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 #1's comments Anonymous Reviewer #1 Received and published: 5 July 2017 Overview

This paper as the other reviewer has pointed out potentially has an amazing dataset which is really needed for greater understanding of air pollution and its impacts in agricultural regions. The paper could be hugely improved by moving away from the gas-particle ratio analysis to more detailed atmospheric chemistry and physics which would allow insight into the processes occurring and whether current understanding of emission, transformation and deposition can explain the observations. There is an overuse of "the data suggests..." and "this indicates..." without backup of information.

Answer: Thank you for your comments and suggestions, which are valuable in improving the quality of our manuscript. 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:

Introduction:

I think the ambition of the paper (as described in the last paragraph) needs to be more detailed and then the critical analysis done in the paper.

P3 More details of instrumentation is needed, in particular the calibration and response time of the NH3 instrument is required. Did the authors see an influence on the response time from PM deposition on the inlet and instrument filters (see Bobrutski et al 2009 and other papers for details of this issue). Some raw data and calibrations would be useful – ACP is not figure limited. Though rainfall is mentioned as a key meteorological driver, the method of measurement and the data are not shown at all.

Answer: We have added some more details about the instrumentation and issues regarding quality control. We paid attention to the influences on NH₃ measurements from the inlet and PM deposition on it and tried to reduce such influences. Although we do not exclude some unperceivable influences from adsorption and desorption, these influences should be much smaller than the high NH₃ values we observed and cause mainly slightly slower response or a lag in the recorded NH₃ concentration, which may not impact our analysis based on hourly average data. Some figures are added in the revised

manuscript and supplementary materials to provide information about calibration, meteorological condition, etc. Section 2.2 "Sampling and analysis" has been rewritten as follows:

"Ambient NH₃ was measured using an ammonia analyser (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, NH₃ 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 NH_3 (25.92 ppm with an accuracy of $\pm 2\%$) 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 NH₃ concentrations, and repeated accurately (within the uncertainty) the supplied NH₃ concentrations. The NH₃ 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 NH₃ measurements because the mirror reflectivity is continually monitored and the measurement is compensated using the mirror ringdown time. Interferences to NH₃ 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 NH₃ 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 NH₃ concentration is very high, and cause mainly a lag in the recorded NH₃ concentration.

A set of commercial instruments from Thermo Environmental Instruments, Inc. were used to measure O_3 (TE 49C), NO/NO₂/NO_x (TE 42CTL), CO (TE 48C), and SO₂ (TE 43CTL). All instruments were housed in an air-conditioned room in the observation building at the site. Two parallel inlet tubes (Teflon, 4.8 mm ID×8 m length) were shared by the analyzers. The height of the inlets was 1.8 m above the roof of the building and about 8m above the ground. The inlet residence time was estimated to be less than 5 s (Lin et al., 2009). Zero and span checks were performed weekly on the analyzers of these trace gases to identify possible analyzer malfunctions and zero drifts. Multipoint calibrations of SO₂, NO_x, CO and O₃ analyzers were performed on the instruments at approximately 1-month intervals. Measurement records were saved as 1-min averages After the correction of data on the basis of the multipoint calibrations, hourly average data were calculated and used for the analysis.

An Ambient Ion Monitor (AIM) (URG 9000D Series, USA) was deployed at the site to measure hourly concentrations of water-soluble inorganic components in PM_{2.5} during 15 June–11 August, 2013. A detailed description of performance evaluation of AIM-IC system is reported by Han et al., (2016). Briefly, ambient air was introduced in to the AIM with a 2 meter Teflon coated aluminum pipe and particles larger than 2.5 μ m were removed by a cyclone at a flow rate of 3 L/min. A liquid diffusion denuder was used to remove the interfering acidic and basic gases, in combination with a Steam-Jet Aerosol Collector followed by an Aerosol Sample Collector, until the particles can be injected into the ion chromatograph (Hu et al., 2014). The detection limit of NH₄⁺, SO₄²⁻ and NO₃⁻ were 0.05 μ g m⁻³, 0.04 μ g m⁻³ and 0.05 μ g m⁻³, respectively. For the AIM, multipoint calibrations were performed weekly by using calibration standard solutions. Acceptable linearity of ions was obtained with an R² of ≥0.999. The flow rate of the AIM was checked weekly at the sample inlet with a certified flow meter. The flow rate of the AIM was kept at 3 L/min with standard derivation of <1%. Hourly data were obtained for the concentrations of water-soluble inorganic ions in summer 2013.

