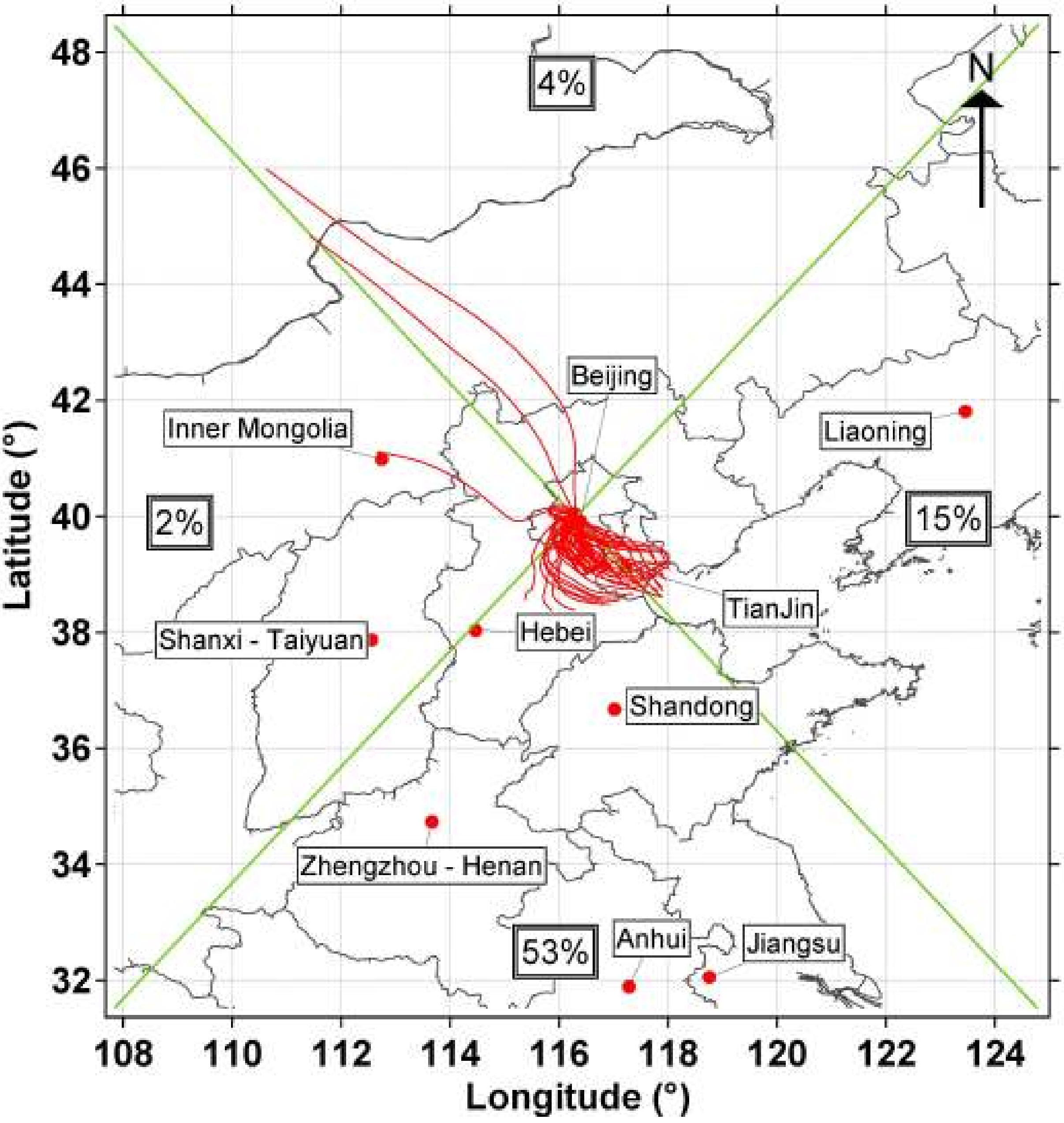

Fig. 11. Geographical map showing the 24-h backward trajectories arriving at Beijing during the intensive summer measurements, reconstructed using the NOAA ARL HYSPLIT trajectory model (htpp://ready.arl.noaa.gov./HYSPLIT.php).

References:

Chan C. Y., Xu X. D., Li Y. S., Wong K. H., Ding G. A., Chan L. Y., Cheng X. H.: Characteristics of vertical profiles and sources of $PM_{2.5}$, PM_{10} and carbonaceous species in Beijing, Atmos. Environ., 39, 5113-5124, 2005.

Chen D., Wang Y., McEltroy M. B., He K., Yantosca R. M., Le Sager P.: Regional CO pollution and export in China simulated by the high-resolution nested-grid GEOS-Chem model, Atmos. Chem. Phys., 9, 3825-3839, 2009.

EMEP Webdab emission data hosted by the Centre on Emission Inventories and Projections (CEIP): http://www.ceip.at/, last access: 20 August 2009, 2009.

Hao J., He D., Li L., Wu Y., Fu L., He K.: A study of the emission and concentration distribution of vehicular pollutants in the urban area of Beijing, Atmos. Environ., 34, 453-465, 2000.

