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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.

Z. Y. Meng et al.

jxmxpb@mail.tsinghua.edu.cn

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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 #2 As the authors suggest, there are few observations of ammonia available and that much more monitoring is called for. And following from this, I think the authors have done a wonderful job by assembling this data set. Further, I think that passives are a good way to proceed, given today's limited budgets and the ability to locate passives at highly diverse locations with or without electricity. In my opinion, the most important problem with this paper is with the discussion of sampling and laboratory methods. Ammonia is a notoriously difficult gas to deal with (contamination in

particular), therefore you must go to extreme lengths to ensure that no contamination occurred. I don't think there is near enough discussion on these particular points. For example: You need to show your blank results. Contamination is constantly a problem with passive samplers and with ammonia. How large were your blanks? How many of your concentrations were negative after subtracting blanks? Any contamination problems?

Answer: We have added more description and discussion of sampling and laboratory methods in the text according to the referee's comments.

Did you run any duplicate analyses to determine your internal variability of your observations? How accurate are your observations? How precise?

Answer: The information about duplicate analyses is added in section 2.3 in our revised version according to the referee's comments.

The quality not only depends on the sampler, but also on the analysis and the evaluation of results. The coefficient of variation is a statistical measure of precision based on the difference between duplicate samples. In this study, the coefficients of variation (COV) are defined as the median relative standard deviation, assuming a normal distribution of the deviation between parallel samples. The coefficients of variation of all duplicates were 9.9% and 6.5% for urban and rural site, which is acceptable for indicative monitoring.

Define what you call a field blank; what you call a travel blank. Did you take lab blanks? Did you do filter blanks? What were your results of all of this.

Answer: We have given the definitions of field blank and lab blank. More discussion is added as follows.

The field blank was a loaded sampler taken to and from the field with other samplers but never removed from its air-tight vial. Field blank measurements were made each month at SDZ site. The laboratory blank remained frozen in a refrigerator in the laboratory until

ACPD

11, C2953–C2965, 2011

analyzed. Both of these blanks were prepared and processed at the same time and in the same way as the deployed samplers to determine if contamination occurred during the sampler loading, transport, or analysis. In the laboratory, the exposed samples as well as the field and laboratory blank samples were extracted and analyzed. The values of laboratory blank ranged from 0.02 to 0.57, with the average of 0.178.

The exposed samplers and field samplers of NH3, SO2 and NO2 in the thermometer screen at the site is showed in Supplement Figure.

Did you assemble the samplers in a clean bench; if so, what kind? Did you track ammonia contamination in your lab? In your bench? What were the results? How were samples stored in the field? How were they stored in the labs? Shipping times back and forth? Were they shipped cold? Exactly how were they shipped?

Answer: Before and after exposure, all the samplers remained frozen in a refrigerator in the site and laboratory. Shipping time is about two hours from CMA to SDZ.

How were samples packed going back and forth? Pictures? Did you use a filter to trap ammonia? Did you double bag? Did your citric acid degrade in the heat over time?

Answer: During the transport, the samplers were sealed in airtight vials and packed in a cooling box containing four blue ice blocks (2.4 kg). All the samplers remained frozen in a refrigerator in the laboratory until analyzed.

Did you soak/sonicate the samplers between use? Again blanks should be shown. Lab blanks would have been a good idea? Where these done?

Answer: The disassembled components of the passive sampler were thoroughly cleaned prior to each use (to avoid contamination and carryover) by sonicate, rinsing thoroughly with deionized water in the laboratory.

I think much more of the laboratory methods could be added, and are important to add. For example, give specifics of the IC method that you used, blanks, standards, cleaning routines for the housings, etc.

ACPD

11, C2953–C2965, 2011

Answer: We have added more description of laboratory methods in section 2.2.

The ammonium extract was analyzed using Dionex ICS-3000 Ion Chromatography (Dionex, USA) with a CG12A 4 mm guard column and a CS12A 4 mm analytical column. The CSRS (cation self-regenerating suppressor) was set at 50 mV. The detector used was a CD conductivity detector. The eluent was methanesulfonic acid (MSA).

Automated Ammonia sampler: For this analyzer, what method does it use, how does it work? Has it been shown to be correct? Has it been tested against known systems?

