Response to comments by editor and anonymous reviewers

We appreciate the editor and anonymous reviewers' comments and helpful suggestions. We have revised the manuscript according to their comments and suggestions. We hope the revised manuscript can meet the quality requirements of *Atmospheric Chemistry and Physics*.

Response to Reviewer #2's comments

Anonymous Reviewer #2

Received and published: 31 May 2017

This manuscript presents a comprehensive ambient measurement dataset, including various trace gases and particulate species, for over four months at a rural site in the North China Plain (NCP). Ammonia (NH3) is the focus of this study for its role in the formation of secondary inorganic aerosols, which accounts for a major fraction of PM2.5 in NCP. The hourly resolution, higher than many of the previous ambient ammonia measurements, enables detailed studies on individual pollution events and the diurnal variations. However, I hope the authors can take better advantage of this dataset, and go deeper into Atmospheric Chemistry and Atmospheric Physics, as indicated by the journal name. For example, this work aims to understand the impact of ammonia on secondary ammonium aerosols (page 1, line 20), facilitate developing future ammonia emission control policies (page 1, line 32), and examine the sources of ammonia and ammonium and their chemical conversion mechanism (page 3, line 8). These are all important issues, but I am not convinced that this article has advanced our current knowledge and understanding about these issues after reading it.

Answer: We thank your comments and suggestions. We have made additional data analysis and revised the manuscript according to the comments and suggestions by both reviewers. To gain more insight into the role of ammonia in the formation of secondary inorganic aerosol, simulations were made using the thermodynamic equilibrium model ISORROPIA II. The measurements were used as input of model to simulate the variations of the components in gas, liquid and solid phases, which are useful in the investigation of the gas-aerosol equilibrium characteristics.

Major comments

1. It takes a significant part of this manuscript to explain the observed concentrations. However many of the explanations are qualitative and even speculative. Further quantitative evidences are needed. To name a few:

Page 8, lines 5-6, "the monthly concentration of SO2, NOx, and CO in July and August decreased because of raid photochemical reduction, additional removal by rainfall, and excellent vertical mixing." What are the evidences of photochemistry, wet scavenging, and vertical mixing?

Answer: We have added the analysis of some related meteorological conditions and show figures with measurements of rainfall and the NO_2 photolysis frequency (jNO_2) during June-August 2013 as supplementary materials. Changes are made to text as follows:

"The monthly concentrations of SO_2, NO_x, and CO in July and August decreased compared to those in June. In addition to less influences from biomass burning, meteorological conditions were also in favor of lowering the concentrations of these gases. Figure S2 shows the monthly average diurnal variations of jNO2 and the time-series of hourly rainfall during June-August 2013. As can be seen, the average jNO2 increased from June to August, indicating better conditions for photochemical reduction in July and August. There was also a slight increase in rainfall from June to August, which may promote removal of the pollutants."

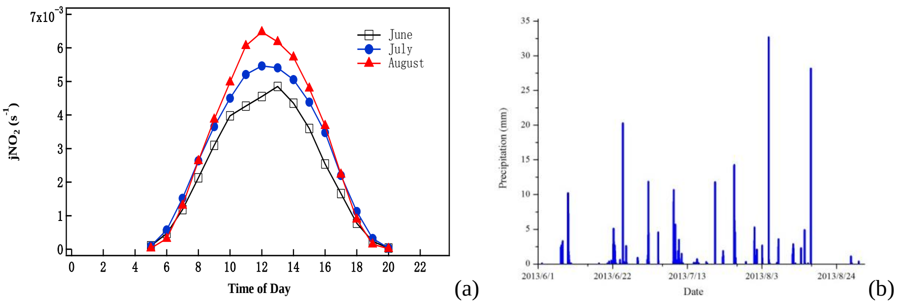


Figure S2. Monthly average diurnal variations of the NO_2 photolysis frequency (jNO_2) (a) and hourly rainfall (b) observed at Gucheng during June-August 2013.

Page 8, lines 8-9, the ozone was highest in June because of "photochemical production, intense burning of biomass, and transport of regional pollution". What are the evidences of more photochemistry, biomass burning, and regional transport in June? Shouldn't July have larger photochemical rates?

Answer: After careful consideration we think the statement should be revised. The sentence is changed to "For the secondary pollutant O_3, the highest concentration was observed in June. This is consistent with previous results from Gucheng (Lin et al., 2009) and should be related with the annual maximum of background O_3 in the NCP, which occurs in June (Lin et al., 2008; Ding et al., 2008). "

Ding, A. J., Wang, T., Thouret, V., Cammas, J.-P., and Nédélec, P.: Tropospheric ozone climatology over Beijing: analysis of aircraft data from the MOZAIC program, Atmos. Chem. Phys., 8, 1-13, 2008.

Lin, W., Xu, X., Zhang, X., and Tang, J.: Contributions of pollutants from North China Plain to surface ozone at the Shangdianzi GAW Station, Atmos. Chem. Phys., 8, 5889–5898, 2008.

Lin, W., Xu, X., and Zhang, X.: Characteristics of gaseous pollutants at Gucheng, a rural site southwest of Beijing, J. Geophys. Res., 114, 10339, 2009.

Page 8, lines 26-27, the downward mixing of the residual layer containing higher ammonia concentration could lead to an increase of ammonia in the morning. This would require a very large pool of ammonia in the residual layer. Why did it not happen in other months?

Answer: Indeed, the interpretation about the morning peak is mainly based on the opinions in cited references, which are mostly speculations. We think more investigations are necessary to be able to clearly and quantitatively explain the morning peak phenomenon. We have revised the 2nd and 3rd paragraphs in section 3.2.2 as follows:

"The morning peak of NH_3 was also observed elsewhere and could be resulted from emissions from fertilized soils and plant stomata, evaporation of dew, and human sources, as well as mixing down of ammonia from the residual layer (Trebs et al., 2004; Norman et al., 2009; Bash et al., 2010; Ellis et al., 2011). Figure 3b reveals that the relative humidity (90%-89%) and temperature (21.5-22.1 ℃) remained relatively constant before 06:00, but increased later in the morning. The increasing temperature can heat the earth’s surface and vegetation leaves and reduce the RH, potentially leading to evaporation of NH3 from soil and plants and volatilization of ammonium aerosol (Trebs et al., 2004; Norman et al., 2009; Ellis et al., 2011), which may increase NH_3 concentrations in the morning. When the emission was occurring into a shallow boundary layer, NH_3 increase would be more prominent. In addition, the morning rise might also be due to the break-up of the nocturnal boundary layer. During the sampling period, the majority of peaks of ammonia over 50 ppb occurred at night, which were attribute to local emissions, such as from agricultural activity, into a shallow nocturnal boundary layer. It was supposed by Ellis et al. (2011) that the downward mixing of air containing higher NH_3 from the residual layer could lead to an increase of surface NH_3 after the breakup of the nocturnal boundary layer. "

