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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characteristics of atmospheric ammonia over Beijing, China" *by* Z. Y. Meng et al.

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We would like to thank the anonymous referee for his comments and constructive suggestions. We have revised the whole manuscript according to his comments and suggestions.

Anonymous Referee #1 This manuscript describes a 2+ year record of ammonia measurements made at 2 sites (urban and rural) in Beijing with some ancillary measurements. This is clearly a useful dataset and the preliminary analysis shown here appears sound. While there are limitations to the analysis possible (i.e no particle measurements made at the urban site), I feel there are at least 2 avenues that could be further explored by the authors to put their observations in better context for future follow-on work. I have indicated these as "major revisions" as I believe they could take a bit of time for the authors to address. 1. The manuscript would benefit from a more thorough meteorological analysis, including information on wind direction (particularly relative to agricultural vs urban areas), wind speed and precipitation. Wind roses or back trajectories would be helpful in this context. Section 3.1.2 invokes precipitation as a major control on NH3 concentrations, but without data this argument is not convincing. Similarly the argument regarding the correlation of CMA and SDZ observations at the end of Section 3.1.2 would be reinforced by some analysis of synoptic meteorological conditions and wind patterns. It is unclear what parameters were measured at the site - if met measurements at the site are not available, I would encourage the authors to take a look at some assimilated met products for this analysis.

Answer: We have revised Section 3.1.2 and 3.2 by adding more meteorological analysis and discussions according to the referee's comments.

In section 3.1.2, the corresponding data of air temperature and precipitation are analyzed together with the measurement results. To present meteorological data more clearly, we have drawn rainfall and relative humidity figures in Figure 3.

In section 3.2, wind roses are calculated to help the interpretation of measurement results. Backward trajectories are calculated and clustered to interpret the variations of NH3 concentrations at urban site and the results are put in the new Section 3.3.

Following is the revised context of section 3.1.2:

At CMA, NH3 increased gradually from April and reached the highest values on July, and then decreased until the following March. NH3 values had a small peak in April as the temperature increased suddenly to cause the accumulated emission of NH3 from natural and fertilized soils, vegetation, and human sources in city centre in winter. The peak NH3 value was 85.1 ppb on 20-24 July 2009 and the lowest concentrations of NH3 (0.7 ppb) appeared on 18-24 February 2009 for over two-year period 2008-2010 (Fig. 3a). The annual average temperatures were 14.0, 14.1 and 14.4 in 2007, 2008 and 2009, respectively, with the highest monthly temperature (27.9) in July of 2008

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

and the lowest temperature (-3.5) in January of 2010 at CMA (Fig. 3b). The maximum value of NH3 concentration is consistent with the highest ambient temperature in July. The lowest NH3 value was in February 2009 which might be attributable to the cold temperatures, moderate snowfall and less human activity because lots of mobile population moving back to their hometowns during Chinese Spring Festival.

At SDZ, the peak NH3 value was 42.9 ppb on 11-21 July 2010 and the lowest concentrations of NH3 (0.8 ppb) appeared on 19-29 December 2008 from January 2007 to June 2010. The annual average temperatures at SDZ site were 11.3, 10.7 and 10.9 in 2007, 2008 and 2009, respectively, with the highest monthly temperature (25.1) in July of 2008 and the lowest temperature (-8.4) in January of 2010. In summer, high temperatures will favor ammonia volatilization from urea and ammonium dibasic phosphate applied to crops.

In CMA, the highest annual rainfall (626.0 mm) was found in 2008 during observation period (Fig. 3c). In 2008, the monthly rainfalls were 125.3, 79.3 and 132.1 mm in June, July and August, respectively. NH3 concentrations were 17.9, 26.5 and 19.9 ppb in June, July and August of 2008, respectively. Much lower NH3 concentrations were observed (7.4 and 9.7 ppb, respectively) on 2-10 June 2008 and 1-8 June 2009, those were rainy days. The highest annual rainfall (633.9 mm) was also found in 2008 in SDZ during observation period (Fig. 3d). In 2008, the monthly rainfalls were 104.7, 77.8 and 223.7 mm in June, July and August, respectively. NH3 concentrations were 19.6, 21.6 and 5.2 ppb in June, July and August of 2008, respectively. The lower NH3 levels were consistent with the more heavy rain in summer months, reflecting the important role wet removal plays in influencing the temporal variation in ambient NH3 levels.