Meteorological parameters were measured at the site. Air temperature and relative humidity were monitored using a humidity and temperature probe (HMP155, Vaisala, Finland); wind speed and direction were measured using an anemometer (ZQZ-TFD12, Jiangsu Radio Scientific Institute Co., Ltd, China); rainfall was measured using a tilting rain gauge (SL2-1, Tianjin Meteorological Instrument Factory, China). Global radiation observation was made at the site but showed a drift by the end of July,

2013. Instead we use the photolysis rate jNO_2 observed using a 2-pi-actinic-flux spectrograph (CCD type, Meteorologie Consult GmbH, Germany) to indicate radiation condition for photochemistry. Hourly meteorological data were calculated from the in-situ measurements and used in this paper. Planetary boundary layer height values at 14:00 were derived from the ERA-Interim data using the Bulk Ricardson number method (Guo et al., 2016; Miao et al., 2017)."



Figure S1 Confirmation of the performance of NH_3 analyzer using diluted standard gas (mixture NH_3/N_2). (a) Instrument response to changed NH_3 concentration and stability; (b) repeated multipoint calibrations.



Figure S2. Monthly average diurnal variations of the NO₂ photolysis frequency (jNO_2) (a) and hourly rainfall (b) observed at Gucheng during June-August 2013.

- Han, B., Zhang, R., Yang, W., Bai, Z., Ma, Z., and Zhang, W.: Heavy haze episodes in Beijing during January 2013: inorganic ion chemistry and source analysis using highly time-resolved measurements from an urban site, Sci. Total Environ., 544, 319-329, 2016.
- 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.
- 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.
- Wu, W. S. and Wang, T.: On the performance of a semi-continuous PM_{2.5} sulphate and nitrate instrument under high loadings of particulate and sulphur dioxide. Atmos. Environ. 41, 5442-5451, 2007.

P 11 section 3.4: Relationship between ammonium and ammonia: This discussion is very brief and limited. In particular after noting previously (and probably correctly) that local ammonia emissions dominate the chemical speciation observed, the authors then infer "NH3 dominates NHx deposition". With the dataset they have they could have performed calculations of deposition vs emission over the 4 month period would have given much more insight, i.e. the process is bidirectional therefore it is uncertain whether any net deposition would occur under the ambient conditions. This is a missed opportunity to explore the atmospheric chemistry and physics of the system.

Answer: Thank you for your valuable comments. Indeed it would be great if we could use our measurements to systematically explore the atmospheric chemistry and physics over the our site and to gain more insight, including the emission and deposition of NH_3 and NH_4^+ . However, we did not observe the emission and deposition of NH_3 and NH_4^+ . The air/surface exchange of NH3 is very complex, bidirectional and highly variable, and is influenced by many factors (e.g., Schrader et al., 2016). Given the parameters we observed, it is hardly possible to obtain robust and quantitative results about the emission vs deposition purely based on available measurements. To well understand the processes of emission, conversion and deposition of NHx species in the polluted NCP region, it is highly needed to design observational and 3D modeling studies. Our in-situ measurements present in this paper can be used as supporting data in future modeling studies.

Schrader, F., Brümmer, C., Flechard, C.R., Wichink Kruit, R.J., van Zanten, M.C., Zöll, U., Hensen, A., and Erisman, J.W.: Non-stomatal exchange in ammonia dry deposition models: comparison of two state-of-the-art approaches, Atmos. Chem. Phys., 16, 13417–13430, 2016.

Given that there are several thermodynamic models freely available, it would have been useful to explore the dataset against what is predicted by models. What is the ion balance – are

dicarboxylic acids needed to explain aerosol neutralisation? (is it neutral?). Is the atmospheric chemistry at the site dominated by thermodynamic equilibrium or is there kinetic limitations on the processes? The authors have missed an opportunity with the dataset to fully understand the chemistry and rely in the results and discussions to discuss the ratios between gas and aerosol partitioning to explain scientific concepts which are known and therefore not surprising.