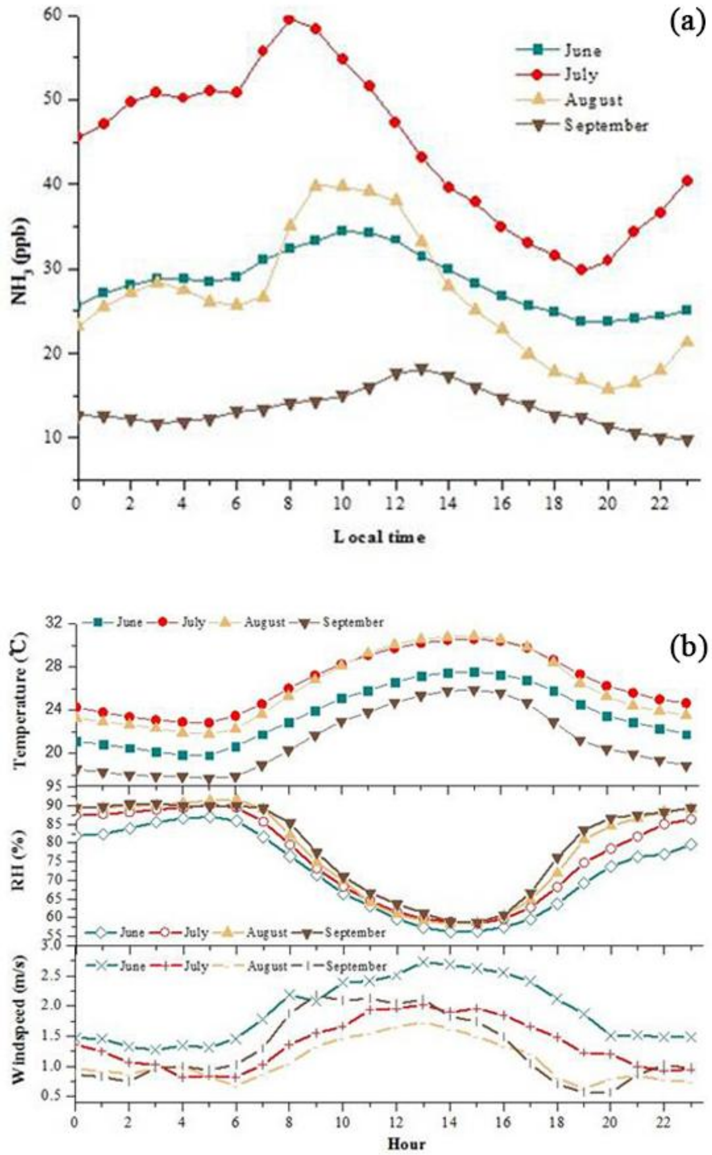


Figure 3. Diurnal variation (a) NH_3 and (b) meteorological parameters during the sampling period.

Bash, J. O., Walker, J. T., Katul, G. G., Jones, M. R., Nemitz, E., and Robarg, W. P.: Estimation of In-Canopy Ammonia Sources and Sinks in a Fertilized Zea mays Field, Environ. Sci. Tech., 44, 1683-1689, 2010.

Ellis, R. A., Murphy, J. G., Markovic, M. Z., VandenBoer, T. C., Makar, P. A., Brook, J., and Mihele, C.: The influence of gas-particle partitioning and surface-atmosphere exchange on ammonia during BAQS-Met, Atmos. Chem. Phys., 11, 133-145, 2011.

Norman, M., Spirig, C.,Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., and Neftel, A.: Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), Atmos. Chem. Phys., 9, 2635–2645, 2009.

Schwab, J.J.: Ambient Gaseous Ammonia: Evaluation of Continuous Measurement Methods Suitable for Routine Deployment, Final Report Prepared for the New York State Energy Research and Development Authority (NYSERDA)，Final Report 08-15, New York, October 2008.

Trebs, I., Meixner, F. X., Slanina J., Oties, R. P., and Andreae, M. O.: Real-time measurements of ammonia, acidic trace gases and water-soluble inorganic aerosol species at a rural site in the Amazon Basin, Atmos. Chem. Phys., 4, 967–987, 2004.

Page 9, line 5, the author explains the earlier ammonia morning peak in July by increased emissions. Further evidence?

Answer: We have no direct evidence of emissions. However, the Gucheng site is an experiment station for agrometeorological studies. Corn is the main crop in the station area and nearly all the agricultural areas in the surrounding. According the climate in the NCP, corn is planted around the middle of June and grows rapidly in July. Therefore, July is the key period for the application of nitrogen fertilizers like urea. For example, during last ten days of July 2013, 225-300 kg of urea were applied per hectare of station area (Meng et al., 2015), causing huge NH3 spikes during the end of July (Fig. 2). In addition, the highest nighttime temperature in July (Fig. 3b) could promote the soil emission of NH_3 and the relatively lower wind speed (Fig. 3b) and lowest PBLH (Fig. S3) in July was in favor of the accumulation of NH_3 in surface air. We have revised the 4th and 5th paragraphs in section 3.2.2 as follows:

"~~-~~From Fig. 3a, it can be seen that in July the NH_3 level was the highest and peaked earliest. One reason for this might be the increased emissions of local agricultural NH_3 sources in July compared with those in June, August, and September. On the average, the level NH3 in July had a maximum nighttime increase (20.0 ppb from 20:00 to 06:00), which is much large than those in June (5.2 ppb), August (9.9 ppb) and September (1.8 ppb). The early morning increase of NH_3 in July started from a much higher level than in other months, resulting a earliest NH_3 peak in July.

There is no direct evidence of increased agricultural NH_3 emission in July. However, the Gucheng site is an experiment station for agrometeorological studies. Corn is the main crop in the station area and nearly all the agricultural areas in the surrounding. According the climate in the NCP, corn is planted around the middle of June and grows rapidly in July. Therefore, July is the key period for the application of nitrogen fertilizers like urea. ~~For example~~As mentioned above, ~~during last ten days of~~the urea application in the station on 20 July 2013 and a precipitation process afterwards~~, 225-300 kg of urea were applied per hectare of station area (Meng et al., 2015),~~ caus~~ing~~ed huge NH_3 spikes during the end of July (Fig. 2b). In addition, the highest nighttime temperature in July (Fig. 3b) could promote the soil emission of NH_3, and the relatively lower wind speed (Fig. 3b) and lowest PBLH (Fig. S3) in July was in favor of the accumulation of NH_3 in surface air.

In summary, ambient NH_3 at Gucheng showed interesting diurnal cycles, which look significantly different in different summer months. We believe the interplay of some processes, such as emissions from agricultural sources, meteorological conditions (temperature, relativity humidity, wind speed, and

BHL height, etc.) as well as chemical conversion are important in the determination of levels and diurnal patterns of NH_3 at the site. Whether or not these processes are all important in the morning variation of NH_3? How important are they? And what makes the difference in the peaking time and concentration of NH_3 in different months? These are questions to be answered in the future."

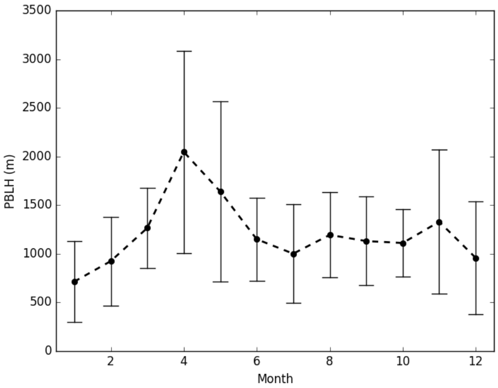


Figure S3. The monthly planetary boundary layer heights at 14:00 during 2013 at Gucheng.

Guo, J., Miao, Y., Zhang, Y., Liu, H., Li, Z., Zhang, W., He, J., Lou, M., Yan, Y., Bian, L., and Zhai, P.: The climatology of planetary boundary layer height in China derived from radiosonde and reanalysis data, Atmos. Chem. Phys., 16, 13309-13319, 2016.

Miao, Y., Guo, J., Liu, S., Liu, H., Li, Z., Zhang, W., and Zhai, P.: Classification of summertime synoptic patterns in Beijing and their associations with boundary layer structure affecting aerosol pollution, Atmos. Chem. Phys., 17, 3097-3110, 2017.

2. A high observed concentration can always be explained by more emission, less mixing, or less removal. I think a publication in ACP should go beyond reporting the concentrations of these short-lived species, as the concentrations are highly variable. This study used the ratio between ammonium and NHx to infer the gas-particle conversion of ammonia. However the ammonium and ammonia may be from different sources, where ammonium is formed in the city with NOx and SO2, and ammonia is emitted locally. In other words, what if NHx and NH3 are decoupled?

Answer: We have made simulations using the ISORROPIA II model and analyzed the model results together measurements. We think we have gained more insight than before but also acknowledge that there are limitations in our observation, modeling and data analysis. Some open issues remain to be addressed in future studies.

