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

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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 NH$_3$ 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 NH$_3$ values we observed and cause mainly slightly slower response or a lag in the recorded NH$_3$ 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 NH$_3$ 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, NH$_3$ data were recorded as 100-s average. In principle, the NH$_3$ 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 NH$_3$ 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 ±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.

A set of commercial instruments from Thermo Environmental Instruments, Inc. were used to measure O$_3$ (TE 49C), NO/NO$_2$/NO$_x$ (TE 42CTL), CO (TE 48C), and SO$_2$ (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 8 m 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 SO$_2$, NO$_x$, CO and O$_3$ 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 μm were removed by a cyclone at a flow rate of 3 L min$^{-1}$. 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 NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ were 0.05 μg m$^{-3}$. 
0.04 μg m$^{-3}$ and 0.05 μg m$^{-3}$, respectively. For the AIM, multipoint calibrations were performed weekly by using calibration standard solutions. Acceptable linearity of ions was obtained with an $R^2$ of $\geq 0.999$. 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$^{-1}$ 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 $j_{NO_2}$ 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 (PBLH) values at 14:00 were derived from the ERA-Interim data using the Bulk Richardson 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$_2$). Instrument response to changed NH$_3$ concentration and stability (a) and repeated multipoint calibrations (b).
Figure S2. Monthly average diurnal variations of the NO₂ photolysis frequency ($j$NO₂) (a) and hourly rainfall (b) observed at Gucheng during June-August 2013.

The references are added in the revised manuscript.


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 NH$_3$ 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 NH$_3$ 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.


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/index.php?title=Main_Page). The concentrations of the measured NH$_3$ 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. 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 (Guo et al., 2015; Bougiatioti et al., 2016; Liu et al., 2017). In this study, the aerosol properties as acidity and the water content of the aerosol are needed to investigate the aerosol acidity characteristics and role of heterogeneous chemistry in nitrate formation. The pH of aerosol water was calculated using the following equation:

$$pH = -\log_{10} \frac{1000H^+_\text{air}}{AWC}$$  \hspace{1cm} (4)$$

where $H^+_\text{air}$ ($\mu$g m$^{-3}$) is the ion concentration of equilibrium particle hydronium and AWC ($\mu$g m$^{-3}$) is the aerosol water content from the ISORROPIA-II simulation. The evaluation of AWC prediction showed a good performance compared with observed particle water (Bian et al., 2014; Guo et al., 2015).
We have added a new section (Section 3.4 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. The model outputs include equilibrium $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_4^+$, $\text{H}^+_\text{air}$, $\text{HNO}_3$, $\text{NH}_3$, AWC, etc. As shown in Fig. 5, the modelled $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{NH}_3$ show excellent correlations with the corresponding measurements, but modelled $\text{NH}_4^+$ is much worse correlated with the measured one. Modelled $\text{NO}_3^-$, $\text{SO}_4^{2-}$, and $\text{NH}_3$ values agree well with the measurements, while the modelled $\text{NH}_4^+$ largely underestimate the measurements. Considering the unbalance between observed $\text{NH}_4^+$ and the sum of observed $\text{SO}_4^{2-}$+$\text{NO}_3^-$+$\text{Cl}^-$, we can confirm that other acids in aerosol particles are important in the conversion of $\text{NH}_3$ to $\text{NH}_4^+$. 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.

![Figure 5](https://via.placeholder.com/150)

Figure 5. Observed and modelled concentrations of $\text{NH}_3$, $\text{NH}_4^+$, $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ in summer 2013.

The average concentration of simulated $\text{HNO}_3$ was 0.7 $\mu\text{g m}^{-3}$, showing a maximum value of 7.41 $\mu\text{g m}^{-3}$ at 11:00 on 19 June 2013. The average diurnal variations of $\text{HNO}_3$ and $\text{H}^+_\text{air}$ are shown in Fig.
6a. A typical high HNO₃ concentrations during daytime and low values at nighttime during the observation period is predicted by the model, which is consistent with other studies (Makkonen et al., 2012; Sudheer et al., 2015). The diurnal cycle of H⁺_{air} is predicted with the highest level around 17:00. The concentrations of NH₃ were closely associated with H⁺_{air}, and higher NH₃ always corresponded to lower H⁺_{air} (Liu et al., 2017). 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. The fine particles were moderately acidic in summer, with an average pH values of 3.5. On average, pH is over 3.5 during nighttime and below 3.5 during daytime (Fig. 6b). Under the medium acidic conditions and high NH₃ concentrations, organic acid like diacids are able to react with ammonia to form 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. S4).

Figure 6. Simulated diurnal variation of HNO₃ and H⁺_{air} (a) and calculated diurnal variation of pH value of aerosol water (b) in summer 2013.

Figure S4. 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 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 calculated parameters during this period are given in Fig. S5. As shown in Figs. 9 and S5, there was a sharp increase of NO$_x$ during the night and early morning of 10 August, followed by that of NH$_3$ (peak value of 64 ppb) at 03:00. In the meantime, a large peak of AWC occurred and gaseous HNO$_3$ decreased to nearly zero (Fig. S5), suggesting rapid uptake of wet aerosol. This event caused the first largest peak of [SO$_4^{2-}$]+[NO$_3^-$]+[NH$_4^+$]. After this event NH$_3$ rose again and reached a even higher peak (76.3 ppb) shortly before noon of 10 August. This peak of NH$_3$ coincided with a valley of NO$_x$, but the HNO$_3$ level increased and pH value decreased was observed in parallel. A few hours later SO$_2$ 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).

![Figure 9. Hourly concentrations of gaseous, ionic species and jNO$_2$ measured in the pollution episode during 7-11 August 2013.](image)
The secondary ions concentrations had similar temporal distributions with slow accumulation and relatively rapid clearing under favorable meteorological conditions. There were good correlation between NH₃ with NH₄⁺, SO₄²⁻ 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 [SO₄²⁻]+[NO₃⁻]+[NH₄⁺], 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.

Figure S5. Time series of predicted fine particle pH, particle water mass, HNO₃, H₂O, NH₃ and inorganic ions during 7-11 August 2013.

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⁻, NO₃⁻ and Cl⁻ due to the very low amount of NH₄Cl. In this study, the level of NH₃ was high enough to neutralize
both SO$_4^{2-}$ and NO$_3^-$, and likely to be form (NH$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. In addition to these substances, it is likely that NH$_3$ also reacted with oxalic acid and other dicarboxylic acid to form ammonium oxalate and other organic ammonium aerosols, as discussed above.

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.

The references are added in the revised manuscript.


Kawamura, K., Barrie, L. A., and Desiree, T.-S.: Intercomparison of the measurements of oxalic acid in


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 O3 loss, aerosol surface, N2O5 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 O3 dry deposition velocity in the NCP region is about 0.3 cm s⁻¹. Assuming a doubled deposition velocity (0.6 cm s⁻¹) 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⁻¹, which is much smaller than the estimated NO titration (37-117 ppb hr⁻¹). If reaction of O₃ with other gases and uptake by aerosol are neglected, a production rate in the range of 35-127 ppb hr⁻¹ is required to balance the titration and deposition losses and cause the observed net change from -10 ppb hr⁻¹ to 12 ppb hr⁻¹. Note that photochemical production during nighttime should be zero. Therefore the “production” during nighttime can be considered as source aloft the surface layer.

![Figure R1](image1.png)

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

We have added “Nighttime formation, aerosol uptake and hydrolysis of N₂O₅ 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).

![Figure R2](image2.png)

**Figure R2.** Diurnal variations of NOₓ and aerosol NO₃⁻ at Gucheng during summer 2013.
By assuming high aerosol surface to mass ratio (33.7 m$^2$ g$^{-1}$, Okuda, 2013) and a high uptake coefficient (0.1, Seinfeld and Pandis, 2006), we estimate the nighttime N$_2$O$_5$ under the conditions over our site to be in the range of about 3-10 ppb, corresponding to a HNO$_3$ production rate of about 1-3 ppb hr$^{-1}$ (or 2.6-7.7 μg m$^{-3}$). This rate of HNO$_3$ 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$_2$O$_5$ chemistry to NH$_3$ conversion needs to be made in the future.

![Figure R3](image.png)

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

The references are added in the revised manuscript.


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

The Gucheng site is located in the densely populated rural area in the NCP, it is influenced by local sources in the surrounding areas and by long range transport of pollutants from the residential and industrial centers around it. 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.