Answer: Thank you for your suggestions. We have used the thermodynamic equilibrium model (ISORROPIA II) to investigate gas-aerosol partitioning characteristics and compared the modeling results with our measurements. The pH values of aerosol, estimated based on the simulated results, are mostly in the range of 2.5-4.5, with an average of 3.5. While simulated sulfate and nitrate are well comparable with the measurements, simulated ammonium substantially underestimates the observed one, indicating the importance of organic acids in the formation of ammonium. 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. Our results also suggest that the gas-aerosol partitioning at the Gucheng site is dominated by thermodynamic equilibrium. We have added a section about the ISORROPIA II model in the revised manuscript and more text about the simulation results and related discussions as follows:

"2.3.2 ISORROPIA II model

Thermodynamic gas-aerosol equilibrium characteristics during summer 2013 were examined using ISORROPIA II model (Fountoukis and Nenes, 2007). ISORROPIA II is a thermodynamic equilibrium model for inorganic gases and aerosols in the atmosphere (available at http://isorropia. eas.gatech.edu). To obtain the best available predictions of aerosol pH, ISORROPIA II, was run in the forward mode with metastable aerosol state salts precipitate once the aqueous phase becomes saturated with respect to salts, which often showed better performance than the stable state solution (solid + liquid) and was commonly applied in previous pH predictions (Liu et al., 2017). The concentrations of the measured NH₃ and water-soluble ions in PM_{2.5} were input into the model as total (gas + aerosol) concentrations, along with simultaneously measured relative humidity and temperature data. The bulk particle pH was calculated using the following equation:

$$pH = -\log_{10} \frac{1000H^+_{air}}{AWC} \qquad (4)$$

where H^+_{air} (µg m⁻³) and AWC (µg m⁻³) are the ISORROPIA-II predicted equilibrium particle hydronium ion concentration per volume air and aerosol water content, respectively. Evaluation of the

AWC prediction have been reported in previous studies and shows a good performance compared with particle water measurements (Bian et al., 2014; Guo et al., 2015). "

We have added a new section (Section 3.3 Results from thermodynamic equilibrium simulation) to present our main modeling results and discussed them also other section.

"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^+_{alr} , H^+_{alr} , 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 $SO_4^{2-}+NO_3^-+CI^-$, 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 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 HNO₃ concentrations was $0.9 \pm 1.1 \ \mu g \ m^{-3}$, showing a maximum value of 7.41 $\mu g \ m^{-3}$ at 11:00 on 19 June 2013. The average diurnal variations of HNO₃ 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 NH₃ 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). "



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 NH₄⁺ with modelled SO₄²⁻, SO₄²⁻+NO₃⁻ and SO₄²⁻+NO₃⁻ +Cl⁻..

We have made another new section (3.6 A case study of a pollution period) to present and discuss the 7-11 August measurement with additional analysis.

"3.6 A case study of a pollution period

On several days during the study period, very high NH₃ 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 NH₃ (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 $[SO_4^{2^2}]+[NO_3^{-1}]+[NH_4^{+*}]$. 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 $[SO_4^{2^2}]+[NO_3^{-1}]+[NH_4^{+*}]$ occurred. These data show that high NH₃ concentration was accompanied by the large increase in concentrations of $SO_4^{2^2}$, NO₃⁻ and NH₄^{+*}, confirming that NH₃ play an important role in PM mass formation and that gas-particle

conversion occurred when NH₃ was available, though $SO_4^{2^-}$ partitions to the aerosol phase regard less of NH₃ 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 NH₃ with NH₄⁺, $SO_4^{2^-}$ and NO₃⁻ (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 NH₄⁺ versus those of SO₄²⁻, the sum of SO₄²⁻ and NO₃⁻ and the sum of SO₄²⁻, NO₃⁻ and Cl⁻ are presented in Fig. 10. It is known that (NH₄)₂SO₄ is preferentially formed and the least volatile, NH₄NO₃ is relatively volatile, while NH₄Cl is the most volatile. NH₄⁺ is thought to be first associated with SO₄²⁻, afterwards, the excess of NH₄⁺ is with nitrate and chloride (Meng et al., 2015). It is noted that the correlation of NH₄⁺ with the sum of SO₄²⁻ and NO₃⁻ (R=0.91, slope=1.23, with P < 0.01) was better than that of NH₄⁺ with SO₄²⁻ (R=0.80, slope=1.65, with P < 0.01), suggesting that both SO₄²⁻ and NO₃⁻ were associated with NH₄⁺. 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 NH₄⁺ with the sum of SO₄²⁻ and NO₃⁻ and the sum of SO₄²⁻ and NO₃⁻, and likely to be form (NH₄)₂SO₄ and NH₄NO₃. 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 $[SO_4^{2^-}]+[NO_3^-]+[CI^-]$ 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 NH₃ and measured inorganic ions during 7-11 August 2013