The ratios NHR (NH_4^+/NHx), SOR (SO_4^{2-}/(SO_4^{2-}+SO_2)) and NOR (NO_3^-/(NO_3^-+NOx)) were calculated as measures of chemical conversion of NH_3, SO_2 and NOx. You are right that NHx and NH3 may be decoupled. Sources of NH_3, SO_2 and NOx may be dislocated. The lifetimes of these gases are different and hence the dispersion areas. F~~In f~~ine aerosol particles may travel much longer than the precursor gases. In the real situation we always observe gases and aerosols originating both from cities and from rural areas, emitted by different sources, and chemically produced. Wherever we measure, we measure is a mixture impacted by different sources~~,~~ from locations and processes. In this sense, we should not attribute our results only to local impacts or local situation. When our observation at a site covers a longer period, our results should be applicable to ~~......~~ areas in varying size~~—~~.

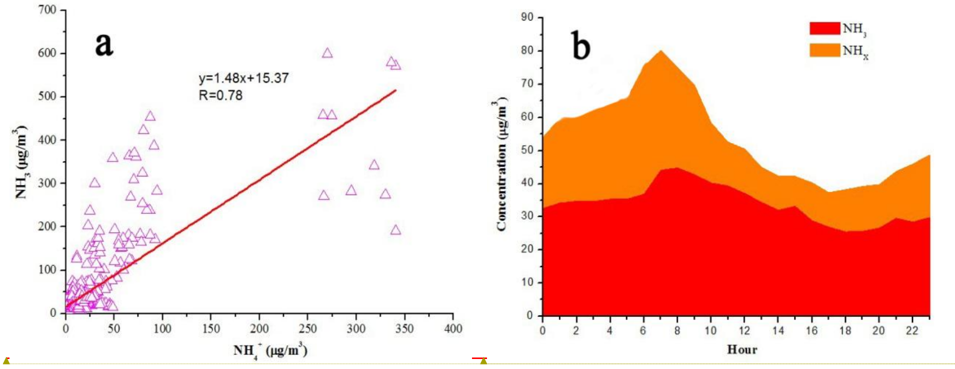
~~The ratio of NH_3 to NH_x (NH_3+NH_4^+) has been used to identify the source of NH_x and the relative contribution of NH_3 to NH_x deposition (Lefer et al., 1999; Walker et al., 2004). The parameter NHR defined here could be a measure of the extent of transformation from NH_3 to NH_4^+ in areas with significant local NH_3 sources, although it encompasses both transformation and local equilibrium, the latter dominating further downwind from the source (Hu et al., 2014).~~

~~We have drawn the Figure 8 and added following interpretation in response to reviewer's comment, as follow:~~

~~In this study, NH_4^+ concentrations correlated significantly and positively with NH_3 with a correlation coefficient of 0.78 and a slope of 1.48 (Fig.8a, n=915, P<0.01), suggesting that NH_3 played a important precursor role in NH_4^+ in $PM_{2.5}$ formation.~~

~~According to hourly average concentrations, the ratio of NH_3/NH_x varied from 0.22 to 0.97, with a mean ratio of 0.69±0.14, suggesting that NH_3 remained predominantly in the gas phase rather than the aerosol phase in summer 2013 at Gucheng.~~

~~The diurnal changes in gaseous precursors and aerosol species are controlled by emission and deposition processes, horizontal and vertical transport and gas-particle partitioning. To investigate gas-particle conversion further, diurnal variation of NH_x was showed in Fig. 8b. Between 08:00–18:00, a decrease in NH_3 would result in an increase in NH_4^+, which coincided with higher sulfate concentrations (see Section 3.4). The decrease in gas phase ammonia is likely the result of uptake onto aerosols to from $(NH_4)_2SO_4$. The diurnal variability of NH_x may be controlled by transport and vertical exchange. Between the hours of 08:00-18:00, NH_3 decreased by 43% while NH_x decreased by 49%, suggested that NH_3 remained predominantly in the gas phase. Between 19:00 and 07:00, NH_3 increased by 42% and NH_x increased by 51%, indicating that gas-particle partitioning contributes significantly to the decrease in gas phase ammonia during this time.~~



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~~Figure 8. Relationship between NH_3 and NH_4^+ (a) and diurnal variation of NH_x (b) in summer 2013.~~

At page 10, line 13, it is summarized that "This observation emphasizes the important role of NH3 in the formation of secondary SO4, NO3 and NH4 aerosols, which should be further

explored...". The title of this manuscript is about the role of ammonia on secondary inorganic aerosols, but what exactly is this role? It is not satisfying to only know it is important and needs further exploration.

Answer: We have deleted this sentence. New results from model simulation and data analysis are added and discussed in the revised manuscript. In particular~~selected the cases to analyze the detailed impact of NH_3 on fine particulate formation in our revised version in response to reviewer's comment~~, we have added two new sections:

"**3.4 Results from thermodynamic equilibrium simulation**

We have used the thermodynamic equilibrium model ISORROPIA II to investigate gas-aerosol partitioning characteristics. NO_3^-, SO_4^{2-} and NH_4^+. The model outputs include equilibrium NO_3^-, SO_4^{2-}, NH_4^+. H^+_{air}, HNO_3, NH_3, AWC, etc. As shown in Fig. 5, the modelled NO_3^-, SO_4^{2-}, NH_3 show excellent correlations with the corresponding measurements, but modelled NH_4^+ is much worse correlated with the measured one. Modelled NO_3^-, SO_4^{2-}, and NH_3 values agree well with the measurements, while the modelled NH_4^+ largely underestimate the measurements. Considering the unbalance between observed NH4+ and the sum of observed SO_4^{2-}+NO_3^-+Cl^-, we can confirm that other acids in aerosol particles are important in the conversion of NH_3 to NH_4^+. These other acids may be oxalic acid and other dicarboxylic acids. Although we did not measure organic acids in aerosol, the presence of oxalic acid and other low molecular weight dicarboxylic acids in aerosols is often reported (e.g., Hsieh et al., 2007; Kawamura et al., 2010, 2013; Sauerwein and Chan, 2017). There is no doubt about the presence of significant amount of dicarboxylic acids over the North China Plain particularly during summer (Kawamura et al., 2013). Therefore, it is highly possible that neutralizing dicarboxylic acids in aerosol particles contributed significantly to the conversion of ammonia to ammonium.

The simulated HNO_3 concentrations was 0.9 ± 1.1 μg m^{-3}, showing a maximum value of 7.41 μg m^{-3} at 11:00 on 19 June 2013. The average diurnal variations of HNO_3 and H^+_{air} are shown in Fig. S4. The fine particles were moderately acidic in summer, with an average pH values of 3.5. The pH values of aerosol water, estimated based on the simulated results using equation (4), are mostly in the range of 2.5-4.5, with an average of 3.5. On average, pH is over 3.5 during nighttime and below 3.5 during daytime (Fig. 6). Under the medium acidic conditions and high NH_3 concentrations, organic acid like diacids are able to reaction with ammonia to for ammonium. Because we used ISORROPIA-II for inorganic aerosol composition and no organic acids measurements are available, we cannot analyze in detail the role of organic acids though the model performed quite well (Fig. S5).