![Figure 11. The average NH$_3$, NH$_4^+$ concentrations and meteorological data roses in different wind sectors during summer 2013.](image)
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.

Oxidised nitrogen chemistry and the gas-aerosol partitioning dynamic are mentioned in passing but are key to understanding whether NH$_3$ 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 NH$_3$ 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$_2$SO$_4$, HNO$_3$ and HCl) are well balanced by NH$_3$ (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 NH$_4^+$. In other words, nearly 0.44 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.
Figure R4. Correlation of simulated NH$_4^+$ with simulated SO$_4^{2-}$, NO$_3^-$ and Cl$^-$. 

As shown in Fig. R3, the average NHR values were around 0.30, indicating NH$_3$ was not a factor limiting the PM formation. Some recent studies suggest that the formation of sulfate in aerosol can be 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 NH$_3$. 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.

Figure R5. Correlation of observed NH$_4^+$ with observed SO$_4^{2-}$, SO$_4^{2-}$+NO$_3^-$ and SO$_4^{2-}$+NO$_3^-$ +Cl$^-$. 
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 (Fig. R6) show that open burning occurred mainly in June and July, which is usually the period of burning wheat straw.

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

During a few days around middle and end June, we observed relatively higher concentrations of CO and aerosol $K^+$ (Fig. R7), which may be resulted from biomass burning.

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

The $K^+$ concentration is fairly well correlated with the PM$_{2.5}$ concentration (Fig. R8), 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 R8. Correlation between K\(^+\) and PM\(_{2.5}\) concentrations.](image)


Minor corrections:

P1 Line 22 The observation that NH\(_3\) drives NH\(_4\) 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 NH$_3$, SO$_2$ and NO$_x$ were 36.2 (0.1-862.9), 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 O$_3$ and
NO₂ are shown to provide information about photochemistry. We have reviewed the some recent papers (Guo et al., 2015; Sudheer and Rengarajan, 2015; Wen et al., 2015; Han et al., 2016; Tang et al., 2016; Zhao et al., 2016; Xu et al., 2017) and cited them in the revised manuscript.

Figure R9. Hourly concentrations of gaseous, ionic species and jNO₂ measured in the pollution episode during 7-11 August 2013.

The references are added in the revised manuscript.


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: 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

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 NO₂ photolysis frequency (jNO₂) during June-August 2013 as supplementary materials. Changes are made to text as follows:

The monthly concentrations of SO₂, NOₓ, 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](image)

Figure S2. Monthly average diurnal variations of the NO₂ photolysis frequency (jNO₂) (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 O₃, 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 O₃ in the NCP, which occurs in June (Lin et al., 2008; Ding et al., 2008).
The references are added in the revised manuscript.


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°C) 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 NH$_3$ 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 breakup 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 NH$_3$ (a) and meteorological parameters (b) during the sampling period.


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 NH$_3$ 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 lower 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 NH$_3$ 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 an earliest NH$_3$ peak in July.

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. As mentioned above, the urea application in the station on 20 July 2013 and a precipitation process afterwards caused 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 lower 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 PBLH, 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.

The references are added in the revised manuscript.


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\textsubscript{4}/NH\textsubscript{x}), SOR (SO\textsubscript{4}\textsuperscript{2−}/(SO\textsubscript{4}\textsuperscript{2−}+SO\textsubscript{2}) and NOR (NO\textsubscript{3}/(NO\textsubscript{3}+NO\textsubscript{x})) were calculated as measures of chemical conversion of NH\textsubscript{3}, SO\textsubscript{2} and NO\textsubscript{x}. You are right that NH\textsubscript{x} and NH\textsubscript{3} may be decoupled. Sources of NH\textsubscript{3}, SO\textsubscript{2} and NO\textsubscript{x} may be dislocated. The lifetimes of these gases are different and hence the dispersion areas. Fine 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.

At page 10, line 13, it is summarized that “This observation emphasizes the important role of NH\textsubscript{3} in the formation of secondary SO\textsubscript{4}, NO\textsubscript{3} and NH\textsubscript{4} 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, 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\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−} and NH\textsubscript{x}. The model outputs include equilibrium NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−}, NH\textsubscript{x}, H\textsuperscript{+}, HNO\textsubscript{3}, NH\textsubscript{3}, AWC, etc. As shown in Fig. 5, the modelled NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−}, NH\textsubscript{3} show excellent correlations with the corresponding measurements, but modelled NH\textsubscript{x} is much worse correlated with the measured one. Modelled NO\textsubscript{3}, SO\textsubscript{4}\textsuperscript{2−}, and NH\textsubscript{3} values agree well with the measurements, while the modelled NH\textsubscript{x} largely underestimate the measurements. Considering the unbalance between observed NH\textsubscript{x} and the sum of observed SO\textsubscript{4}\textsuperscript{2−}+NO\textsubscript{3}+Cl\textsuperscript{−}, we can confirm that other acids in aerosol particles are important in the conversion of NH\textsubscript{3} to NH\textsubscript{x}. 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.

Figure 5. Observed and modelled concentrations of NH$_3$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in summer 2013.

The average concentration of simulated HNO$_3$ was 0.7 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$^+$ are shown in Fig. 6a. A typical high HNO$_3$ concentrations during daytime and low values at nighttime during the observation period is predicted by the model, which is consistent with other studies (Makkonen et al., 2012; Sudheer et al., 2015). The diurnal cycle of H$^+$ is predicted with the highest level around 17:00. The concentrations of NH$_3$ were closely associated with H$^+$, and higher NH$_3$ always corresponded to lower H$^+$ (Liu et al., 2017). 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. The fine particles were moderately acidic in summer, with an average pH values of 3.5. On average, pH is over 3.5 during nighttime and below 3.5 during daytime (Fig. 6b). 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. S4).
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 calculated parameters during this period are given in Fig. S5. As shown in Figs. 9 and S5, there was a sharp increase of NO$_x$ during the night and early morning of 10 August, followed by that of NH$_3$ (peak value...
of 64 ppb) at 03:00. In the meantime, a large peak of AWC occurred and gaseous HNO₃ decreased to nearly zero (Fig. S5), suggesting rapid uptake of wet aerosol. This event caused the first largest peak of [SO₄²⁻]+[NO₃⁻]+[NH₄⁺]. After this event NH₃ rose again and reached a even higher peak (76.3 ppb) 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 [SO₄²⁻]+[NO₃⁻]+[NH₄⁺] occurred. These data show that high NH₃ concentration was accompanied by the large increase in concentrations of SO₄²⁻, 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 SO₄²⁻ partitions to the aerosol phase regard less of NH₃ level (Gong et al., 2013).

Figure 9. Hourly concentrations of gaseous, ionic species and jNO₂ measured in the pollution episode during 7-11 August 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 NH$_3$ 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.

![Diagram](image)

Figure S5. Time series of predicted fine particle pH, particle water mass, HNO$_3$, H$_{air}^+$, NH$_3$ and inorganic ions during 7-11 August 2013.

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$_4$)$_2$SO$_4$ is preferentially formed and the least volatile, NH$_4$NO$_3$ is relatively volatile, while NH$_4$Cl 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 NH₄Cl. In this study, the level of NH₃ was high enough to neutralize both 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 10. Correlations between [NH₄⁺] and [SO₄²⁻] (left), [NH₄⁺] and [SO₄²⁻]+[NO₃⁻] (middle) and [NH₄⁺] and [SO₄²⁻]+[NO₃⁻]+[Cl⁻] (right) during 7-11 August 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 3.7 to "Long range transport and local source of ammonia and ammonium" and revised the text as follows:

The Gucheng site is located in the densely populated rural area in the NCP, it is influenced by local sources in the surrounding areas and by long range transport of pollutants from the residential and industrial centers around it. Dependence of the concentrations of NH₃ 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 NH₃ 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 NH₃ concentrations were observed under winds from other sectors. Since NH₃ is either readily converted to NH₄⁺ 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, NH₃ concentrations might be generally lower at higher wind speeds because of turbulent diffusion.

Figure 11. The average NH₃, NH₄⁺ concentrations and meteorological data roses in different wind sectors during summer 2013.


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). According to the maps from Lin et al. (2009) shown below, the Gucheng site is surrounded by farms, dense villages/towns, and the transportation network 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.

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 information revised the related text as follows:

Ambient NH₃ 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, 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 ±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.