At both sites, highest relative humidity and lowest wind speed are often found in summer, while lowest relative humidity and highest wind speed usually occur in spring and part of the winter (Figs. 3b, c and d).

Following is the meteorological analysis has been added in section 3.2:

ACPD
11, C2933–C2950, 2011

Figure 5 shows the rose maps of hourly average NH3 concentrations, wind direction frequencies and wind speeds in different seasons at CMA and SDZ.

As shown in figure 5b and 5c, the dominant winds are from NNE-NE sectors and SE-SSE-S sectors, but the strongest winds are from WNW-NW-NNW-N sectors. In summer, the average NH3 concentrations in the NNE, NE, ENE, and E sectors are 42.3, 41.9, 39.1, and 40.2 ppb, respectively (Fig. 5a). They are about 10 ppb higher than that in W-N sectors, in which the wind speeds are much stronger. When winds come from northeast direction, the emissions of NH3 from the agricultural areas such as Shunyi district which locates in the northeast suburb of CMA site might contribute higher levels of NH3. The higher average NH3 concentrations in W and WSW sectors might be attributed to transport of industrial emission from Shijingshan district.

Since NH3 is either readily converted to NH4+ or subjected to dry deposition, high concentrations are found only close to the surface and near to emission sources. Thus, NH3 concentrations might be generally lower at higher wind speeds because of turbulent diffusion. The wind speeds were high more than 5m/s during spring and winter, with the higher values in summer and autumn in NW-WNW sectors (Fig. 5c). As can be seen in Fig. 5a, the lowest concentrations in four seasons were in these sectors. Previous studies have reported an inverse relationship between ground-level concentrations of trace gases, such as ammonia, and wind speed (Robarge et al., 2002).

At SDZ, the prevailing winds are northeasterly in autumn and winter and southwesterly in spring and summer (Fig. 5d). The wind direction distribution at SDZ is typical of the larger-scale situation in the North China plain. Therefore, polluted air masses from urban areas and even those regions in south of Beijing at North China Plain, can be easily transported to SDZ under southwesterly winds, while relatively clean air masses are transported to the site with winds from other directions.

Following is the new section 3.3:

3.3 The impact of different air mass transport on the surface NH3 concentrations

To gain an insight into the impact of transport on NH3 at CMA, 72-h backward trajectories were calculated using the HYSPLIT 4 model (HYbrid Single-Particle Lagrangian Integrated Trajectory model version 4.7, http://www.arl.noaa.gov/ready/hysplit4.html). The trajectory calculations were done for four times of each day from July 2009 to June 2010, with the start times of 00, 06, 12, and 18 UTC, respectively. As can be seen in Fig. 6, cluster 2 from the North China Plain region (NCP) was most important for the Beijing urban site, contributing 33% of air masses. To know the seasonal variations in the trajectories, monthly occurrence frequencies of each type of air masses arriving at CMA were calculated and are shown in Table 3. Based on this table, trajectories in cluster 2 can occur in any month but mostly in the summer months.

To characterize the dependences of the pollutants concentrations on air masses, statistics of hourly average concentrations of NH3 were made for corresponding clusters of backward trajectories and are also summarized in Table 3. Large differences in the concentrations of NH3 exist among the clusters, with cluster 2 corresponding to the highest NH3 levels, and cluster 5 corresponding to the second highest NH3 levels.

A detailed estimates of NH3 emission in Beijing and surrounding areas in 2005, carried out by Ianniello et al. (2010) has shown that the largest sector contributor to NH3 emissions in the NCP is agriculture (99%), while mineral fertilizer use contributing 54% to the total NH3 emission, and livestock sources contributing the remaining 46% in the NCP. Of the total agricultural ammonia emissions in the NCP, the Hebei, Henan and Shandong provinces take the larger part (Zhang et al., 2010). Contributions of NH3 emissions from livestock and fertilizer activities were also found in Inner Mongolia (Klimont, 2001; Ju et al., 2004).

Since cluster 2 represents air masses originating from NCP, it is not surprising that the highest NH3 levels were observed in this cluster of air mass. Air masses in cluster 5 traveled over China's key coal mining and power generation regions in Inner Mongolia, Shanxi Province, and Hebei Province (e.g., Datong, Zhangjiakou, etc.). This explains the second highest NH3 levels corresponding to cluster 5. The cluster 1 has the third

Full Screen / Esc

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Discussion Paper

highest concentration of NH_3. The data in Table 3 suggest that the NH_3 concentrations corresponding to clusters 4 and 6 were low. This is attributable to the less polluted air over the northwest sector and its higher traveling heights and velocities.