Answer: The EC9842 Nitrogen Oxides/Ammonia Analyzer uses gas-phase chemiluminescence detection to perform continuous analysis of ammonia, oxides of nitrogen and total nitrogen compounds. Ammonia is measured by conversion of the NH3 in the sample to NO, followed by detection directly by a chemilluminescent reaction.

For NH3 analyzers, zero and span checks were done every week to check for possible analyzer malfunction and calibration drift. The multi-point calibrations were performed at approximately 1-month interval.

How did you collect PM 2.5 filters for your analysis? Ammonia filled air flowing through a particulate filter I would think would allow gaseous NH3 to collect on to the particulate and onto the filter. How do you know that the particulate NH4 value didn't change? Did you lose any particulate ammonia during the time the sample sat on the filter sampler (decomposition of ammonium nitrate), or absorb NH3 from the atmosphere?

Answer: Daily aerosol PM2.5 samples are collected independently using the MiniVol portable sampler. NH3 is also collected solely by passive sampler, with no influence on the concentrations of NH4+ in PM2.5.

SDZ sampler. I think it is very important to discuss precisely how the sampler was sited; how high off the ground, surrounding landscape (farm field, forest, etc), what crops are nearby, what fertilizers are used, CAFOs present? All is necessary so that the reader knows what the local conditions were exactly.

ACPD

11, C2953–C2965, 2011

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 of the hill about 2 km south is the Shangdianzi village with about 1200 inhabitants. The main agricultural products include corn, wheat, vegetables and fruit. Ammonium dibasic phosphate and urea are used as fertilizers.

The information above has been added in our revised version.

The sample collection schedule is somewhat unclear. Additionally, what does your sampler housing look like? Airflow around it, through it? Were sample concentrations and mass flow rates corrected for temperature, particularly in the winter?

Answer: The prepared samplers were sealed in individual airtight storage vials in the laboratory and shipped in a cooling box to SDZ site. The samplers were deployed by trained station operators in the thermometer screen (1.5 m above the ground), which protect the samplers from rain and direct sunshine. At SDZ, each sampler was exposed about 10 days and samples were collected once per month from January 2007 to August 2009 and three times per month from September 2009 to July 2010.

My general point is that with ammonia, you have to prove that you didn't collect contamination because it is so very easy to do.

Answer: It is very important that the sampling and analysis protocols are followed to avoid potential contamination.

The authors tend to repeat the table results (e.g. annual means, correlations in season) when discussing specific points. I think it would be clearer to only bring the numbers out of the table when important. For example, the only strong correlation with season is for winter. I would focus on that one.

Answer: We have revised the manuscript according to the referee's comments. I would expect the authors, when discussing seasonality, would address why the average

NH3 concentration is high in April in Beijing. After you remove the expected seasonality,

ACPD

11, C2953–C2965, 2011

that is very interesting; why is it there?

Answer: NH3 values had a small peak in April as the temperature increase suddenly to cause the accumulated emission of NH3 from natural and fertilized soils, vegetation, and human sources in city centre in winter.

The authors do not discuss the likely condition of wintertime inversions (and low mixing depth) and large summertime mixing depth. I think this is a very important concept generally missing from the discussion.

Answer: Thank you for your suggestion. The discussion of mixing depth has been added in our revised version.

Other Page 3043, 20; I do not understand “and the largest columns are observed”.

Answer: Clarisse et al (2009) have reported global NH3 integrated concentrations retrieved from satellite measurements in 2008. NH3 concentrations were presented with column (mg m-2). We have rewritten the sentences as follows.

Clarisse et al (2009) have presented global NH3 integrated concentrations retrieved from satellite measurements in 2008. They have identified several ammonia hotspots with column above 0.5 mg m-2 in middle-low latitudes across the globe.

Page 3044, 1-4; very complicated sentences beginning “Cao et al “and ending with respectively. It ends up being very unclear and difficult to read/understand.

Answer: We have rewritten the sentences as follows.

Cao et al. (2009) reported the variation of ammonia concentrations in Xi’an. It was found that the average concentrations of NH3 were 18.5 and 20.2 ppb at the urban and suburban sites in Xi’an from April 2006 to April 2007.