On several days during the study period, very high NH_3 and inorganic $PM_{2.5}$ concentrations were observed. As shown in Fig. 6a, the peak NH_3 value of 76.3 ppb at 09:00 on 10 August was observed, with SO_2 and NO_x concentrations of 3.33 ppb and 14.72 ppb, respectively. A few hours later, the concentration of SO_4^{2-} increased by a factor of 2.0 from 18.3 to 35.9 μg m^{-3} and NH_4^+ concentration rose by a factor of 1.6 from 15.9 to 24.8 μg m^{-3}, with NO_3^- concentration from 14.3 to 15.7 μg m^{-3} at 13:00 on 10 August. High NH_3 concentration was accompanied by the large increase in concentrations of SO_4^{2-}, NO_3^- and NH_4^+ during this period.Several pollution episodes of precursor gases, SO_4^{2-}, NO_3^- and NH_4^+ in $PM_{2.5}$ were observed during the study period. As shown in Fig. 46a, the peak values of NH_3, SO_2 and NO_x (76.3 ppb at 09:00, 14.9 ppb at 14:00 on and 42.2 ppb at 00:00 on 10 August, respectively) were observed, which were accompanied by the large increase in concentrations of SO_4^{2-}, NO_3^- and NH_4^+ during 7-11 August 2013. This suggests that NH_3 played an important role in PM mass formation and that gas particle conversion occurred when NH_3 was available, though SO_4^{2-} partitions to the aerosol phase regard less of NH_3 level (Gong et al., 2013). Due to the atmospheric conditions favoring the accumulation of pollutants, the concentrations of NH_4^+, SO_4^{2-} and NO_3^- (24.8, 35.9 and 15.7 μg m^{-3}, respectively) at 13:00 on 10 August were detected and higher compared with the average concentrations during 7-11 August 2013 by around 127%, 81% and 83%, respectively. These secondary ions concentrations had similar temporal distributions with slow accumulation and relatively rapid clearing under favourable meteorological conditions. There were good correlation between NH_3 with NH_4^+, SO_4^{2-} and NO_3^- (R=0.33, 0.27 and 0.49, respectively, with $P < 0.01$). Our study and other research reveal that reducing NH_3 concentrations could be an effective method for alleviating secondary inorganic $PM_{2.5}$ pollution in the NCP, besides the reduction of primary SO_2, NOx and aerosol emissions.This observation emphasizes the important role of NH_3 in the formation of secondary SO_4^{2-}, NO_3^- and NH_4^+ aerosols, which should be further explored to solve the current air pollution problems in NCP and other regions of the world.

During 7-11 August 2013, the relationships of the observed NH_4^+ versus those of SO_4^{2-}, the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- are presented in Fig. 46balso analyzed. It is known that $(NH_4)_2SO_4$ is preferentially formed and the least volatile, NH_4NO_3 is relatively volatile, while NH_4Cl is the most volatile. NH_4^+ is thought to be first associated with SO_4^{2-}, afterwards, the excess of NH_4^+ is with nitrate and chloride (Meng et al., 2015). It is noted that the correlation of NH_4^+ with the sum of SO_4^{2-} and NO_3^- (R=0.91, slope=1.23, with $P < 0.01$) was better than that of NH_4^+ with SO_4^{2-}

(R=0.80, slope=1.65, with $P < 0.01$), suggesting that both SO_4^{2-} and NO_3^- were associated with NH_4^+. As shown in Fig.4b, sulfate and nitrate were almost completely neutralized with most of the data above the 1:1 line. A few scattered data below the 1:1 line . Little different was found between the regression slopes of NH_4^+ with the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- due to the very low amount of NH_4Cl. In this study, NH_4^+ was enough to neutralize both SO_4^{2-} and NO_3^-, and likely to be in the form of $(NH_4)_2SO_4$, NH_4HSO_4, and NH_4NO_3.

The analysis of water soluble ions in $PM_{2.5}$ at NCP rural site also indicated that biomass burning was a crucial source of aerosol species. This attribution is supported by the concentrations of K^+ in $PM_{2.5}$, an excellent indicator for biomass burning emission. The monthly concentrations of K^+ in $PM_{2.5}$ were 2.17, 1.62 and 0.98 g m^{-3} in June, July and August, respectively, with the highest concentration in June 2013. During the period of 16–19 June, 2013, elevated concentrations of K^+ (33.28 g m^{-3} at 08:00 on 16 June), NH_4^+ (33.28 g m^{-3}), SO_4^{2-} (24.53 g m^{-3}), and NO_3^- (29.79 g m^{-3}) were observed, which is consistent with the increase of CO, SO_2, NO_x and NH_3 at the same time.

The comparison of the model and measurement results of the partitioning between NH_3 and inorganic ions in $PM_{2.5}$ was shown in Fig. 5. The model predictions and measurements were in reasonable agreement, and the agreement on NH_3 was better than the NO_3^-, SO_4^{2-} and NH_4^+. According to Fig. 5, the simulated NH_3 was in good agreement with observation with an R^2=0.94 and normalized mean bias (NMB) of 26.9% for all the data, implying a good performance of ISORROPIA II. Howheve, in most cases the model tended to under-predict aerosols species, especially for NH_4^+ in summer. During sampling period, aerosols water content (AWC), ranged between 2.3 and 910 μg m^{-3}, with an average concentration of 78.7 ± 74.3 μg m^{-3}, which was primarily due to both high RH and denser fine particles in the atmospheric boundary layer (Bian et al., 2014). "

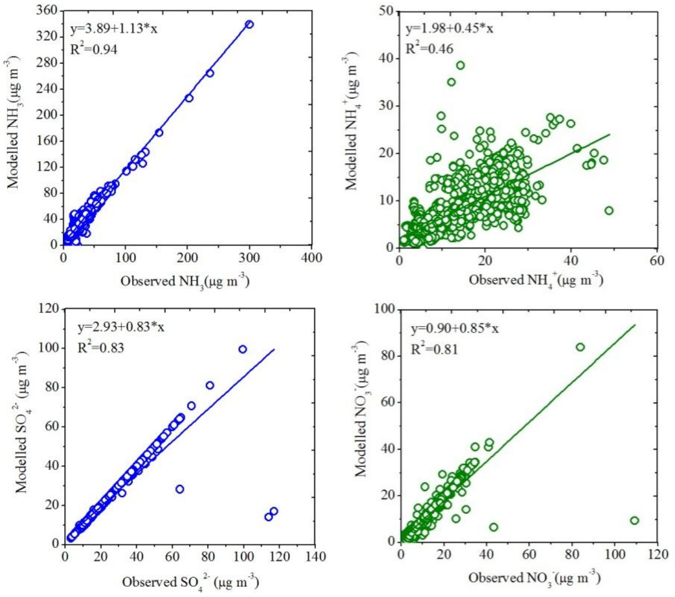

Figure 5. Observed and modelled concentrations of NH_3, NH_4^+, SO_4^{2-} and NO_3^- in summer 2013.

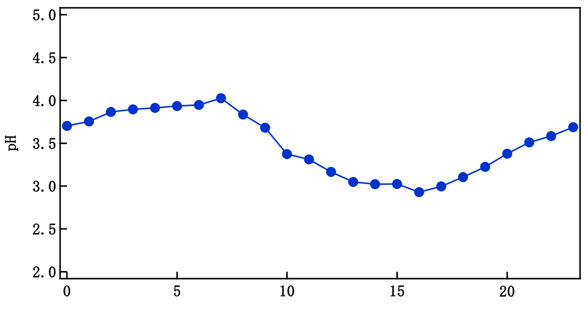

Figure 6. Calculated diurnal variation of pH value of aerosol water.

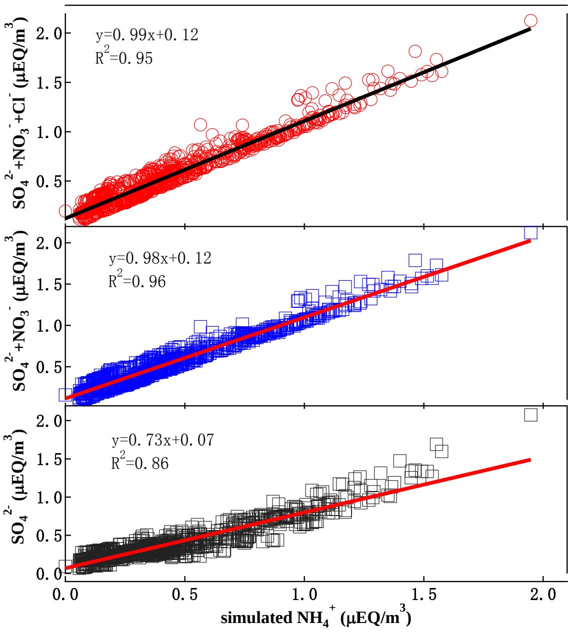

Figure S5 Correlation of modelled NH_4^+ with modelled SO_4^{2-}, $SO_4^{2-}+NO_3^-$ and $SO_4^{2-}+NO_3^-+Cl^-$..