Figure S1 Confirmation of the performance of NH$_3$ analyzer using diluted standard gas (mixture NH$_3$/N$_2$). Instrument response to changed NH$_3$ concentration and stability (a) and repeated multipoint calibrations (b).

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\textsubscript{3} concentration is very high, and cause mainly a lag in the recorded NH\textsubscript{3} concentration.

The references are added in the revised manuscript.


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".

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

Answer: This was one of the typos. We have 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 revised our expression as follows:

In recent year a few publications about China's national and regional emission inventories of NH\textsubscript{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\textsubscript{3} emissions. Ground based observations of NH\textsubscript{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\textsubscript{3} emission inventory.


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 as shown below:

Figure 2. Time series of hourly data of NH₃, other trace gases and meteorological parameters measured during the sampling period (a) and a blow-up of the period with extremely high NH₃ values during 27-31 July 2013 (b).
Page 7, line 6: where the urea was applied and how large was the applied area?

Answer: We have added the required information and revised the text 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 NH₃ concentration increased rapidly on the seventh day after the urea application on 20 July, peaking during the 27-30 July period (Fig. 2b).

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

Answer: We have added "such as NOₓ and CO" at the end of "trace gases" to in our revised version.

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

Answer: We have deleted the paragraph there.

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

Answer: We have deleted this sentence and changed the sentence before to "On the other hand, NH₃ was more efficient in summer to react with SO₂ to form (NH₄)₂SO₄. The average concentration of NO₃⁻ in PM₂.₅ 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 high RH conditions in summer might dissolve a significant fraction of HNO₃ and NH₃ in humid particles, therefore increasing the concentrations of NO₃⁻ and NH₄⁺ in the atmosphere (Krupa et al., 2003; Trebs et al., 2004; Ianniello et al., 2010). The high NO₃⁻ concentrations were also mostly associated with large aerosol water content, which indicates the importance of heterogeneous hydrolysis in the production of nitrate (Pathak et al., 2009).

The reference is added in the revised manuscript.


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 added a figure to show the correlations as you suggested and revised the text accordingly.

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$_4$)$_2$SO$_4$ is preferentially formed and the least volatile, NH$_4$NO$_3$ is relatively volatile, while NH$_4$Cl 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$_4$Cl. 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$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. In addition to these substances, it is likely that NH$_3$ also reacted with oxalic acid and other dicarboxylic acid to form ammonium oxalate and other organic ammonium aerosols, as discussed above.

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

Answer: 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 added the reference.

Role of ambient ammonia in particulate ammonium formation at a rural site in the North China Plain

Zhao yang Meng1, Xiaobin Xu1, Weili Lin2, Baozhu Ge3, Yulin Xie4,5, Bo Song4, Shihui Jia6, Rui Zhang7,8, Wei Peng1, Ying Wang1, Hongbin Cheng1, Wen Yang2, Huarong Zhao1

1 State Key Laboratory of Severe Weather & Key Laboratory for Atmospheric Chemistry of CMA, Chinese Academy of Meteorological Sciences, Beijing 100081, China
2 CMA Meteorological Observation Centre, Beijing 100081, China
3 State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China
4 University of Science and Technology Beijing, Beijing 100083, China
5 Baotou Steel Group Mining Research Institute, Baotou 014010, China
6 South China University of Technology, Guangzhou 510641, China
7 Chinese Research Academy of Environmental Sciences, Beijing 100012, China
8 Beijing Municipal Research Institute of Environmental Protection, Beijing 100037, China

Correspondence to: Zhao yang Meng (mengzy@camscma.cn)

Abstract. The real-time measurements of NH3 and trace gases were conducted, in conjunction with semi-continuous measurements of water-soluble ions in PM2.5 at a rural site in the North China Plain (NCP) from May to September 2013 in order to better understand of chemical characteristics for ammonia, and of the impact on formation of secondary ammonium aerosols in the NCP. Extremely high NH3 and NH4+ concentrations were observed after a precipitation event within 7-10 days following urea application. Elevated NH3 levels coincided with elevated NH4+, indicating that NH3 likely influenced particulate ammonium mass. For the sampling period, the average oxidation/conversion ratios for SO2−(SOR), NO3−(NOR) and NH4+(NHR) were estimated to be 0.64, 0.24 and 0.30, respectively. The increased NH3 concentrations mainly from agricultural activities and regional transport, coincided with the prevailing meteorological conditions. The high NH3 level with NHR about 0.30 indicate that the emission of NH3 in the NCP is much higher than needed for aerosol acids neutralization and NH3 plays an important role in the formation of secondary aerosols as a key neutralizer. The hourly data obtained were used to investigate gas-aerosol partitioning characteristics using the thermodynamic equilibrium model ISORROPIA II. Modelled NO3−, SO2−, and NH3 values agree well with the measurements, while the modelled NH4+ largely underestimate the measurements.
Our observation and modelling results indicate that strong acids in aerosol are completely neutralized. Additional NH₄⁺ exists in aerosol, probably a result of presence of substantial amount of oxalic and other diacids.

Keywords: Ambient ammonia; ammonium in PM₁₀; the conversion ratio of NH₄⁺; thermodynamic equilibrium; agricultural activity; North China Plain.

1 Introduction

Ammonia (NH₃) is a very important alkaline constituent in the atmosphere, plays an important role in atmospheric chemistry and is closely related to ecosystems. NH₃ has both direct and indirect impacts on critical environmental issues, including regional fine particles, acid rain, and eutrophication (Roelle and Aneja, 2002; Krupa, 2003; Reche et al., 2015). In addition, NH₃ is a key species for neutralising H₂SO₄ and HNO₃ in the atmosphere and forming (NH₄)₂SO₄, NH₄HSO₄, and NH₄NO₃ (Erisman and Schaap, 2004; Walker et al., 2004), which are major inorganic components of fine particulate matters and contribute to regional haze (Ye et al., 2011; Meng et al., 2014; Wei et al., 2015). Global ammonia emission has more than doubled since pre-industrial times, mainly because of agricultural intensification (Galloway et al., 2003). The total ammonia emission in China in 2006 was estimated to be 16.07 million tons (Mt) (Dong et al., 2010). Such high emission makes NH₃ one of the key species related to atmospheric environmental problems. Some studies have indicated that reducing NH₃ concentrations could be an effective method for alleviating secondary inorganic PM₂.₅ pollution in China (Cao et al., 2009; Park et al., 2014; Wang et al., 2015; Xu et al., 2017).

As global food production requirements increase, agriculture plays an increasingly important role in local, regional, and global air quality (Walker et al., 2006). The North China Plain (NCP) is a highly populated region with intensive agricultural production as well as heavy industry. The region has been affected by severe haze and photochemical pollution in recent years (Guo et al., 2010; Wang et al., 2010; Luo et al., 2013). Covering only 3.3% of the national area, the NCP region provides 40% and 25% of China’s wheat and corn production. To sustain such high agricultural productivity, chemical fertilisers have been intensively applied. Less than 30% efficiency in N application causes approximately 40% N loss through various routes including the leaching of NO₃⁻ and emission of NH₃.
N₂O, and N₂(Zhang et al., 2010). So far, only a few limited studies have paid attentions to impacts of NH₃ on air pollution in the NCP region. According to some studies (Dong et al., 2010; Ianniello et al., 2010; Meng et al., 2011; Shen et al., 2011; Meng et al., 2015), the high NH₃ emission intensities observed in the NCP have been caused by high fertiliser application rates and numerous intensive livestock farms. However there were few simultaneous high time resolution measurements of NH₃, and NH₄⁺ in PM₂.₅, and investigating the role in fine particulate formation in China. These studies are necessary to improve our understanding of ammonia pollution on regional air quality, and of the impact on formation of secondary ammonium aerosols in the NCP.

During May-September 2013, the intensive field measurements of NH₃ and other trace gases, water-soluble ions in PM₂.₅, and meteorological parameters took place at a rural site in the NCP. In this article, we report the results on NH₃, trace gases and major water-soluble ions in PM₂.₅. We discuss temporal variations and diurnal patterns of NH₃ and NH₄⁺. We also show results from thermodynamic equilibrium simulations and compared them with observations.