Page 3044, 14: English “Recent the measurements”.

Answer: We have corrected the word “Recent” to “Recently”.

ACPD

11, C2953–C2965, 2011

Page 3045, 4: Elevation of the monitor (50 meters) is pretty high. Are there any implications for the measurements, vs. 2 meters?

Answer: The measurement at 2 meters is influenced by many local conditions and cannot represent the area features. Therefore, our measurement at 50 m is more representative of the area characteristics of ammonia.

Table 2: you will need to add the state names to the USA entries for Walker et al.

Answer: We have added the state name "Carolina".

Page 3048, 1-19: here again, the authors repeat all the values form the table. I would recommend just discussing the general findings, etc.

Answer: We have revised the sentences in Page 3048 according to reviewer's comment.

Page 3048, 24: "therefore: : :.Beijing" I don't think we know enough to say that air masses changes are responsible for the observations. This next sentence is true and contradictory to this sentence.

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

ACPD

11, C2953–C2965, 2011

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 highest concentration of NH3. The data in Table 3 suggest that the NH3 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 NH3, and the air masses traveling over the coal mining and power generation

ACPD
11, C2953–C2965, 2011

regions west of Beijing contain the second highest concentrations of ammonia. Therefore, transport of air masses from these regions is responsible for the high concentrations of NH3 at CMA.

Page 3049, 11-14: I agree that water removal is an important part of the understanding, but I don't think you have enough information to say that June and August are reduced due to heavy rain. Your urban July is high I agree, but on average, does it not rain in June at the rural site (Figure 4)? Seasonality: I would seem to me that an important part of your observations could be due to vertical mixing, inversions, etc., and it therefore should be addressed more fully. i.e., your observation of a high correlation in the winter, and traffic source not being important in summer.

Answer: We have revised Section 3 by adding more meteorological analysis and discussions according to the referee's comments.

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 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 concen-

ACPD

11, C2953–C2965, 2011

trations 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).

Page 3054, 5: you also have increased photochemistry in the summer, and higher NOx emissions.

Answer: NH4+ concentrations were high in summer may reflect the influences of primary air pollutants such as NOx on the formation of secondary ammonium particles.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C2953/2011/acpd-11-C2953-2011-

ACPD
11, C2953–C2965, 2011

supplement.pdf

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

ACPD

11, C2953–C2965, 2011

Interactive Comment

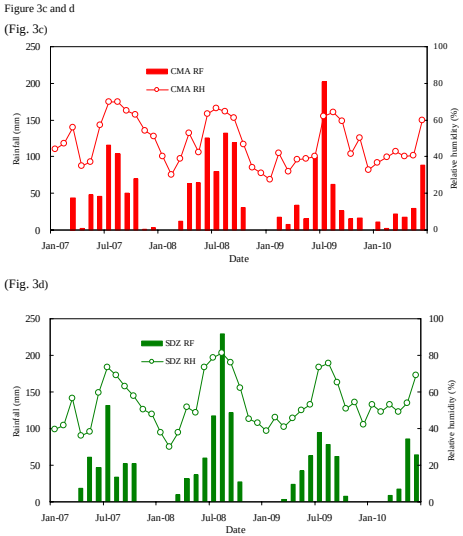

Fig. 1. Fig.3c and d

ACPD
11, C2953–C2965, 2011

Figure 6

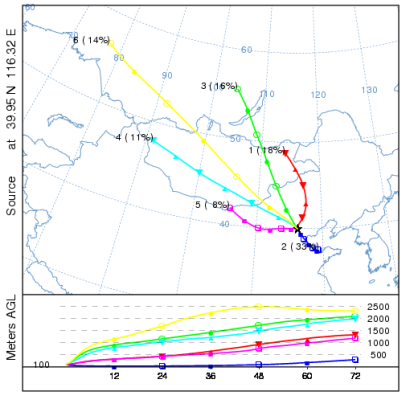

Fig. 6. Air mass backward trajectories for 100 m above ground at Beijing urban site during July 2009-June 2010.

Fig. 2. Fig.6

ACPD
11, C2953–C2965, 2011