- Hsieh, L.Y., Kuo, S.C., Chen, C.L., Tsai, Y.I.: Origin of low-molecular-weight dicarboxylic acids and their concentration and size distribution variation in suburban aerosol, Atmos. Environ., 41, 6648-6661, 2007.
- Kawamura, K., Tachibana, E., Okuzawa, K.,Aggarwal,S.G., Kanaya, Y., and Wang, Z. F.: High abundances of water-soluble dicarboxylic acids, ketocarboxylic acids and α-dicarbonyls in the mountaintop aerosols over the North China Plain during wheat burning season, Atmos. Chem. Phys., 13, 8285–8302, 2013.
- Kawamura, K., Barrie, L.A., and Desiree, T.-S.: Intercomparison of the measurements of oxalic acid in aerosols by gas chromatography and ion chromatography, Atmos. Environ., 44, 5316-5319, 2010.
- Sauerwein, M. and Chan, C. K.: Heterogeneous uptake of ammonia and dimethylamine into sulfuric and oxalic acid particles, Atmos. Chem. Phys., 17, 6323–6339, 2017

The references are added in the revised manuscript.

- Bian, Y. X., Zhao, C. S., Ma, N., Chen, J., and Xu, W. Y.: A study of aerosol liquid water content based on hygroscopicity measurements at high relative humidity in the North China Plain, Atmos. Chem. Phys., 14, 6417-6426, https://doi.org/10.5194/acp-14-6417-2014, 2014.
- Bougiatioti, A., Nikolaou, P., Stavroulas, I., Kouvarakis, G., Weber, R., Nenes, A., Kanakidou, M., and Mihalopoulos, N.: Particle water and pH in the eastern Mediterranean: Source variability and implications for nutrient availability, Atmos. Chem. Phys., 16, 4579–4591, 2016.
- Fountoukis, C. and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+ -Ca²⁺-Mg²⁺-NH₄⁺-Na⁺-SO₄²⁻ -NO₃⁻-Cl⁻-H₂O aerosols, Atmos. Chem. Phys., 7,

4639-4659, doi:10.5194/acp-7-4639-2007, 2007.

- Fountoukis, C., Nenes, A., Sullivan, A., Weber, R., Van Reken, T., Fischer, M., Matias, E., Moya, M., Farmer, D., and Cohen, R. C.: Thermodynamic characterization of Mexico City aerosol during MILAGRO 2006, Atmos. Chem. Phys., 9, 2141–2156, doi:10.5194/acp-9-2141-2009, 2009.
- Liu, M., Song, Y., Zhou, T., Xu, Z., Yan, C., Zheng, M., Wu, Z., Hu, M., Wu, Y., and Zhu, T.: Fine particle pH during severe haze episodes in northern China, Geophys. Res. Lett., 44, doi:10.1002/2017GL073210, 2017.

In the places in the manuscript which use atmospheric chemistry to explain data (e.g. 3.4.2), there are no calculations to check if what is observed is what would be expected under the conditions. Is ozone being lost to the surface or is there a haze which allows aqueous processing in the atmosphere, what might be the role of organics...), what is the surface area of PM (given composition and RH) and hence can N2O5 hydrolysis explain the observations completely? There are lots of questions which are not touched upon, though they are key to understanding the role of NH3.