2 Description of Experiment

2.1 Measurement site

The measurements were performed from May to September 2013 at Gucheng (39°08′N, 115°40′E, 15.2 m a.s.l.), a rural site in the NCP, which is an Integrated Ecological Meteorological Observation and Experiment Station of the Chinese Academy of Meteorological Sciences. In Fig. 1, the location of the site is shown on the NCP map with the NH₃ emission distribution for the year 2012 from the multi-resolution emission inventory of China (http://meicmodel.org/index.html). The measurement site chosen is situated for monitoring regional background concentrations of air pollutants in the North China Plain, has good regional representativeness (Lin et al., 2009). The site is approximately 110 km southwest of Beijing, 130 km west of Tianjin, and 160 km northeast of Shijiazhuang City in Hebei Province. The site is surrounded by farms, dense villages/towns, and the transportation network in the NCP. The main crops in the area surrounding the site are wheat (winter and spring) and corn (summer and fall). The site is influenced by high NH₃ emissions from fertiliser use and animal husbandry in the surrounding area. Being in the warm temperate zone, the site has a typical temperate continental monsoon climate. Precipitation occurs mainly between May to August.

2.2 Sampling and analysis

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 NH3/N2 (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 NH3 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 NH3 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 O3 (TE 49C), NO/NO2/NOx (TE 42CTL), CO (TE 48C), and SO2 (TE 43CTL). All instruments were housed in an air-conditioned room in the observation building at the Gucheng site. Two parallel inlet tubes (Teflon, 4.8 mm IDx8 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.
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 8 m 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, NOₓ, 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 PM₂.₅ 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 into the AIM with a 2 meter Teflon coated aluminum pipe and particles larger than 2.5 μm were removed by a cyclone at a flow rate of 3 L min⁻¹. 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 μg m⁻³, 0.04 μg m⁻³ and 0.05 μg 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⁻¹ 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 j(NO₂) 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 (PBLH) values at 14:00 were derived from the ERA-Interim data using...
the Bulk Richardson number method (Guo et al., 2016; Miao et al., 2017).

2.3 Data analysis

2.3.1 Chemical conversions of species

Sulfate and nitrate oxidation ratios (SOR and NOR) are defined as the molar ratio of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) in PM\(_{2.5}\) to the total oxidized S and N, respectively (Zhang et al., 2011).

\[
\text{SOR} = \frac{\text{SO}_4^{2-}}{\text{SO}_4^{2-} + \text{SO}_2} \quad (1)
\]

\[
\text{NOR} = \frac{\text{NO}_3^-}{\text{NO}_3^- + \text{NO}_x} \quad (2)
\]

Similarly, the conversion ratio of ammonium (NHR) is expressed in terms of the ratio of ammonium to total ammonia (NH\(_3\)), which could be a measure of the extent of transformation from NH\(_3\) to NH\(_4^+\) in areas with major local NH\(_3\) sources (Hu et al., 2014).

\[
\text{NHR} = \frac{\text{NH}_4^+}{\text{NH}_4^+ + \text{NH}_3} \quad (3)
\]

2.3.2 Thermodynamic equilibrium

Thermodynamic gas-aerosol equilibrium characteristics during summer 2013 were examined using ISORROPIA II model (Fountoukis and Nenes, 2007; Fountoukis et al., 2009). ISORROPIA II is a thermodynamic equilibrium model for inorganic gases and aerosols in the atmosphere (available at http://isorropia.eas.gatech.edu/index.php?title=Main_Page). The concentrations of the measured NH\(_3\) 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. 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 (Guo et al., 2015; Bougiatioti et al., 2016; Liu et al., 2017). In this study, the aerosol properties as acidity and the water content of the aerosol are needed to investigate the aerosol acidity characteristics and role of heterogeneous chemistry in nitrate formation. The pH of aerosol water was calculated using the following equation:

\[
\text{pH} = -\log_{10} \left( \frac{1000H^+_{\text{air}}}{\text{AWC}} \right) \quad (4)
\]

where \( H^+_{\text{air}} \) (μg m\(^{-3}\)) is the ion concentration of equilibrium particle hydronium and AWC (μg m\(^{-3}\)) is
the aerosol water content from the ISORROPIA-II simulation. The evaluation of AWC prediction showed a good performance compared with observed particle water (Bian et al., 2014; Guo et al., 2015).

2.3.3 Trajectory calculation

The 72-h backward trajectories were calculated using the HYSPLIT 4.9 model (http://www.arl.noaa.gov/ready/hysplit4.html). The trajectories terminated at the height of 100 m above the ground. The trajectory calculations were done for four times (00:00, 06:00, 12:00, and 18:00 UTC) per day in summer 2013. Individual back trajectories were grouped into five clusters. The number of clusters is identified according to the changes of total spatial variance (TSV). Five is chosen as the final number of clusters considering optimum separation of trajectories (larger number of clusters) and simplicity of display (lower number of cluster). The corresponding concentrations of trace gases and water soluble ions were averaged over the period of 3 h ahead and after the arrival time for each backward trajectory for further analysis.

3 Results and discussion

3.1 Overview of concentration levels of measured species

During 15 May–25 September 2013, the average concentrations (ranges) of NH₃, SO₂ and NOₓ were 36.2 (0.1-862.9), 5.0 (0-86.8) and 15.4 (2.7-67.7) ppb, respectively. As listed in Table 1, the concentration of NH₃ at the NCP rural site was lower than those reported in Asian and Africa urban sites such as Lahore (Pakistan) (Biswas et al., 2008), Colonelganj (India) (Behera et al., 2010) and Cairo (Egypt) (Hassan et al., 2013), but higher than those from other areas in China, Europe and North American (Plessow et al., 2005; Yao et al., 2006; Lin et al., 2006; Walker et al., 2006; Hu et al., 2008; Meng et al., 2011; Shen et al., 2011; Schaap et al., 2011; Makkonen et al., 2012; Behera et al., 2013; Gong et al., 2013; Meng et al., 2014; Li et al., 2014). For example, the NH₃ at the NCP rural site was higher than those found at Shangdianzi regional background station in the NCP (Meng et al., 2011), Lin’an regional background station in the Yangtze River Delta (YRD) in Eastern China (Meng et al., 2014) and the rural site in Beijing (Shen et al., 2011). The relatively high concentrations of NH₃ observed in this study were attributed to agricultural activities involving fertiliser use, vegetation, and livestock, as well as human excrement and waste disposal in the surrounding region.

According to an inventory study (Zhang et al., 2010), the total agricultural NH₃-N emission in 2004 in the NCP was 3071 kt yr⁻¹, accounting for 27% of the total emissions in China with the 1620 kt yr⁻¹
of NH$_3$–N emissions caused by fertiliser applications, which is the largest emission source accounting for more than half of the total agricultural emissions. In recent years, there were 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.

The observed concentration of SO$_2$ at the NCP rural site was markedly lower than those reported for the same period in 2006-2007 (Lin et al., 2009). Because of a series of emission reduction measures implemented in recent years, SO$_2$ levels have decreased markedly in the NCP (Lin et al., 2011). The average concentration of NO$_x$ was higher than those at Shangdianzi (Meng et al., 2011) and Lin’an (Meng et al., 2014) regional background stations in the NCP and YRD region of China, which might be due to emission form agricultural activities and motor vehicle sources (Lei and Wuebbles, 2013; Liu et al., 2013) in the NCP, but was lower than those at urban sites in India (Behera et al., 2010) and Egypt (Hassan et al., 2013).

The average concentrations (ranges) of NH$_4^+$, SO$_4^{2−}$, and NO$_3^−$ in PM$_{2.5}$ were 19.8±(1.07-340.6), 20.5±(3.30-116.9) and 11.3±(1.09-109.3) µg m$^{-3}$, respectively, at the NCP rural site during 15 June-11 August 2013. The average concentration of NH$_4^+$ in PM$_{2.5}$ was higher than those observed at the rural or urban sites in the NCP (Meng et al., 2011), YRD (Meng et al., 2014), Beijing (Shen et al., 2011), Guangzhou (Hu et al., 2008), and Hong Kong (Yao et al., 2006) in China, and comparable to that at urban site in India (Behera et al., 2010). The average concentration of SO$_4^{2−}$ in PM$_{2.5}$ was higher than those at rural sites in the NCP (Meng et al., 2011) and YRD (Meng et al., 2014) in China, but was lower than that observed at rural sites in Guangzhou (Hu et al., 2008) in China, as well as urban sites in India (Behera et al., 2010) and Egypt (Hassan et al., 2013). The average concentration of NO$_3^−$ in PM$_{2.5}$ was higher than those observed at the rural sites in the YRD and Guangzhou (Hu et al., 2008) in China, and lower than those at urban sites in India (Behera et al., 2010) and Pakistan (Biswa et al., 2008). The elevated NH$_3$ and NH$_4^+$ in PM$_{2.5}$ concentrations at the NCP rural site demonstrate severe ammonia and fine particulate ammonium pollution in this area.