Overall, the air masses from the North China Plain region contain the highest concentration of NH_3, and the air masses traveling over the coal mining and power generation regions west of Beijing contain the second highest concentrations of ammonia. Therefore, transport of air masses from these regions is responsible for the high concentrations of NH_3 at CMA.

2. It would be highly informative to investigate to what degree acids were neutralized by ammonia at the rural site. Analysis of the PM2.5 filters for sulfate, nitrate and chloride, would allow the authors to comment on whether the NH_4^+ fully neutralized these species and/or whether excess NH_3 is available in summer as a result.

Answer: We have added the analysis of inorganic ions in PM2.5.

Table 4 summarizes the mean, median, and minimum and maximum daily values of inorganic ions in PM2.5. The average concentrations of NO_3^-, SO_4^{2-} and Cl^- were 11.57, 15.00 and 1.33 μg/m3, and total concentration of inorganic (NH_4^++NO_3^-+SO_4^{2-}+Cl^-) was 34.93μg/m3 from June 2008 to December 2009.

With respect to percentage of the total mass, SO_4^{2-} was the most important species on average in PM2.5 at SDZ. Nitrate contributes more significantly to total mass during colder months when SO_2 oxidation rates are reduced in response to lower concentrations of oxidants such as OH. The average molar ratios of NH_4^+ to SO_4^{2-}, NO_3^- to NH_4^+ and Cl^- to NH_4^+ - were 1.8, 0.5 and 0.1, respectively.

In this study, the average molar ratio of NH_4^+ to SO_4^{2-} varies from 0.2 to 5.8 from June 2008 to December 2009. Since a ratio of 2 indicates that all of aerosol is present as $(NH_4)_2SO_4$, this signifies differing degrees of aerosol neutralization. The mean molar ratio approaches 2, suggesting that SO_4^{2-} is completely neutralized at SDZ.

Minor Comments 1. Abstract: Lines 5,7,9,17: Missing 'the' in front of 'rural site' or 'urban site'

Answer: We have added "the" in front of 'rural site' or 'urban site'.

2. Page 3042, Lines 23-25: The list of neutralized species is incomplete (eg. Ammonium bisulfate). I suggest that the authors indicate that the species given are examples of salts.

Answer: We have corrected the sentence in our revised version according to reviewer's comment.

3. Page 3043: Lines 9-11 and line 25: According to what inventory? Indicate reference for specific percentages reported.

Answer: We have given the reference in our revised version according to reviewer's comment.

References: Clarisse, L., Clerbaux, C., Dentener, F., Hurtmans, D. and Coheur, P.F.: Global ammonia distribution derived from infrared satellite observations, Nature geosciences, 2, 478-483, doi: 10.1038/NGEO551, 2009. Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., Fu, Q., He, D., Klimont, Z., Nelson, S. M., Tsai, N. Y., Wang, M. Q., Woo, J. H., and Yarber, K. F.: An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, J. Geophys. Res.-Atmos., 108, (D21), 8809, doi:10.1029/2002JD003093, 2003.

4. Page 3044, Line 14: grammar: "Recently, measurements of ammonia"

Answer: We have corrected the sentence according to reviewer's comment.

5. Page 3045, Lines 5-11: Could you tell us about agricultural activity in the area? Where and what type?

Answer: The site is on the gentle slope of a small hill. The geography surrounding the station is characterized by rolling hills with farmland, orchard and forests. On the foot

ACPD

11, C2933–C2950, 2011

of the hill about 2 km south is the Shangdianzi village with about 1200 inhabitants. The main agricultural products include corn, Setaria italica, vegetables and fruit. Ammonium dibasic phosphate and urea are used as fertilizers. The information above has been added in our revised version.

6. Page 3045, Line 21: grammar: "The concentrations of NH3 were measured in parallel by a : : :"

Answer: We have corrected the sentence according to reviewer's comment.

7. Page 3045, line 23: grammar: "2010 at the top of the CMA Training Center Building (50 m), 200 m away: : :"

Answer: We have corrected the sentence according to reviewer's comment.