Answer: It is true we did not calculate the O_3 loss, aerosol surface, N_2O_5 hydrolysis, etc. Having these results would be very helpful in understanding the role of NH3 in ammonium formation and other aspects of atmospheric chemistry at the site. However, our project was not designed for a "closure study" of gas-aerosol chemistry over the site. Many key parameters were not observed, such as deposition of O3, NH3, etc., concentrations of radical species, organic aerosols, aerosol surface and size distribution, changes in boundary layer, etc. In the absence of these parameters, many assumptions have to be made, which will lead to large uncertainties in the results. We think a comprehensive modeling study is needed to obtain quantitative assessments of all the chemical and physical processes. Such a modeling is beyond the scope of this observation-based study. Nevertheless, we have made some calculations and obtained some semi-quantitative results as answer to the reviewer's questions (Fig. R1). According to Verbeke et al. (2015), the annual mean O_3 dry deposition velocity in the NCP region is about 0.3 cm/s. Assuming a doubled deposition velocity (0.6 cm/s) in summer and a constant PBLH of 200 m (this may cause an overestimate during daytime), dry deposition of O3 is estimated to be in the range of 1.5-9 ppb/hr, which is much smaller than the estimated NO titration (37-117 ppb/hr). If reaction of O_3 with other gases and uptake by aerosol are neglected, a production rate in the range of 35-127 ppb/hr is required to balance the titration and deposition losses and cause the observed net change from -10 ppb/hr to 12 ppb/hr. Note that photochemical production during nighttime should be zero. Therefore the "production" during nighttime can be considered as source aloft the surface layer.

We have added "Nighttime formation, aerosol uptake and hydrolysis of N_2O_5 are highly uncertain as has been pointed out (e.g., Xue et al. 2014). The NOx concentration during nighttime was higher than during daytime, while the NO₃⁻ level during nighttime was only slightly higher than that during daytime (Fig. R2). By assuming high aerosol surface to mass ratio (33.7 m²/g, Okuda, 2013) and a high uptake coefficient (0.1, Seinfeld and Pandis, 2006), we estimate the nighttime N₂O₅ under the conditions over our site to be in the range of about 3-10 ppb, corresponding to a HNO3 production rate of about 1-3 ppb/hr (or 2.6-7.7 µg/m³). This rate of HNO₃ production would cause an obvious night production of NH_4^+ . Indeed we can see increases in the NH_4^+ concentration and NHR during night (Fig. R3). However, a more or less accurate estimate of the relative contribution of the night N_2O_5 chemistry to NH_3 conversion needs to be made in the future."



Figure R1 Estimated budget of surface O3 at Gucheng during summer 2013.



Figure R2 Diurnal variations of NO_x and aerosol NO₃⁻ at Gucheng during summer 2013.



Figure R3 Average diurnal cycles of NHR, SOR. NOR, gaseous precursors, major water soluble ions, and meteorological factors in summer 2013.

- Okuda, T.: Measurement of the specific surface area and particle size distribution of atmospheric aerosol reference materials, Atmos. Environ., 75, 1-5, 2013.
- Seinfeld, J. H. and Pandis, S. N.: Atmospheric chemistry and physics: from air pollution to climate change (2nd ed.), Wiley Interscience, New Jersey, 2006.
- Verbeke, T., Lathière, J., Szopa, S., and de Noblet-Ducoudr é, N.: Impact of future land-cover changes on HNO3 and O3 surface dry deposition, Atmos. Chem. Phys., 15, 13555-13568, 2015.
- Xue, L. K., Wang, T., Gao, J., Ding, A. J., Zhou, X. H., Blake, D. R., Wang, X. F., Saunders, S. M., Fan, S. J., Zuo, H. C., Zhang, Q. Z., and Wang, W. X.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14, 13175–13188, doi:10.5194/acp-14-13175-2014, 2014.

Having read the paper I am still not sure what the authors want a reader to learn from the gas-particle ratios. I would suggest the authors revise to include pollution/wind rose diagrams to look at the pollution footprint (e.g. ones are available on Open air and other packages), use current thermodynamics and kinetics of the system to see if current models would accurately represent the observations, if not what may be missing?

Answer: We have drawn the Figure of NH_3 rose and added the analysis of local source in Section 3.5 (now section 3.7) as follows:

"3.5 Local and long-rang transport source of ammonia and ammonium aerosol

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."

Oxidised nitrogen chemistry and the gas-aerosol partitioning dynamic are mentioned in passing but are key to understanding whether NH3 is driving the PM formation or it is a reservoir gas which grows PM when the presence of the other pollutants is there. Biomass burning is mentioned and K and CO as the indicators. With the dataset they could estimate the fraction of PM due to biomass burning, how much of the PM is explained by biomass burning, and does the biomass burning "seed" larger PM events. Finally the discussion and conclusion would be enhanced if some discussion about the impacts and potential solutions to the impacts. What is the evidence that limiting the NH3 emission would improve the air quality - it may well achieve this, but to make the case, evidence or hypothesis is needed to back the statements up.