"3.6 A case study of a pollution period

On several days during the study period, very high NH_3 and inorganic $PM_{2.5}$ concentrations were observed. Here make a case study of a pollution period during 7-11 August 2013. Data of gases, major aerosol ions and some key meteorological parameters are presented in Fig. 9. Some other measure and calculated parameters during this period are given in Fig. S6. As shown in Figs. 9 and S6, there was a sharp increase of NOx during the night and early morning of 10 August, followed by that of NH_3 (peak value 64 ppb at 03:00. In the meantime, a large peak of AWC occurred and gaseous HNO3 decreased to nearly zero (Fig. S6), suggesting rapid uptake of wet aerosol. This event caused the first largest peak of $[SO_4^{2-}]+[NO_3^-]+[NH_4^{+-}]$. After this event NH3 rose again and reached a even higher peak (76.3) shortly before noon of 10 August. This peak of NH3 coincided with a valley of NOx, but the HNO3 level increased and pH value decreased was observed in parallel. A few hours later SO2 showed a large peak and the second largest peak of $[SO_4^{2-}]+[NO_3^-]+[NH_4^{+-}]$ occurred. These data show that high NH_3 concentration was accompanied by the large increase in concentrations of SO_4^{2-}, NO_3^- and NH_4^+, confirming that NH_3 play an important role in PM mass formation and that gas-particle conversion occurred when NH_3 was available, though SO_4^{2-} partitions to the aerosol phase regard less of NH_3 level (Gong et al., 2013). The secondary ions concentrations had similar temporal distributions with slow accumulation and relatively rapid clearing under favourable meteorological conditions. There were good correlation between NH_3 with NH_4^+, SO_4^{2-} and NO_3^- (R=0.33, 0.27 and 0.49, respectively, with P < 0.01). However, there was also situation when high NH3 did not associate with high $[SO_4^{2-}]+[NO_3^-]+[NH_4^{+-}]$, as indicated by the data around noon of 8 August (Fig. 9). During this case, AWC was extremely low and RH was around 40%. These conditions do not favor heterogeneous reactions.

During 7-11 August 2013, the relationships of the observed NH_4^+ versus those of SO_4^{2-}, the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- are presented in Fig. 10. It is known that $(NH_4)_2SO_4$ is preferentially formed and the least volatile, NH_4NO_3 is relatively volatile, while NH_4Cl is the most volatile. NH_4^+ is thought to be first associated with SO_4^{2-}, afterwards, the excess of NH_4^+ is with nitrate and chloride (Meng et al., 2015). It is noted that the correlation of NH_4^+ with the sum of SO_4^{2-} and NO_3^- (R=0.91, slope=1.23, with P < 0.01) was better than that of NH_4^+ with SO_4^{2-} (R=0.80, slope=1.65, with P < 0.01), suggesting that both SO_4^{2-} and NO_3^- were associated with NH_4^+. As shown in Fig.10, sulfate and nitrate were almost completely neutralized with most of the data above the 1:1 line. A few scattered data below the 1:1 line may be caused by uncertainties in measurements. Little different was found between the regression slopes of NH_4^+ with the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- due to the very low amount of NH_4Cl. In this study, the level of NH_3 was high enough to neutralize both SO_4^{2-} and NO_3^-, and likely to be form $(NH_4)_2SO_4$ and NH_4NO_3. In addition to these substances, it is likely that NH3 also reacted with oxalic acid and other dicarboxylic acid to form ammonium oxalate and other organic ammonium aerosols, as discussed above."

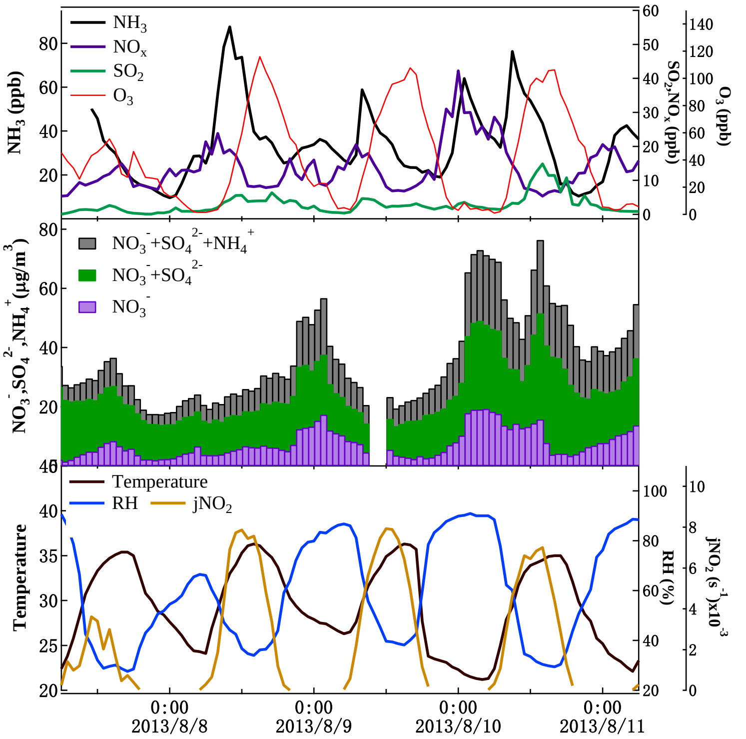

Figure 9. Hourly concentrations of precursor gas and ionic species measured in the pollution episode (a) temporal variations and (b) correlations of [NH_4^+] versus [SO_4^{2-}], [SO_4^{2-}]+[NO_3^-] and [SO_4^{2-}]+[NO_3^-]+[Cl^-] during 7 –11 August 2013.

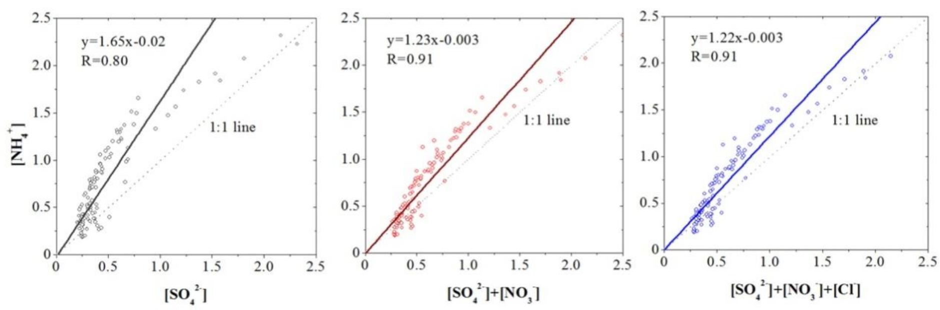

Figure 10. Correlations between [NH_4^+] and [SO_4^{2-}] (left), [NH_4^+] and [SO_4^{2-}]+[NO_3^-] (middle) and [NH_4^+] and [SO_4^{2-}]+[NO_3^-]+[Cl^-] (right) during 7-11 August 2013.