8. Page 3045, line 26: grammar "on top of the CMA Training Center Building." Answer: We have corrected the sentence according to reviewer's comment.

9. Page 3046, line 19, grammar: "and glass ware.."

Answer: We have corrected the sentence according to reviewer's comment.

10. Table 2: It would be helpful to understand what measurement techniques were employed when comparing previous studies to yours, could you add this information to Table 2?

Answer: According to reviewer's suggestion, we have added the measurement techniques in Table 2.

11. Page 3049, line 10: grammar: "going back to their hometowns during: : :"

Answer: We have corrected the sentence according to reviewer's comment. 12. Figures 5 & 6: As the concentrations shown are independent the authors should use a 2-sided regression (reduced major axis technique) for their regression statistics

Answer: Thank you for your suggestion. We have redrawn figures using 2-sided re-

ACPD

11, C2933–C2950, 2011

Interactive Comment

gression. It seems that 2-sided regression lines are more reasonable than the previous one. The slope value of 0.84 for NH3/NOx in summer indicates the comparable levels of NH3 with NOx. In autumn and winter, NH3 was about one third of the levels of NOx. The intercepts tell us the regional background of NH3 in spring, summer, and autumn were within 4-14 ppb with the maximum one in summer. The regional background of NH3 in winter was less than 1 ppb.

13. Page 3051, lines 15-19: I'm confused by these 2 sentences. The first indicates that 35% of local NOx emissions comes from vehicles and the second indicates that 74% of "ground NOx" results from vehicular emissions. Do the authors mean concentrations when they say "ground NOx"? How are the numbers consistent with the previous sentence?

Answer: We have deleted the second sentences in our revised version.

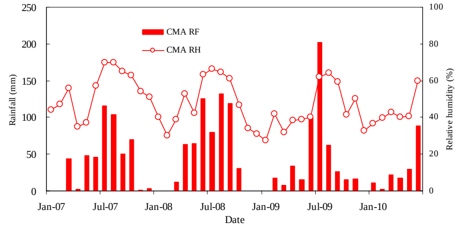
14. Page 3053, line 12: Suggest that you re-phrase this sentence which (as written) suggests that there is a weaker summertime traffic cycle, which may not be the case, it may simply be swamped by other sources. I believe that this is the authors' intent and suggest this modification: "No bimodal pattern is seen in summer, which implies that traffic is not the dominant: : :"

Answer: We have modified the sentence according to reviewer's comment. No bimodal pattern is seen in summer, which implies that traffic is not the dominant source of NH3.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 3041, 2011.

Figure 3c and d

(Fig. 3c)



(Fig. 3d)

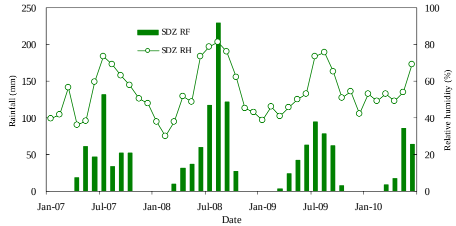


Fig. 1. Fig.3c and d

ACPD
11, C2933–C2950, 2011

Interactive Comment

Figure 5

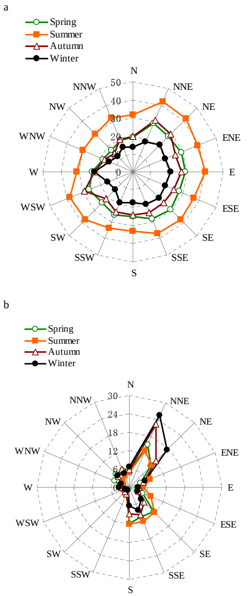


Fig.5 Seasonal average NH_3 concentrations at CMA (a), wind frequency at CMA (b), wind speed at CMA (c) and wind frequency at SDZ (d) distributions in different wind direction sectors during 2009-2010.

Fig. 2. Fig.5a and b

ACPD
11, C2933–C2950, 2011

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Discussion Paper

ACPD

11, C2933–C2950, 2011

Interactive Comment

Figure 5

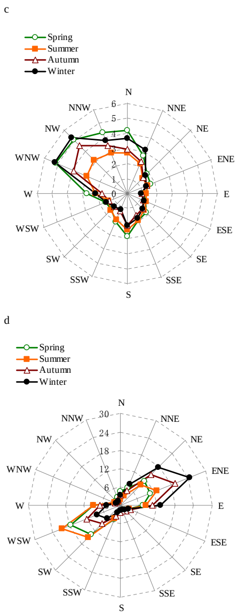

Fig.5 Seasonal average NH_3 concentrations at CMA (a), wind frequency at CMA (b), wind speed at CMA (c) and wind frequency at SDZ (d) distributions in different wind direction sectors during 2009-2010.