### 3.2 Ambient ammonia
3.2.1 Temporal variation of NH₃

The time series of hourly averages of NH₃ and other trace gases together with meteorological parameters during 15 May-25 September 2013 at Gucheng are shown in Fig. 2. NH₃ concentrations varied considerably during the observation period, ranging from 0.1 to 862.9 ppb. 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 NH₃ concentration increased rapidly on the seventh day after the urea application on 20 July, peaking during the 27-30 July period (Fig. 2b). The highest hourly value of NH₃ (862.9 ppb) was observed at 04:00 local time on 29 July 2013, with the second highest concentration observed at 06:00 on the same day. The extremely high NH₃ concentrations were probably caused by intensified soil emissions after rainfall on 26 July, which enhanced the soil moisture. Precipitation and the resulting soil water dynamics are known to strongly affect urea hydrolysis and subsequent NH₃ emissions (Reynold and Wolf, 1987; Aranibar et al., 2004). The general increase in NH₃ emissions was observed when soils with high moisture content began to dry because of increased diffusion (Burch et al., 1989). In addition, high temperatures in summer promote NH₃ volatilisation from urea and ammonium dibasic phosphate applied to crops.

The monthly concentration of NH₃ depends on its source and meteorological conditions. The monthly average values of NH₃ were 28.4, 73.9, 26.4, and 13.5 ppb in June, July, August, and September 2013, respectively. In summer, high temperature promotes the emission of NH₃ from natural and fertilised soils, as well as vegetation. The concentration of NH₃ in July was approximately five times higher than that in September, which was influenced by higher temperature and increased emission rates of local agricultural NH₃ sources in July.

SO₂ and NOₓ are the main precursors of sulfate and nitrate aerosols, and O₃ play an important role in atmospheric chemistry because they act as sources of OH radicals through photolysis. The maximum hourly average concentrations of SO₂ and NOₓ were 86.8 ppb at 00:00 on 21 May and 67.7 ppb at 10:00 on 17 September, respectively. O₃ monthly levels were high in June (44.3 ppb) and July (43.7 ppb), with a maximum hourly average value of 149.9 ppb at 15:00 on 25 July 2013.

In contrast to NH₃, the highest monthly levels of SO₂ (7.0 ppb) and CO (885 ppb) were observed in June, which could be due to the open burning of agricultural waste (straw, cornstalk, and other crops).
after harvest in the surrounding area. Previous studies have shown that the burning of crop residues is a crucial source of trace gases such as NO\textsubscript{x} and CO in the NCP during summer (Meng et al., 2009; Lin et al., 2011). The obvious impact of biomass burning was observed during 16-19 June 2013 period. As CO is mainly emitted from anthropogenic sources such as the burning of biomass, the elevated CO concentrations (2529 ppb at 22:00 on 16 and 2488 ppb at 22:00 on 17 June) were observed. During this pollution episode, the average concentrations of NH\textsubscript{3}, SO\textsubscript{2}, NO\textsubscript{x}, O\textsubscript{3} and CO were 42.6, 7.69, 18.8, 44.0 and 1092 ppb, respectively, which were about 1.2-1.5 times than the average values for the whole study period. The monthly concentrations of SO\textsubscript{2}, NO\textsubscript{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 NO\textsubscript{2} and the time-series of hourly rainfall during June-August 2013. As can be seen, the average NO\textsubscript{2} 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. For the secondary pollutant O\textsubscript{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\textsubscript{3} in the NCP, which occurs in June (Ding et al., 2008; Lin et al., 2008).

### 3.2.2 Diurnal variations of NH\textsubscript{3}

The average diurnal variations of NH\textsubscript{3} during June to September 2013 are shown in Fig. 3. As indicated in Fig. 3a, NH\textsubscript{3} concentration maxima and minima were observed during 08:00-13:00 and 19:00-23:00, respectively. As for July, NH\textsubscript{3} concentrations showed a considerably more pronounced diurnal pattern with a maximum of 59.5 ppb at 08:00. The concentration of NH\textsubscript{3} gradually increased during 00:00-03:00, remained relatively constant during 04:00-06:00, and then rapidly increased from 06:00 (beginning just after sunrise). After peaking at approximately 08:00, a decrease was observed until it reached the minimum of 29.8 ppb at 19:00.

The morning peak of NH\textsubscript{3} was also observed elsewhere and could be resulted from emissions from fertilised 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°C) 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 NH$_3$ 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 breakup 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.

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 NH$_3$ in July had a maximum nighttime increase (20.0 ppb from 20:00 to 06:00), which is much larger 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 an earliest NH$_3$ peak in July.

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 fertilisers like urea. As mentioned above, the urea application in the station on 20 July 2013 and a precipitation process afterwards caused 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 lower 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, relative humidity, wind speed, and PBLH, 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.
3.3 Ambient ammonium aerosol

Secondary inorganic aerosols form from gas-phase precursors, which are mostly from anthropogenic activities such as industrial, agricultural, and motor vehicle emissions. Therefore, the major precursors (NH₃, SO₂ and NOₓ) are responsible for the formation of particulate ammonium, sulphate, and nitrate.

The hourly NH₄⁺ concentrations during 15 June-11 August 2013 ranged from 1.07 to 340.6 μg m⁻³, with an average concentration of 19.8 μg m⁻³. The highest monthly level of NH₄⁺ appeared in July and the lowest level appeared in June 2013. Similar to NH₃, the concentration of NH₄⁺ also increased sharply after urea fertilisation, with the highest value (340.6 μg m⁻³) observed at 09:00 on 28 July 2013. The temporal variations of NH₄⁺ basically coincided with SO₄²⁻ and NO₃⁻ (discussed in Sect. 3.6), reflecting that NH₄⁺ largely originated from the neutralization between NH₃ and acidic species.

The highest hourly SO₄²⁻ concentration (116.9 μg m⁻³) was observed at 10:00 on 9 July and the second highest value was 111.4 μg m⁻³ at 18:00 on 6 August, 2013, with an average concentration of 20.5±13.6 μg m⁻³. Despite the lower concentrations of NOₓ, higher SO₄²⁻ concentrations in summer were attributed to the higher temperature, O₃ concentration and solar radiation, which increase the photochemical activities, the atmospheric oxidation and markedly faster conversion of SO₂ to SO₄²⁻.

The average concentration of NO₃⁻ in PM₁₀ 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 high RH conditions in summer might dissolve a significant fraction of HNO₃ and NH₃ in humid particles, therefore increasing the concentrations of NO₃⁻ and NH₄⁺ in the atmosphere (Krupa et al., 2003; Trebs et al., 2004; Ianniello et al., 2010). The high NO₃⁻ concentrations were also mostly associated with large aerosol water content, which indicates the importance of heterogeneous hydrolysis in the production of nitrate (Pathak et al., 2009). On the other hand, NH₃ was more efficient in summer to react with SO₂ to form (NH₄)₂SO₄.

Figure 4 shows correlations of observed NH₄⁺ with the sum of observed with observed SO₄²⁻, SO₄²⁻+NO₃⁻ and SO₄²⁻+NO₃⁻+Cl⁻. Although all the correlations are significant, the slopes of the regression lines are far from unit. This cannot be due bias in measurements. The major ion balance shows ratio of 1.05:1.0 for cation:anion. The slope is 0.56 when all three strong acid are considered, suggesting that the neutralization of the strong acids explain 56% of the observed NH₄⁺. In other words, nearly 44% of the observed NH₄⁺ was due to the presence of other acids in aerosol particles.

3.4 Results from thermodynamic equilibrium simulation
We have used the thermodynamic equilibrium model ISORROPIA II to investigate gas-aerosol partitioning characteristics. The model outputs include equilibrium NO$_3^-$, SO$_4^{2-}$, NH$_4^+$, H$^+$, 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 NH$_4^+$ 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 average concentration of simulated HNO$_3$ was 0.7 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$^+$ are shown in Fig. 6a. A typical high HNO$_3$ concentrations during daytime and low values at nighttime during the observation period is predicted by the model, which is consistent with other studies (Makkonen et al., 2012; Sudheer et al., 2015). The diurnal cycle of H$^+$ is predicted with the highest level around 17:00.