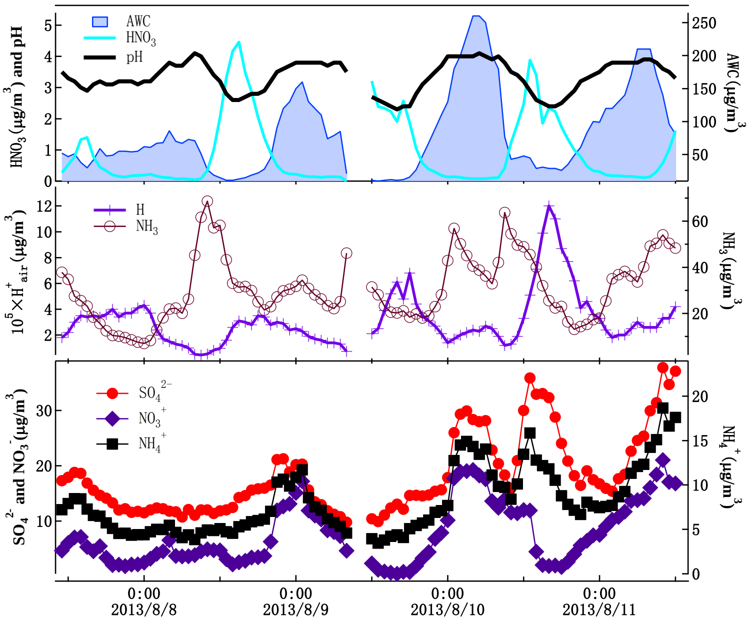

Figure S6. Time series of predicted fine particle pH, predicted particle water mass, predicted H_{air}^{+} and measured NH_3 and measured inorganic ions during 7-11 August 2013

~~On several days during the study period, very high NH_3 and inorganic $PM_{2.5}$ concentrations were observed. As shown in Fig. 6a, the peak NH_3 value of 76.3 ppb at 09:00 on 10 August was observed, with SO_2 and NO_x concentrations of 3.33 ppb and 14.72 ppb, respectively. A few hours later, the concentration of SO_4^{2-} increased by a factor of 2.0 from 18.3 to 35.9 g m^{-3} and NH_4^+ concentration rose by a factor of 1.6 from 15.9 to 24.8 g m^{-3}, with NO_3^- concentration from 14.3 to 15.7 g m^{-3} at 13:00 on 10 August. High NH_3 concentration was accompanied by the large increase in concentrations of SO_4^{2-}, NO_3^- and NH_4^+ during this period. This suggests that NH_3 played an important role in PM mass formation and that gas-particle conversion occurred when NH_3 was available, though SO_4^{2-} partitions to the aerosol phase regard less of NH_3 level (Gong et al., 2013).~~

Specific comments

Page 1, line 29: please define “transport of air mass from the North China Plain region”, as the site itself is in the middle of NCP.

Answer: Yes, the site is located in the middle of NCP. The concentrations of pollutant levels at Gucheng site are not only driven by local sources but also affected by long range transport. We have changed the title of Section 3.5 to "Long rang transport and local source of ammonia and ammonium" and revised the text as follows:

"Dependence of the concentrations of NH_3 on wind direction at Gucheng is studied to get insight into the distribution of local emission sources around the monitoring site. As shown in Fig. 11, during the sampling period, the prevailing surface winds at Gucheng were northeasterly and southwesterly. High NH_3 originated from the southwest sector of the measurement site, which may be due to a local unidentified agricultural or industrial source or transport from the Xushui township, which is approximately 15 km away from Gucheng. Lower NH_3 concentrations were observed under winds from other sectors. Since NH_3 is either readily converted to NH_4^+ or subjected to dry deposition, high concentrations are found only close to the surface and near the emission sources. Previous studies have reported an inverse relationship between ground-level concentrations of trace gases, such as ammonia, and wind speed (Robarge et al., 2002; Lin et al., 2011). Thus, NH_3 concentrations might be generally lower at higher wind speeds because of turbulent diffusion.

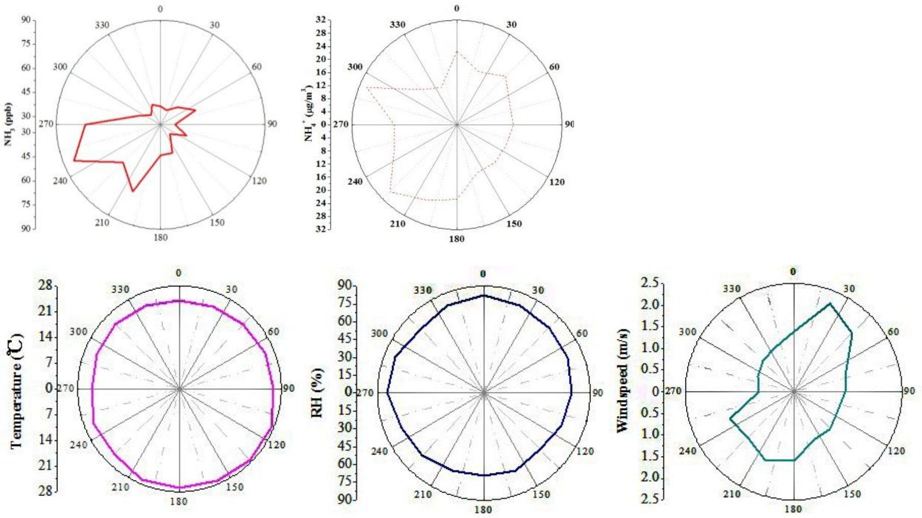

Figure 11. The average NH_3, NH_4^+ concentrations and meteorological data roses in different wind sectors during summer 2013."

Lin, W., Xu, X., Ge, B., and Liu, X.: Gaseous pollutants in Beijing urban area during the heating period 2007-2008: variability, sources, meteorological and chemical impacts, Atmos. Chem. Phys., 11, 8157-8170, 2011.

Robarge, W. P., Walker, J. T., McCulloch, R. B., and Murray, G.: Atmospheric concentrations of ammonia and ammonium at an agricultural site in the southeast United States, Atmos. Environ., 36, 16611-1674, 2002.

Page 3, line 22: how large is the "surrounding area" that impacts the measurements of this site?

Answer: The site is situated in the middle of a large agricultural region with many villages. The information of Gucheng site in details can be found in Lin et al. (2009). Accord~~ru~~ing to the maps ~~drawn by~~from Lin et al. (2009) shown below, the Gucheng site is surrounded by farms, dense villages/towns, and the transportation network~~s~~ in the NCP. The accurate size of the surrounding area that really impacts the measurements at Gucheng is not easy to define and varies with meteorological condition, particularly wind speed. One can do footprint analysis by setting criteria, but this is out of the scope of this paper.

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(a)

(b)

Figure 1. Location of Gucheng site and the topography of the surrounding region (a) from Google Earth imagery (copyright Google Inc., used with permission) and (b) from NASA satellite map (Community Landsat7 visible color; http://worldwind.arc.nasa.gov).

Section 2.2: what's the response time of the Los Gatos instrument? What is the concentration and accuracy of the calibration gas?

Answer: We have added ~~following~~ information ~~in our~~ revised ~~version in response to reviewer's comment,~~ the related text as follows:

"Ambient NH_3 was measured using an ammonia analyzer (DLT-100, Los Gatos Research, USA), which utilize a unique laser absorption technology called Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS). The analyzer has a precision of 0.2 ppb at 100 sec average and a maximum drift of 0.2 ppb over 24 hrs. The response time of the analyzer is less than 2 s (with optional external N920 vacuum pump). During the campaign, NH_3 data were recorded as 100-s average. In principle, the NH3 analyzer does not need external calibration, because the measured fractional absorption of light at an ammonia resonant wavelength is an absolute measurement of the ammonia density in the cell (Manual of Economical Ammonia Analyzer - Benchtop Model 908-0016, Los Gatos Research). However, we confirmed the good performance of the NH3 analyzer using a reference gas mixture NH_3/N_2 (Scottgas, USA) traceable to US National Institute for Standards and Technology (NIST). The reference gas of NH3 (25.92 ppm with an accuracy of ±2%) was diluted to different concentrations using zero air and supplied to the analyzer and a sequence with 5 points of different NH_3 concentrations (including zero) were repeated for several times to check the performance of the analyzer. As shown in Fig. S1, the analyzer followed rapidly to changes of the NH_3 concentration, produced stable response under stabilized NH_3 concentrations, and repeated accurately (within the uncertainty) the supplied NH_3 concentrations. The NH_3 analyzer contains an internal inlet aerosol filter, which was cleaned before our campaign. Nevertheless, some very fine particles can deposit on the mirrors of the ICOS cell, leading to gradual decline in reflectivity. However, slight mirror contamination does not cause errors in NH_3 measurements because the mirror reflectivity is continually monitored and the measurement is compensated using the mirror ringdown time. Interferences to NH_3 measurements can be from the sample inlets, for example, due to water condensation or adsorption/desorption effects (e.g., Schwab, 2008; Norman et al., 2009). Such interferences were not quantified but reduced as possibly as we could. PTFE tubing (4.8 mm ID), which is one of the well suited materials for NH_3 measurement (Norman et al., 2009), was used to induced ambient air. The length of the tubing was kept as short as possible (about 5 m) to limit the residue time to less than 3 s. The aerosol filter at the inlet was changed every two weeks. Water condensation was avoided. Nevertheless, we cannot exclude the influence from the adsorption and desorption, which can also occur on dry surfaces. However, this influence should be small at our site, where the NH_3 concentration is very high, and cause mainly a lag in the recorded NH_3 concentration. "