Answer: We have made simulations using the thermodynamic equilibrium model ISORROPIA II. The simulated results indicate that the strong acids (H_2SO_4 , HNO_3 and HCl) are well balanced by NH3 (Fig. R4). However, the correlation between observed NH_4^+ and the sum of observed SO_4^{-2} , NO_3^- and Cl^- (Fig. R5) suggests that the neutralization of the strong acids explain 56% of the observed NH4+. In other words, nearly 44% of the observed NH_4^+ was due to the presence of other acids in aerosol particles. As mentioned above these acids may be oxalic acid and other dicarboxylic acids. The level of NH_3 at Gucheng in summer 2013 was very high. Under the NH_3 -rich condition acid neutralization was easily achieved. As shown in Fig. R3, the average NHR values were around 30%, indicating NH_3 was not a factor limiting the PM formation. Some recent studies suggest that the formation of sulfate in aerosol can been largely enhanced by NO_2 oxidation under higher pH values (e.g., Xie et al., 2015; Cheng et al., 2016). Higher pH in aerosol water can be caused by high dust aerosol or NH3. The pH values in aerosol water at Gucheng during our observations was estimated to mostly range from 2.5 to 4.5, based on the ISORROPIA modeling results. Our data do not indicate any increase in sulfate content with the increased NO_2 . Therefore, high NH_3 at our site was not driving more PM formation and it served as a reservoir gas to neutralize acids present in aerosol and gas phases.

Open biomass burning occurred occasionally in the NCP region during our campaign though open burning of agricultural wastes had been prohibited. We observed no significant open fires nearby Gucheng. However, fires in the surrounding areas may impact the measurements at the site. The fire maps show that open burning occurred mainly in June and July, which is usually the period of burning wheat straw. During a few days around middle and end June, we observed relatively higher concentrations of CO and aerosol K^+ , which may be resulted from biomass burning. The K+ concentration is fairly well correlated with the PM_{2.5} concentration (Fig. R7), suggesting an impact of biomass burning on particle pollution. The concentration of K^+ is not correlated with those of Na and Ca. Therefore, the observed K^+ in aerosol should be mainly from biomass burning. Although the slope of the K-PM_{2.5} regression line is small (0.026), the total contribution of biomass burning to PM_{2.5} may be much larger than a few percentages considering carbonaceous aerosols and other species emitted by biomass burning (Cheng et al., 2013).



Figure R4 Correlation of simulated NH_4^+ with simulated SO_4^{2-} , NO_3^- and Cl^- .



Figure R5 Correlation of observed NH_4^+ with observed SO_4^{2-} , $SO_4^{2-}+NO_3^-$ and $SO_4^{2-}+NO_3^-+Cl-..$



Figure R6 Open fires in the NCP region during June-September, 2013. The red triangels indicate the position of the Gucheng site. Data source: https://firms.modaps.eosdis.nasa.gov/firemap/.



Figure R7 K+ in aerosol and CO concentrations observed at Gucheng during summer 2013.



Figure R8 Correlation between K⁺ and PM_{2.5} concentrations.

- Cheng, Y., Engling, G., He, K.-B., Duan, F.-K., Ma, Y.-L., Du, Z.-Y., Liu, J.-M., Zheng, M., and Weber, R. J.: Biomass burning contribution to Beijing aerosol, Atmos. Chem. Phys., 13, 7765–7781, 2013
- Cheng, Y., Zheng, G., Wei, C., Mu, Q., Zheng, B., Wang, Z., Gao, M., Zhang, Q., He, K., Carmichael, G., Pöschl, U., Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China. Sci. Adv. 2, e1601530, 2016.
- Xie, Y., Ding, A., Nie, W., Mao, H., Qi, X., Huang, X., Xu, Z., Kerminen, V.-M., Pet äj ä, T., Chi, X., Virkula, A., Boy, M., Xue, L., Guo, J., Sun, J., Yang, X., Kulmala, M., Fu, C.: Enhanced sulfate formation by nitrogen dioxide: Implications from in-situ observations at the SORPES Station, J. Geophys. Res. 120, 12679-12694, 2015.