Fig. 3. Fig.5c and d

Full Screen / Esc

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Interactive Discussion

Discussion Paper

Figure 6

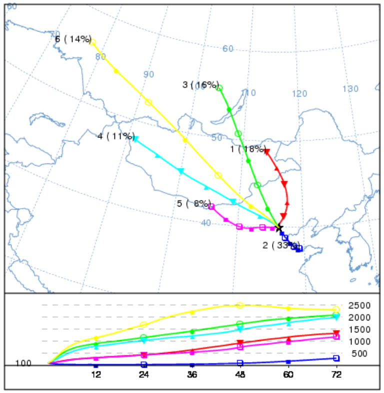

Fig. 6. Air mass backward trajectories for 100 m above ground at Beijing urban site during July 2009-June 2010.

Fig. 4. Fig.6

ACPD
11, C2933–C2950, 2011

Interactive Comment

Figure 7

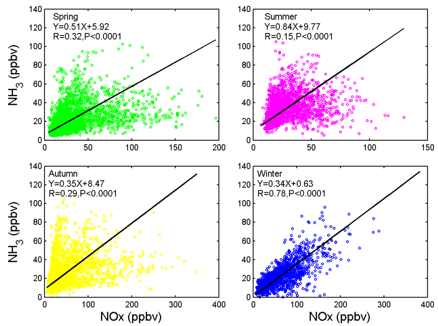

Fig.7 The 2-sided regression of NH_3 versus NOx at CMA from June 2009 to May 2010.

Fig. 5. Fig.7

ACPD
11, C2933–C2950, 2011
Interactive Comment

ACPD
11, C2933–C2950, 2011

Interactive Comment

Figure 8

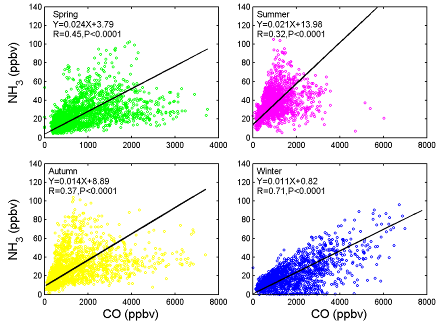

Fig.8 The 2-sided regression of NH_3 versus CO at CMA from June 2009 to May 2010.

Fig. 6. Fig.8

Full Screen / Esc

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Discussion Paper

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

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

Fig. 7. Table 2

ACPD

11, C2933–C2950, 2011

ACPD

11, C2933–C2950, 2011

Table 3. Monthly frequency occurrence, mean NH_3 and NH_4^+ concentrations ($\mu g/m^3$) of each type of air mass arriving at Beijing urban site during July 2009-May 2010

Air mass type	Jul 09	Aug 09	Sep 09	Oct 09	Nov 09	Dec 09	Jan 10	Feb 10	Mar 10	Apr 10	May 10	Jun 10	NH_3
Cluster 1	27	12	14	26	16	15	23	28	39	22	31	10	18.1
Cluster 2	86	74	60	20	1	7	6	10	17	43	45	107	25.7
Cluster 3	1	11	26	22	35	27	25	17	24	28	14	2	11.9
Cluster 4	1	10	5	13	36	22	21	20	18	5	14	0	16.3
Cluster 5	4	17	6	21	20	9	10	9	2	6	5	1	24.4
Cluster 6	0	0	9	18	12	40	39	28	24	16	11	0	12.0

Fig. 8. Table 3

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

Ions	Mean	Standard Deviation	Minimum	25th percentile	75th percentile	Median	Maximum
NH_4^+	7.03	7.76	0.10	1.05	10.67	3.83	36.53
NO_3^-	11.57	11.40	1.14	3.32	17.15	7.10	68.24
SO_4^{2-}	15.00	15.68	0.58	4.48	21.23	8.56	85.31
Cl^-	1.33	1.29	0.01	0.55	1.57	0.96	8.60

Fig. 9. Table 4

ACPD
11, C2933–C2950, 2011