The concentrations of NH$_3$ were closely associated with H$^+$ and higher NH$_3$ always corresponded to lower H$^+$ (Liu et al., 2017). 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. The fine particles were moderately acidic in summer, with an average pH values of 3.5. On average, pH is over 3.5 during nighttime and below 3.5 during daytime (Fig. 6b). Under the medium acidic conditions and high NH$_3$ concentrations, organic acid like diacids are able to reaction with ammonia to form 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. S4).

3.5 Relationship between ammonia and ammonium aerosol

The gas-to-particle conversion between NH$_3$ and NH$_4^+$ has been reported to be strongly affected by temperature, RH, radiation conditions, the concentration of primary acid gas, and other factors. In this
study, \( \text{NH}_3 \) concentrations correlated significantly and positively with \( \text{NH}_3 \) with a correlation coefficient of 0.78 and a slope of 1.48 (Fig. 7a, \( n=915, P < 0.01 \)), suggesting that \( \text{NH}_3 \) played an important precursor role in \( \text{NH}_4^+ \) in PM2.5 formation.

The ratio of \( \text{NH}_3 \) to \( \text{NH}_4^+ \) (NH\(_3\) + NH\(_4^+\)) has been used to identify the source of \( \text{NH}_4 \) and the relative contribution of \( \text{NH}_3 \) to \( \text{NH}_4^+ \) deposition (Lefer et al., 1999; Walker et al., 2004). A value higher than 0.5 signifies that \( \text{NH}_4 \) is mainly from local \( \text{NH}_3 \) sources and that the dry deposition of \( \text{NH}_3 \) dominates the \( \text{NH}_4 \) deposition. Robarge et al. (2002) reported that more than 70% of \( \text{NH}_4 \) was in the form of \( \text{NH}_3 \) at an agricultural site in the South-eastern United States, and concluded that given a larger deposition velocity of ammonia compared with that of ammonium, a considerable fraction of \( \text{NH}_4 \) could be deposited locally rather than be transported out of the region. According to hourly average concentrations, the ratio of \( \text{NH}_3/\text{NH}_4 \) varied from 0.22 to 0.97, with a mean ratio of 0.69±0.14, suggesting that \( \text{NH}_3 \) 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 \( \text{NH}_4 \) was showed in Fig. 7b. Between 08:00-18:00, a decrease in \( \text{NH}_3 \) would result in an increase in \( \text{NH}_4^+ \), which coincided with higher sulfate concentrations. The decrease in gas phase ammonia is likely the result of uptake onto aerosols to form \( (\text{NH}_3)_2\text{SO}_4 \). The diurnal variability of \( \text{NH}_3 \) may be controlled by transport and vertical exchange.

Between the hours of 08:00-18:00, \( \text{NH}_4 \) decreased by 43% while \( \text{NH}_3 \) decreased by 49%, suggested that \( \text{NH}_3 \) remained predominantly in the gas phase. Between 19:00 and 07:00, \( \text{NH}_4 \) increased by 42% and \( \text{NH}_3 \) increased by 51%, indicating that gas-particle partitioning contributes significantly to the decrease in gas phase ammonia during this time.

3.5.1 Gas-to-particle conversion ratio of \( \text{NH}_3 \)

Sulphate and nitrate oxidation ratios (SOR and NOR) are defined in literature to investigate \( \text{SO}_2^2 \) and \( \text{NO}_3^- \) formation and gas-particle transformation (Zhang et al., 2011). The average values of SOR and NOR were estimated to be 0.64 and 0.24 during the observation period at Gucheng, with SOR and NOR being higher than previous measurements (Zhou et al., 2009; Du et al., 2011; Zhang et al., 2011). Yao et al. (2002) pointed out an SOR lower than 0.10 under conditions of primary source emissions and higher than 0.10 when sulphate was mainly produced through the secondary transformation of \( \text{SO}_2 \).
oxidation. The value of SOR reached to 0.70, in August 2013, which may due to the enhanced atmospheric oxidant levels, sufficient ammonia for neutralization, and higher RH in summer at Gucheng (Tang et al., 2016).

To gain further insights into the transformation of NH₃ to NH₄⁺, the conversion ratio of ammonium (NHR) was investigated. NHR is a measure of the extent of transformation from NH₃ to NH₄⁺ in areas with significant local NH₃ sources, although it encompasses both transport and local equilibrium, the latter dominating further downwind from the source. In this study, the average hourly values of NHR ranged from 0.03 to 0.77, with an average of 0.30 during summer 2013. The average NHR level in this study was higher than that observed at an urban site in Beijing (Meng et al., 2017), indicating that high NH₃ concentrations resulting from agricultural activities had a marked influence on the formation of ammonium. 

3.5.2 Diurnal patterns of NHR, SOR and NOR

Fig. 8 presents the diurnal patterns of NHR, SOR, NOR, gaseous precursors, and major water soluble ions, and meteorological factors. As a key species contributing to the oxidation capacity of the atmosphere, O₃ can promote HNO₃ formation, affecting the conversion ratio of NH₃. O₃ exhibited low levels in the morning and enhanced levels in the late afternoon. The lower morning concentrations may be due to the depositional loss of O₃ under stable atmospheric conditions in early morning hours, and the higher levels in the afternoon could be due to the photochemical production of O₃. The NH₄⁺ concentration started to increase from morning, reaching the maximum value (16.1 μg m⁻³) at 18:00, with a diurnal difference of 3.7 μg m⁻³. This diurnal pattern may be due to a combination of high NH₃ concentrations, the intense solar radiation at noon, and the high oxidation capacity of the atmosphere in the afternoon. A clear diurnal cycle of NHR existed, with an amplitude of 0.10 and a peak of 0.35 at 18:00, which is consistent with the higher SOR and RH.

The SO₂ concentration showed a maximum at 09:00, with a secondary peak at 22:00. The concentration of SO₄²⁻ showed small peak at 1:00, 4:00, and 8:00, respectively, but no strong diurnal variation. SOR displayed a diurnal cycle with the highest value of 0.74 observed at 05:00. It is noted that the SOR was lower during daytime when photochemical reaction is intense. Higher SOR during nighttime suggests importance of dark reactions. SO₂ is highly soluble and can easily absorbed by wet aerosol particles. The much RH during night may promoted this process.

As for the diurnal cycle of NO₃, a peak was observed at 06:00 when the mixing layer was stable,
and a broad valley was observed in the daytime, reflecting the influences of a higher mixing layer and stronger photochemical conversion. During the night, NOx concentrations increased again, resulting in the second maximum at 23:00. NO3− concentrations did not show profound diurnal variations, but slightly higher values during the night time, probably because of the hydrolysis of dinitrogenpentoxide (N2O5) and the condensation of HNO3 under the relatively low temperature. NOR displayed a diurnal pattern with a maximum of 0.28 at 10:00, which was likely related to photochemical reactions under the conditions of high O3 concentrations and NO2 levels.

Nighttime formation, aerosol uptake and hydrolysis of N2O5 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. By assuming high aerosol surface to mass ratio (33.7 m2 g−1, 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−1 (or 2.6-7.7 μg m−3). This rate of HNO3 production would cause an obvious night production of NH4+. Indeed we can see increases in the NH4+ concentration and NH3 during night (Fig. 8). However, a more or less accurate estimate of the relative contribution of the night N2O5 chemistry to NH3 conversion needs to be made in the future.

3.6 A case study of a pollution period

On several days during the study period, very high NH3 and inorganic PM2.5 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 calculated parameters during this period are given in Fig. S5. As shown in Figs. 9 and S5, there was a sharp increase of NOx during the night and early morning of 10 August, followed by that of NH3 (peak value of 64 ppb) at 03:00. In the meantime, a large peak of AWC occurred and gaseous HNO3 decreased to nearly zero (Fig. S5), suggesting rapid uptake of wet aerosol. This event caused the first largest peak of [SO42−]+[NO3−]+[NH4+]34. After this event NH3 rose again and reached a even higher peak (76.3 ppb) 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 [SO42−]+[NO3−]+[NH4+]34 occurred. These data show that high NH3 concentration was accompanied by the large increase in concentrations of SO42−, NO3− and NH4+. 
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 NH$_3$ 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 favour 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$_4$)$_2$SO$_4$ is preferentially formed and the least volatile, NH$_4$NO$_3$ is relatively volatile, while NH$_4$Cl 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$_4$Cl. 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$_4$)$_2$SO$_4$ and NH$_4$NO$_3$. In addition to these substances, it is likely that NH$_3$ also reacted with oxalic acid and other dicarboxylic acid to form ammonium oxalate and other organic ammonium aerosols, as discussed above.