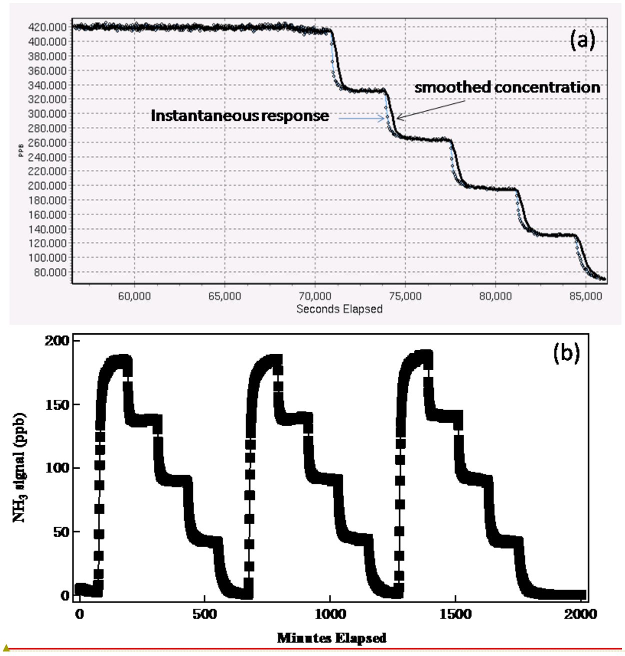

Figure S1 Confirmation of the performance of NH3 analyzer using diluted standard gas (mixture NH3/N2). (a) Instrument response to changed NH3 concentration and stability; (b) repeated multipoint calibrations.

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Norman, M., Spirig, C.,Wolff, V., Trebs, I., Flechard, C., Wisthaler, A., Schnitzhofer, R., Hansel, A., and Neftel, A.: Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), Atmos. Chem. Phys., 9, 2635–2645, 2009.

Schwab, J.J.: Ambient Gaseous Ammonia: Evaluation of Continuous Measurement Methods Suitable for Routine Deployment, Final Report Prepared for the New York State Energy Research and Development Authority (NYSERDA)，Final Report 08-15, New York, October 2008.

~~The response time of the analyzer is less than 2 s (with optional external N920 vacuum pump).~~
~~The concentration of the reference gas of NH_3 is 25.92 ppm with air in balance~~
~~(Certificate Master Class Calibration Standard, with an accuracy of ±2%, from Scottgas, USA).~~

Page 6, line 3: please define "human activity" as it seems a very broad concept.

Answer: We have changed "human activity" to "human excrement and waste disposal~~added following information in our revised version in response to reviewer's comment, as follow:~~".

~~Ammonia emission from human activity include human excrement and waste disposal, etc.~~

Page 6, line 5: there is no "Zhng et al., 2010" in the reference list.

Answer: This was one of the typos. We have ~~revised the reference~~corrected it to "Zhang et al., 2010".

Page 6, line 8-9: please clarify how can these results "be used in improving NH3 emission inventory and making future emission control policies".

Answer: We have ~~added following information in our revised version in response to reviewer's comment,~~revised our expression as follows:

"In recent year a few publications about China's national and regional emission inventories of NH_3 (e.g., Zhou et al., 2015; Xu et al., 2015, 2016; Kang et al., 2016). However, these inventories are based on bottom-up studies, subject to substantial uncertainties in spatial and temporal variations of NH_3 emissions. Ground based observations of NH_3 have been sparse. Our measurements, together with others, can be used for validating and constraining models that use bottom-up inventories, and hence help to reveal potential bias in NH_3 emission inventory."

Kang, K., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., Yan, X., He, H., Zhang, Q., Shao, M., and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, Atmos. Chem. Phys., 16, 2043–2058, 2016.

Xu, P., Zhang, Y., Gong, W., Hou, X., Kroeze, C., Gao, W.,and Luan, S: An inventory of the emission of ammonia from agricultural fertilizer application in China for 2010 and its high-resolution spatial distribution, Atmos. Environ., 115, 141-148, 2015.

Xu, P., Liao, Y. J., Lin, Y. H., Zhao, C. X., Yan, C. H., Cao, M. N., Wang, G. S., and Luan, S. J.: High-resolution inventory of ammonia emissions from agricultural fertilizer in China from 1978 to 2008, Atmos. Chem. Phys., 16, 1207–1218, 2016.

Zhou, Y., Cheng, S., Lang, J., Chen, D., Zhao, B., Liu, C., Xu, R., and Li, T.: A comprehensive ammonia emission inventory with high-resolution and its evaluation in the Beijing-Tianjin-Hebei (BTH) region, China, Atmos. Environ., 106, 305-317, 2015.

~~There are substantial uncertainties in spatial and temporal variations of NH_3 due to the scarcity of ground based observations. our results are expected to be used in improving NH_3 emission inventory and making future emission control policies in the NCP.~~

~~Our study and other research reveal that reducing NH_3 concentrations could be an effective method for alleviating secondary inorganic $PM_{2.5}$ pollution in the NCP, besides the reduction of primary SO_2, NOx~~

~~and aerosol emissions. However, although SO_2, NO_x and $PM_{2.5}$ is routinely measured in large Chinese cities, NH_3, an important precursor of secondary particles, is currently not included in China's emission control policies of air pollution precursors, our findings highlight the important role of NH_3 in secondary inorganic aerosol formation and are expected to facilitate developing future NH_3 emission control policies for the North China Plain.~~

Figure 2: I understand ammonia is shown in log scale because its concentration spanned three orders of magnitude. However I suggest add a sub plot with linear scale so that the variability is comparable at different concentration levels and the individual spikes from pollution episodes are clearer.

Answer: Thank you for your suggestion. We have redrawn Figure 2 ~~in response to reviewer's comment, as follow~~as shown below:

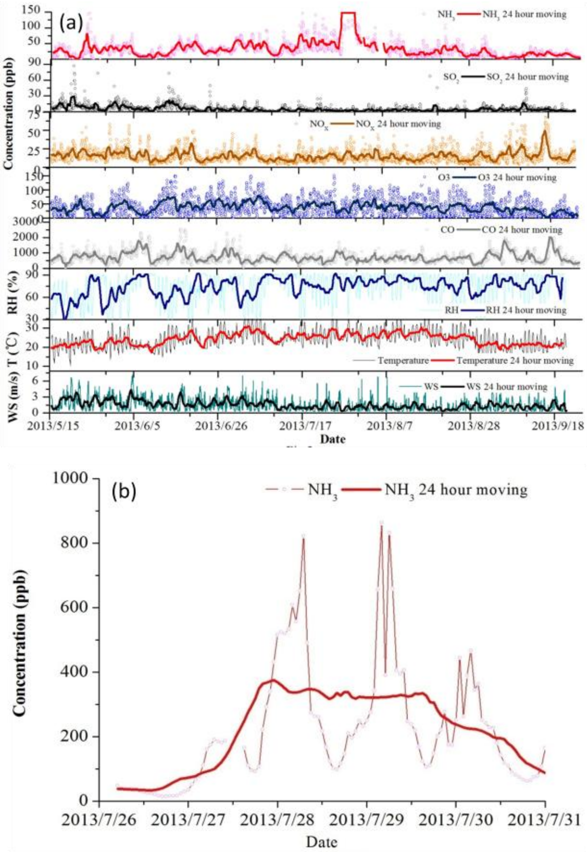

Figure 2. Time series of hourly data of NH_3, other trace gases and meteorological parameters measured during the sampling period (a) and a blow-up of the period with extremely high NH_3 values during 27-31 July 2013.