Minor corrections:

P1 Line 22 The observation that NH3 drives NH4 content of PM is not new, so I do not think the word "suggesting" is appropriate

Answer: We have changed the word "suggesting" to "reflecting".

1 P1 Line 24: This is a percentage not a ratio.

Answer: We have revised the percentage to the ratio according to the reviewer's comments.

P1 Line 25: use previous NCP abbreviation

Answer: We have added "in the NCP" in Line 25 according to the reviewer's comments.

P2 line 15: Actually most atmospheric chemistry text books discuss this, would cite them rather than research papers.

Answer: We have revised the sentence. "Some studies have suggested that reducing NH_3 concentrations could be an effective method for alleviating secondary inorganic $PM_{2.5}$ pollution."

P5, line 19: asymmetric errors would be more appropriate given that one cannot have negative

concentrations.

Answer: We have decided to use the range instead of standard deviation. The sentence reads now "During 15 May–25 September 2013, the average concentrations (ranges) of NH3, SO2 and NOx were 36.2 (0-862.9), 5.0 (0-86.8) and 15.4 (2.7-67.7) ppb, respectively.".

P25 Figure 2: given that it rained during the 4 months, why does the RH never go above 90%?

Answer: To accurately measure high RH is still difficult so that the absolute errors associated the high RH values may be large. The measured RH does include some values over 90%, with the maximum of 93%. There might be negative bias. On the other hand, raining does not necessarily mean the surface air is saturated with water.

P27: for the PM composition it would be useful to have them as stacked so that one can see the variation of composition through time References: There are not many references from 2015 and 2016 despite many papers being published on this subject area. I would suggest the authors review the recent literature.

Answer: The figure on this page has been redrawn. The PM compositions are shown as stacked. Global radiation and wind speed data are removed from the figure. Instead measurements of O3 and jNO2 are shown to provide information about photochemistry. We have reviewed the some recent papers (Guo et al., 2015; Han et al., 2016; Sudheer and Rengarajan, 2015; Tang et al., 2016; Wen et al., 2015; Xu et al., 2017; Zhao et al., 2016) and cited them in the revised manuscript.



Figure R9 Hourly concentrations of gaseous and ionic species and measurements of air temperature,

RH and jNO2 observed during the pollution episode 7-11 August 2013.

- Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr., J. R., Carlton, A. G., Lee, S.-H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211-5228, https://doi.org/10.5194/acp-15-5211-2015, 2015.
- Han, B., Zhang, R., Yang, W., Bai, Z., Ma, Z., and Zhang, W.: Heavy haze episodes in Beijing during January 2013: inorganic ion chemistry and source analysis using highly time-resolved measurements from an urban site, Sci. Total Environ., 544, 319-329, 2016.
- Sudheer, A. K., and Rengarajan, R.: Time-resolved inorganic chemical composition of fine aerosol and associated precursor gases over an urban environment in western India: Gas-aerosol equilibrium characteristics[J]. Atmospheric Environment, 109:217-227, 2015.
- Tang, X., Zhang, X.S., Ci, Z.J., Guo, J and Wang, J. Q.: Speciation of the major inorganic salts in atmospheric aerosols of Beijing, China: Measurements and comparison with model. Atmos. Environ., 133:123-134, 2016.
- Wen, L., Chen, J., Yang, L., Wang, X., Xu, C., & Sui, X., et al.: Enhanced formation of fine particulate nitrate at a rural site on the north china plain in summer: the important roles of ammonia and ozone. Atmos. Environ., 101, 294-302, 2015.
- Xu, W., Song, W., Zhang, Y., Liu, X., Zhang, L., Zhao, Y., Liu, D., Tang, A., Yang, D., Wang, D., Wen, Z., Pan, Y., Fowler, D., Collett Jr., J. L., Erisman, J. W., Goulding, K., Li, Y., and Zhang, F.: Air quality improvement in a megacity: implications from 2015 Beijing Parade Blue pollution control actions, Atmos. Chem. Phys., 17, 31-46, https://doi.org/10.5194/acp-17-31-2017, 2017.
- Zhao, M., Wang, S., Tan, J., Hua, Y., Wu, D., and Hao, J.: Variation of Urban Atmospheric Ammonia Pollution and its Relation with PM2.5 Chemical Property in Winter of Beijing, China. Sci. Total Environ., 16(6), 1378-1389, 2016.