### 3.7 Long rang transport and local ammonium and ammonium

The Gucheng site is located in the densely populated rural area in the NCP, it is influenced by local sources in the surrounding areas and by long range transport of pollutants from the residential and industrial centers around it. 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 location.
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; Meng et al., 2011). Thus, NH$_3$ concentrations might be generally lower at higher wind speeds because of turbulent diffusion.

To identify the impact of long-range air transport on the surface air pollutants levels and secondary ions at Gucheng, the 72-h backward trajectories were calculated using the HYSPLIT 4.9 model. As can be seen in Fig. 1, the Clusters 1, 2 and 3 represent relatively low and slow moving air parcels, with cluster 2 coming from northwest areas at the lowest transport height among the five clusters. The air mass of Cluster 1 and 3 originate from southeast of Gucheng. The Cluster 4 and 5 represent air parcels mainly from the far northwest. The trajectories in Clusters 2 came from the local areas around Gucheng, and it was the most important cluster to the Gucheng site, contributing 56% to the air masses. Based on the statistics, the number of trajectories in Cluster 1, 2 and 3 accounts to 88% of the all trajectories. As more than 80% air masses originated from or passing over the North China Plain region can influence the surface measurements at Gucheng, the observation results at Gucheng can well represent the regional situation of atmospheric components in the North China Plain region.

Since the emission sources of pollutants are unevenly distributed in the areas surrounding the Gucheng site, air masses from different directions containing different levels of pollutants. The corresponding mean concentrations of NH$_3$, SO$_2$, NO$_2$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in PM$_{2.5}$ in different clusters of backward trajectories are also included in Table 2 in order to characterize the dependences of the pollutants concentrations on air masses.

Large differences in the concentrations of NH$_3$, SO$_2$, NO$_2$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in PM$_{2.5}$ existed among the different clusters, with cluster 2 corresponding to the highest NH$_3$ (48.9 ppb) and second highest NO$_2$, NH$_4^+$ and SO$_4^{2-}$(14.4 ppb, 17.5 µg m$^{-3}$ and 22.1 µg m$^{-3}$, respectively). The cluster 1 corresponds to highest SO$_2$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ (7.9 ppb, 22.3 µg m$^{-3}$, 22.6 µg m$^{-3}$ and 17.7 µg m$^{-3}$, respectively), the second highest NH$_3$ level (32.8 ppb). The cluster 3 had the highest
NO$_x$ level (15.1 ppb), the second highest SO$_2$ and NO$_x$ (4.8 ppb and 11.8 $\mu$g m$^{-3}$, respectively), and had the third highest concentration of NH$_3$, NH$_4^+$ and SO$_4^{2-}$ levels (28.5 ppb, 14.6 $\mu$g m$^{-3}$, and 20.2 $\mu$g m$^{-3}$, respectively).

Based on Table 2, the lowest NH$_3$, SO$_2$, NO$_x$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ levels were corresponding to clusters 5, which was expected to bring cleaner air masses into surface. As demonstrated by backward trajectory, more than half of the air masses during the sampling period from North China Plain region contributed to the atmospheric NH$_3$ variations, and both regional sources and long-distance transport from southeast played important roles in the observed ammonium aerosol at the rural site in the NCP.

### 4 Conclusions

Online measurements of NH$_3$, trace gases, and water-soluble ions in PM$_{2.5}$ were conducted during May-September 2013 at a rural site in the NCP, where a large amount of ammonia was emitted because of agricultural activities. The average concentrations (ranges) of NH$_3$ and NH$_4^+$ in PM$_{2.5}$ were 36.2 (0.1-862.9) ppb during 15 May-25 September, 2013, and 19.8 (1.07-340.6) $\mu$g m$^{-3}$ during 15 June-11 August, 2013, respectively; these are considerably higher than those reported at other sites in China, Europe and North American. Extremely high NH$_3$ and NH$_4^+$ concentrations were observed, which was attributed to high soil moisture level due to rainfall on these days following the urea application. Elevated NH$_3$ levels coincided with elevated NH$_4^+$, indicating the contribution of atmospheric NH$_3$ to secondary inorganic aerosols during periods of agricultural activity. NH$_3$ contributed 69% to the total NH$_4^+$ in summer, suggesting that NH$_3$ remained predominantly in the gas phase rather than the aerosol phase in summer 2013 at Gucheng.

The average conversion/oxidation ratio for NH$_4^+$ (NHR), SO$_4^{2-}$ (SOR), and NO$_3^-$ (NOR) were estimated to be 0.30, 0.64, and 0.24 in summer 2013, respectively. Results reveal that the concentrations of NH$_3$, NH$_4^+$, and NHR had clear diurnal variations during the observation period. High NH$_3$ and NH$_4^+$ were observed during late night and early morning period. NHR also showed higher values during night, suggesting the importance of heterogeneous reactions driven by high nighttime RH. The hourly data obtained were used to investigate gas-aerosol partitioning characteristics using the thermodynamic equilibrium model ISORROPIA II. Modelled NO$_x^+$, SO$_4^{2-}$, and NH$_3$ values agree well with the measurements, while the modelled NH$_4^+$ largely underestimate the measurements.

Our measurement and modelling results indicate that the strong acids in aerosol particles over the rural site were well neutralized by NH$_3$. Nearly a half of the ammonium was not associated with strong acids.
but probably with oxalic acid and other diacids, which may present under the medium aerosol acidity (pH around 3.5).

The back trajectory analysis indicates that the transport from the North China Plain region contributed for 56% of air mass with high NH$_3$ levels, meanwhile the long-distance transport from southeast accounted for 32% of air mass with high NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ at the rural site in the NCP.

NH$_3$ is currently not included in China’s emission control policies of air pollution precursors though people have been discussing the necessity for years. Our findings highlight the important role of NH$_3$ in the participation of secondary inorganic and organic aerosol formation. As the emission and concentration of NH$_3$ in the NCP are much higher than needed for aerosol acids neutralization, we speculate that a substantial amount of reduction in NH$_3$ emission is required to see its effect on the alleviation of PM$_{2.5}$ pollution in the NCP. Therefore, further strong reduction of the emissions of primary aerosol, NH$_3$, SO$_2$, NO$_x$, and VOCs is suggested to address the serious occurrence of PM$_{2.5}$ pollution on the North China Plain.

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Table Captions

Table 1. The comparisons of the concentration of trace gases (ppb) and water-soluble ions in PM$_{2.5}$ ($\mu$g m$^{-3}$) at Gucheng with other researches.

Table 2. Occurrence frequency and mean values of NH$_3$, other trace gases and water-soluble ions in PM$_{2.5}$ for each type of air masses arriving at Gucheng during summer 2013.

Figure Captions

Figure 1. Sampling location in the North China Plain with emission distributions of NH$_3$ for the year 2012 from the multi-resolution emission inventory of China (http://meicmodel.org/index.html).

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 (b).

Figure 3. Diurnal variation of NH$_3$ (a) and meteorological parameters (b) during the sampling period.

Figure 4. Correlation of observed NH$_4^+$ with observed SO$_4^{2-}$, SO$_4^{2-}$+NO$_3^-$ and SO$_4^{2-}$+NO$_3^-$+Cl$^-$.

Figure 5. Observed and modelled concentrations of NH$_3$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in summer 2013.

Figure 6. Simulated diurnal variation of HNO$_3$ and H$^+$ (a) and calculated diurnal variation of pH value of aerosol water (b) in summer 2013.

Figure 7. Relationship between NH$_3$ and NH$_4^+$ (a) and diurnal variation of NH$_3$ (b) in summer 2013.

Figure 8. Diurnal variation of NHR, SOR, NOR, gaseous precursors, major water soluble ions, and meteorological factors in summer 2013.

Figure 9. Hourly concentrations of gaseous, ionic species and NO$_2$ measured in the pollution episode 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 11. The average NH$_3$, NH$_4^+$ and meteorological data rises in different wind sectors during summer 2013.