Page 7, line 6: where the urea was applied and how large was the applied area?

Answer: We have added the required information and ~~following interpretation in our~~ revised the text

~~version in response to reviewer's comment,~~ as follows:

"The Gucheng station has a farmland of 8.67 hectares. The observation period was in the time of the wheat harvest and corn seeding and growing. Corn was sown and fertilized with about 600 kg of fertilizer per hectare in late June. On 20 July corn was additionally fertilized with 225 to 300 kg of urea per hectare. After this fertilization, there was a raining period. The NH_3 concentration increased rapidly on the seventh day after the urea application on 20 July, peaking during the 27–30 July period (Fig. 2b)."

~~The Gucheng station has a farmland of 8.67 hectares. The observation period was in the time of the wheat harvest and corn seeding. Corn was sown and fertilized, with about 600 kg of fertilizer per hectare in late June. The additional fertilizer was applied to corn, with 225 to 300 kg of urea per hectare on 20 July. After applying fertilizer, there was a precipitation process, increasing soil moisture and resulting in nitrogen conversion and volatilization in soil with a large amount of~~ ~~NH_3~~ ~~emissions into the atmosphere.~~

Page 7, line 29: what are these "trace gases"?

Answer: We have added "such as NO_x and CO~~-~~"at the end of "trace gases" to in our revised version~~-in response to reviewer's comment~~.

Page 8, lines 14-15 and page 8, lines 30: these two sentences seem contradict each other.

Answer: We have deleted the ~~sentence of line 30 in Page in response to reviewer's comment~~paragraph there.

Page 10, line 1: higher NO3 level than what?

Answer: We have deleted this sentence and changed~~revised~~ the sentence~~s in response to reviewer's comment, as follow:~~ before to " On the other hand, NH_3 was more efficient in summer to react with SO_2 to form $(NH_4)_2SO_4$. The average concentration of NO_3^- in $PM_{2.5}$ was 11.3 ±9.1 μg m^{-3}. The highest value of 109.3 μg m^{-3} was observed at 14:00 on 22 June 2013 at the highest RH (93%) and AWC (910 μg m^{-3})".

~~The average concentration of~~ ~~NO_3^-~~ ~~in~~ ~~$PM_{2.5}$~~ ~~was 11.3 ± 9.1 g~~ ~~m^{-3}~~~~. The highest value of 109.3 g~~ ~~m^{-3}~~ ~~was observed at 14:00 on 22 June 2013, with high RH of 93% and the highest aerosol water content (AWC) of 910 g~~ ~~m^{-3}~~~~. This suggested that the nitrate concentration increased with an almost similar increase in excess ammonium via the gas-phase homogeneous reaction between the ambient ammonia and nitric acid in the ammonium rich condition, thus forming nitrate or the nitrate sulfate salts of ammonium (Pathak et al., 2009).~~

Page 10, line 20-25: I suggest add a figure showing the slope and correlations. The SO4 should be normalized with its number of charge. What is the evidence for the existence of NH4HSO4?

Answer: We have ~~drawn Fig.6b~~added a figure to show the correlations as you suggested and revised the text accordingly~~-and the following information according to the reviewer's comments.~~.

" During 7-11 August 2013, the relationships of the observed NH_4^+ versus those of SO_4^{2-}, the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- are presented in Fig. 10. It is known that $(NH_4)_2SO_4$ is preferentially formed and the least volatile, NH_4NO_3 is relatively volatile, while NH_4Cl is the most volatile. NH_4^+ is thought to be first associated with SO_4^{2-}, afterwards, the excess of NH_4^+ is with nitrate and chloride (Meng et al., 2015). It is noted that the correlation of NH_4^+ with the sum of SO_4^{2-} and NO_3^- (R=0.91, slope=1.23, with $P < 0.01$) was better than that of NH_4^+ with SO_4^{2-} (R=0.80, slope=1.65, with $P < 0.01$), suggesting that both SO_4^{2-} and NO_3^- were associated with NH_4^+. As shown in Fig.10, sulfate and nitrate were almost completely neutralized with most of the data above the 1:1 line. A few scattered data below the 1:1 line may be caused by uncertainties in measurements. Little different was found between the regression slopes of NH_4^+ with the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- due to the very low amount of NH_4Cl. In this study, the level of NH_3 was high enough to neutralize both SO_4^{2-} and NO_3^-, and likely to be form $(NH_4)_2SO_4$ and NH_4NO_3. In addition to these substances, it is likely that NH3 also reacted with oxalic acid and other dicarboxylic acid to form ammonium oxalate and other organic ammonium aerosols, as discussed above."

~~The relationships of the observed NH_4^+ versus those of SO_4^{2-}, the sum of SO_4^{2-} and NO_3^- and the sum of SO_4^{2-}, NO_3^- and Cl^- are presented in Fig. 6b.~~

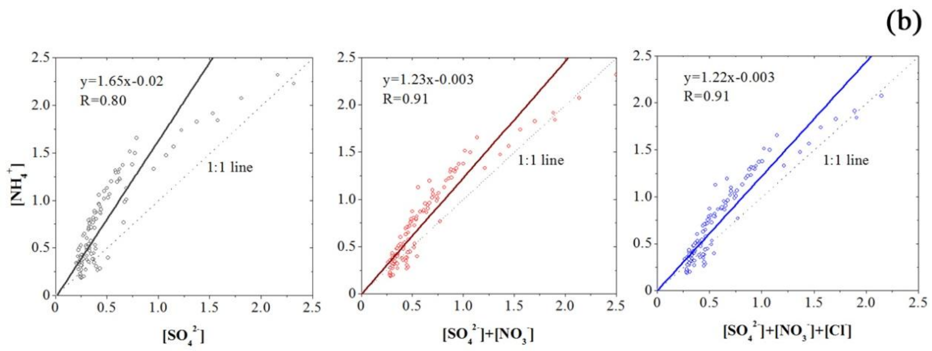

Figure 10. ~~Hourly concentrations of precursor gas and ionic species measured in a pollution episode (a) temporal variations and (b) c~~Correlations ~~of~~between $[NH_4^+]$ ~~versus~~ and $[SO_4^{2-}]$ (a), $[NH_4^+]$ and $[SO_4^{2-}]+[NO_3^-]$ (b) and $[NH_4^+]$ and $[SO_4^{2-}]+[NO_3^-]+[Cl^-]$ (c) during 7-11 August 2013.

Meng, Z. Y., Xie, Y. L., Jia, S. H., Zhang, R., Lin, W. L., Xu, X. B., and Yang W.: The characteristics of atmospheric ammonia at Gucheng, a Rural Site in the North China Plain in summer 2013, J. applied. meteor. sci., 26, 141-150, 2015. (in Chinese).

~~It is noted that the correlation of NH_4^+ with the sum of SO_4^{2-} and NO_3^- (R=0.91, slope=1.23, with $P < 0.01$) was better than that of NH_4^+ with SO_4^{2-} (R=0.80, slope=1.65, with $P < 0.01$), suggesting that both SO_4^{2-} and NO_3^- were associated with NH_4^+. As shown in Fig.4b, sulfate and nitrate were almost completely neutralized with most of the data above the 1:1 line. A few scatter data below the 1:1 line should have a mix of $(NH_4)_2SO_4$ and NH_4HSO_4.~~

Page 11, line 17: again, it is better to have more evidences showing that NH3 dry deposition dominates NHx deposition.

Answer: ~~It is noted that the NH_3 fraction of the reduced nitrogen (NH_3 / NH_x) was used in literature to identify the source of NH_x (Walker et al., 2004; Hu et al., 2014).~~ This is a speculation. No evidence is available. We have deleted this paragraph.

Page 12, line 2: where is the reference Meng et al. 2017?

Answer: We have ~~revised the reference in response to reviewer's comment~~added the reference.

Meng, Z. Y., Lin, W. L., Zhang, R. J., Han, Z. W. and Jiang, X. F.: Summertime ambient ammonia and its effects on ammonium aerosol in urban Beijing, China, Sci. Total Environ., 579, 1521-1530, 2017.