Hao J., Wang L., Li L., Hu J. N., Yu X. C.: Air pollutants contribution and control strategies of energy-use related sources in Beijing, Sci. China, Ser. D 48, (Suppl. II), 138-146, 2005.

Heeb N. V., Saxer C. J., Forss A.-M., Brühlmann S.: Trends of NO-, NO_2-, and NH_3-emissions from gasoline-fueled Euro-3- to Euro-4-passenger cars, Atmos. Environ., 42, 2543-2554, 2008.

Huai T., Durbin T. D., Miller J. W., Pisano J. T., Sauer C. G., Rhee S. H., Norbeck J. M.: Investigation of NH_3 Emissions from New Technology Vehicles as a Function of Vehicle Operating Conditions, Environ. Sci. Technol., 37, 4841-4847, 2003.

Huai T., Durbin T. D., Younglove T., Scora G., Barth M., Norbeck J. M.: Vehicle Specific Power Approach to Estimating On-Road NH_3 Emissions from Light-Duty Vehicles, Environ. Sci. Technol., 39, 9595-9600, 2005.

Ju X., Liu X., Zhang F., Roelche M.: Nitrogen fertilization, soil nitrate accumulation, and policy recommendations in several agricultural regions of China, Ambio, 33, 300-305, 2004.

Klimont Z.: Current and Future emissions of Ammonia in China, 10th International Emission Inventory Conference: One Atmosphere, One Inventory, Many Challenges, US EPA, May 1-3, Denver, USA, http://www.epa.gov/ttn/chief/conference/ei10/ammonia/klimont.pdf, 2001.

Lee H., Kim Y. J., Jung J., Lee C., Heue K.-P., Platt U., Hu M., Zhu T.: Spatial and temporal variations in NO_2 distributions over Beijing, China, measured by imaging differential optical absorption spectroscopy, J. Environ. Manage., 90, 1814-1823, 2009.

Meng Z. Y., Xu X. B., Yan P., Ding G. A., Tang J., Lin W. L., Xu X. D., Wang S. F.: Characteristics of trace gaseous pollutants at a regional background station in Northern China, Atmos. Chem. Phys., 9, 927-936, 2009.

Meng Z. Y., Xu X. B., Wang T., Zhang X.-Y., Yu X.-L., Wang S.-F., Lin W.-L., Chen Y.-Z., Jiang Y.-A., An X.-Q.: Ambient sulphur dioxide, nitrogen dioxide, and ammonia at ten background and rural sites in China during 2007-2008, Atmos. Environ., 44, 2625-2631, 2010.

Reis S., Pinder R. W., Zhang M., Lijie G., Sutton M. A.: Reactive nitrogen in atmospheric emission inventories, Atmos. Chem. Phys., 9, 7657-7677, 2009.

Shen J. L., Tang A. H., Liu X.J., Fangmeier A., Goulding K. T. W., Zhang F. S.: High concentrations and dry deposition of reactive nitrogen species at two sites in the North China Plain, Environ. Poll., 157, 3106-3113, 2009.

Streets D. G., Fu J. S., Jang C. J., Hao J., He K., Tang X., Zhang Y., Wang Z., Li Z., Zhang Q., Wang L., Wang B., Yu C.: Air quality during the 2008 Beijing Olympic Games, Atmos. Environ., 41, 480-492, 2007.

USEPA: National Emission Inventory Tier Summaries: http://www.epa.gov/ttn/chief/eiinformation.html, last access 14 August 2009, 2009.

Wang X., Mauzerall D. L., Hu Y., Russell A. G., Larson E. D., Woo J.-H., Streets D. G., Guenther A.: A high-resolution emission inventory for eastern China in 2000 and three scenarios for 2020, Atmos. Environ., 39, 5917-5933, 2005.

Wang H., Fu L., Lin X., Zhou Y., Chen J.: A bottom-up methodology to estimate vehicle emissions for the Beijing urban area, Sci. Total Environ., 407, 1947-1953, 2009.

Wang B., Shao M., Lu S. H., Yuan B., Zhao Y., Wang M., Zhang S. Q., Wu D.: Variation of ambient non-methane hydrocarbons in Beijing city in summer 2008, Atmos. Chem. Phys., 10, 5911-5923, 2010.

Wang H., Fu L., Lin X., Zhou Y., Du X., Ge W.: Trends in vehicular emissions in China's mega cities from 1995 to 2005, Environ. Poll., 158, 394-400, 2010.

Xia X., Chen H., Zhang W.: Analysis of the dependence of column-integrated aerosol properties on long-range transport of air masses in Beijing, Atmos. Environ., 41, 7739-7750, 2007.

Zheng M., Salmon L. G., Schauer J. J., Zeng L., Kiang C. S., Zhang Y., Cass G. R.: Seasonal trends in $PM_{2.5}$ source contributions in Beijing, China, Atmos. Environ., 39, 3967-3976, 2005.

Zhang Y., Dore A. J., Ma L., Liu X. J., Ma W. Q., Cape J. N., Zhang F. S.: Agricultural ammonia emissions inventory and spatial distribution in the North China Plain, Environ. Pollut., 158, 490-501, 2010.