Figure 12. 72-h backward trajectories for 100 m above ground level at Gucheng during sampling period 2013.
Figure S1. Confirmation of the performance of NH₃ analyzer using diluted standard gas (mixture NH₃/N₂). Instrument response to changed NH₃ concentration and stability (a) and repeated multipoint calibrations (b).

Figure S2. Monthly diurnal variations of photolysis rate coefficient of NO₂ ([NO₂]) (a) and hourly amount of precipitation (b) in summer 2013.

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

Figure S4. Correlation of modelled NH₄⁺ with modelled SO₄²⁻, SO₄²⁻+NO₃⁻ and SO₄²⁻+NO₃⁻+Cl⁻.

Figure S5. Time series of predicted fine particle pH, particle water mass, HNO₃, H₄⁺, NH₃ and inorganic ions during 7-11 August 2013.
Table 1. The comparisons of the concentration of trace gases (ppb) and water-soluble ions in PM$_{2.5}$ (µg m$^{-3}$) at Gucheng with other researches.

<table>
<thead>
<tr>
<th>Location</th>
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<th>NO$_x$</th>
<th>NH$_4^+$</th>
<th>SO$_4^{2-}$</th>
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<td>Lin et al., 2006</td>
</tr>
<tr>
<td>Colonelganj, India</td>
<td>Urban</td>
<td>Summer 2007</td>
<td>41.3±10.5</td>
<td>6.9±1.99</td>
<td>33.8±8.56</td>
<td>18.4±4.7</td>
<td>27.8±7.6</td>
<td>29.2±7.5</td>
<td>Behera et al., 2008</td>
</tr>
<tr>
<td>Singapore</td>
<td>Urban</td>
<td>Sep.-Nov. 2011</td>
<td>3.6</td>
<td>8.3</td>
<td>–</td>
<td>1.76</td>
<td>4.4±1.2</td>
<td>1.29</td>
<td>Behera et al., 2013</td>
</tr>
<tr>
<td>Oberhauersburg, Germany</td>
<td>Forest</td>
<td>Oct.2003-Apr. 2004</td>
<td>0.69</td>
<td>2.34</td>
<td>–</td>
<td>1.55</td>
<td>3.07</td>
<td>2.22</td>
<td>Plessow et al., 2005</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Rural</td>
<td>Aug. 2007 and 2008</td>
<td>12.9</td>
<td>0.5</td>
<td>–</td>
<td>2.4</td>
<td>3.1</td>
<td>5.9</td>
<td>Scharp et al., 2011</td>
</tr>
<tr>
<td>Helsinki, Finnish</td>
<td>Urban</td>
<td>Spring 2010</td>
<td>0.4±0.59</td>
<td>0.29±0.38</td>
<td>–</td>
<td>0.46±0.50</td>
<td>1.64±1.08</td>
<td>1.40±2.04</td>
<td>Makkonen et al., 2012</td>
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<tr>
<td>Cairo, Egypt</td>
<td>Suburban</td>
<td>Summer 2009</td>
<td>6.7</td>
<td>5.39</td>
<td>28.7</td>
<td>7.5</td>
<td>28</td>
<td>4.2</td>
<td>Hassan et al., 2013</td>
</tr>
<tr>
<td>Clinton, USA</td>
<td>Agricultural</td>
<td>Jan.1999-Dec. 2000</td>
<td>8</td>
<td>1.5</td>
<td>–</td>
<td>1.76</td>
<td>4.22</td>
<td>2.05</td>
<td>Walker et al., 2006</td>
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<tr>
<td>Houston, USA</td>
<td>Urban</td>
<td>Aug. 2010</td>
<td>3.0±2.5</td>
<td>–</td>
<td>0.5±1.0</td>
<td>4.5±8.3</td>
<td>0.3±0.2</td>
<td></td>
<td>Gong et al., 2013</td>
</tr>
<tr>
<td>Wyoming, USA</td>
<td>Rural</td>
<td>Dec.2006-Dec. 2011</td>
<td>0.24</td>
<td>–</td>
<td>–</td>
<td>0.26</td>
<td>0.48</td>
<td>0.32</td>
<td>Li et al., 2014</td>
</tr>
</tbody>
</table>
Table 2. Occurrence frequency and mean values of NH$_3$, other trace gases (ppb) and ionic species in PM$_{2.5}$ (μg m$^{-3}$) for each type of air masses arriving at Gucheng in summer 2013.

<table>
<thead>
<tr>
<th>Air mass</th>
<th>Ratio(%)</th>
<th>NH$_3$</th>
<th>SO$_2$</th>
<th>NO$_x$</th>
<th>NH$_4^+$</th>
<th>SO$_4^{2-}$</th>
<th>NO$_3^-$</th>
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<tr>
<td>Clusters 1</td>
<td>15</td>
<td>32.8</td>
<td>7.9</td>
<td>14.0</td>
<td>22.3</td>
<td>22.6</td>
<td>17.7</td>
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<td>Clusters 2</td>
<td>56</td>
<td>48.9</td>
<td>3.7</td>
<td>14.4</td>
<td>17.5</td>
<td>22.1</td>
<td>10.3</td>
</tr>
<tr>
<td>Clusters 3</td>
<td>17</td>
<td>28.5</td>
<td>4.8</td>
<td>15.1</td>
<td>14.6</td>
<td>20.2</td>
<td>11.8</td>
</tr>
<tr>
<td>Clusters 4</td>
<td>10</td>
<td>23.4</td>
<td>2.4</td>
<td>12.8</td>
<td>12.9</td>
<td>15.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Clusters 5</td>
<td>3</td>
<td>16.3</td>
<td>0.6</td>
<td>9.4</td>
<td>7.5</td>
<td>8.1</td>
<td>5.0</td>
</tr>
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</table>
Figure 1. Sampling location in the North China Plain with emission distributions of NH$_3$ for the year 2012 from the multi-resolution emission inventory of China (http://meicmodel.org/index.html).
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 (b).
Figure 3. Diurnal variation of NH$_3$ (a) and meteorological parameters (b) during the sampling period.
Figure 4. Correlation of observed NH$_4^+$ with observed SO$_4^{2-}$, SO$_4^{2-}$+NO$_3^-$, SO$_4^{2-}$+NO$_3^-$+Cl$^-$. 

\begin{align*}
\text{y} &= 0.56x + 0.17 \\
R^2 &= 0.57 \\
\text{y} &= 0.55x + 0.17 \\
R^2 &= 0.56 \\
\text{y} &= 0.56x + 0.17 \\
R^2 &= 0.57
\end{align*}
Figure 5. Observed and modelled concentrations of NH$_3$, NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ in summer 2013.
Figure 6. Simulated diurnal variation of HNO$_3$ and H$^+$ _air (a) and calculated diurnal variation of pH value of aerosol water (b) in summer 2013.
Figure 7. Relationship between NH$_3$ and NH$_4^+$ (a) and diurnal variation of NH$_3$ (b) in summer 2013.
Figure 8. Diurnal variation of NHR, SOR, NOR, gaseous precursors, major water soluble ions, and meteorological factors in summer 2013.
Figure 9. Hourly concentrations of gaseous, ionic species and \( jNO_2 \) measured in the pollution episode 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 11. The average NH$_3$, NH$_4^+$ and meteorological data roses in different wind sectors during summer 2013.
Figure 12. 72-h backward trajectories for 100 m above ground level at Gucheng during sampling period 2013.
Figure S1. Confirmation of the performance of NH\textsubscript{3} analyzer using diluted standard gas (mixture NH\textsubscript{3}/N\textsubscript{2}). Instrument response to changed NH\textsubscript{3} concentration and stability (a) and repeated multipoint calibrations (b).
Figure S2. Monthly diurnal variations of photolysis rate coefficient of NO$_2$ ($j$/NO$_2$) (a) and hourly amount of precipitation (b) in summer 2013.
Figure S3. The monthly planetary boundary layer heights at 14:00 during 2013 at Gucheng.
Figure S4. Correlation of modelled NH$_4^+$ with modelled SO$_4^{2-}$, SO$_4^{2-}$+NO$_3^-$ and SO$_4^{2-}$+NO$_3^-+$Cl$^-$. 

\[ y = 0.99x + 0.12 \quad R^2 = 0.96 \]

\[ y = 0.73x + 0.07 \quad R^2 = 0.86 \]
Figure S5. Time series of predicted fine particle pH, particle water mass, HNO$_3$, H$_3$O$^+$, NH$_3$ and inorganic ions during 7-11 August 2013.