Numerical analysis of the impact of agricultural emissions on PM$_{2.5}$ in China using a high-resolution ammonia emissions inventory

Xiao Han$^{1,2}$, Lingyun Zhu$^5$, Mingxu Liu$^4$, Yu Song$^4$ Meigen Zhang$^{1,2,3}$,

$^1$State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing 100029, China

$^2$College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China

$^3$Center for Excellence in Urban Atmospheric Environment, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China

$^4$State Key Joint Laboratory of Environmental Simulation and Pollution Control, Department of Environmental Science, Peking University, Beijing 100871, China.

$^5$Shanxi Province Institute of Meteorological Sciences, Taiyuan 030002, China

Corresponding author:

Lingyun Zhu
Shanxi Province Institute of Meteorological Sciences
Xinjian Road 65#, Taiyuan, Shanxi province, China
Post code: 030002
Tel: 86-0351-4077738
Fax: 86-0351-4077738
E-mail: zhlyun@126.com

Meigen Zhang
LAPC, Institute of Atmospheric Physics, Chinese Academy of Sciences
HuaYanBeiLi 40#, Chaoyang District
Beijing, China
Post code: 100029
Tel: 86-010-62379620
Fax: 86-010-62041393
E-mail: mgzhang@mail.iap.ac.cn
Abstract

China is one of the largest agricultural countries in the world. The NH$_3$ emissions from agricultural activities in China significantly affect regional air quality and horizontal visibility. To reliably estimate the influence of NH$_3$ on agriculture, a high-resolution agricultural NH$_3$ emissions inventory, compiled with a 1 km × 1 km horizontal resolution, was applied to calculate the NH$_3$ mass burden in China. The key emission factors of this inventory were enhanced by considering the results of many native experiments, and the activity data of spatial and temporal information were updated using statistical data from 2015. Fertilizer and husbandry, as well as farmland ecosystems, livestock waste, crop residue burning, fuel wood combustion, and other NH$_3$ emission sources were included in the inventory. Furthermore, a source apportionment tool, ISAM (Integrated Source Apportionment Method), coupled with the air quality modeling system RAMS-CMAQ (Regional Atmospheric Modeling System and Community Multiscale Air Quality), was applied to capture the contribution of NH$_3$ emitted from total agriculture (Tagr) in China. The aerosol mass concentration in 2015 was simulated, and the results showed that a high mass concentration of NH$_3$, which exceeded 10 μg m$^{-3}$, appeared mainly in the North China Plain (NCP), Central China (CNC), the Yangtze River Delta (YRD), and the Sichan Basin (SCB), and the annual average contribution of Tagr NH$_3$ to PM$_{2.5}$ mass burden in China was 14-18%. Specific to the PM$_{2.5}$ components, Tagr NH$_3$ provided a major contribution to ammonium formation (87.6%) but a tiny contribution to sulfate (2.2%). In addition, several brute-force sensitivity tests were conducted to estimate the impact of Tagr NH$_3$ emissions reduction on the PM$_{2.5}$ mass burden. Compared with the results of ISAM, it was found that even though the Tagr NH$_3$ only contributed 10.1% of nitrate under current emissions scenarios, the reduction of nitrate could reach 98.8% upon removal of the Tagr NH$_3$ emissions. The main reason for this deviation could be that the NH$_3$ contribution to nitrate is small under "rich NH$_3$" conditions and large in "poor NH$_3$" environments. Thus, the influence of NH$_3$ on nitrate formation could be enhanced with the decrease of ambient NH$_3$ mass concentration.
1. Introduction

Ammonia (NH$_3$) is an important pollution species which principal neutralizing agent for the acid aerosols, SO$_4^{2-}$ and NO$_3^-$ formed from the SO$_2$ and NO$_x$ (Chang, 1989; McMurry et al.; 1983). In addition, NH$_3$ also influences the rate of particle nucleation (Ball et al.; 1999; Kulmala et al.; 2002) and enhances secondary organic aerosols (SOA) yields (Babar et al.; 2017). The widespread haze events have frequently occurred in most regions of eastern China in recent years, and several studies have reported that the secondary inorganic salts, including sulfate, nitrate, and ammonium, were the majorities of the total aerosols in the urban and rural regions (Tao et al.; 2014; Wang et al.; 2016; Zhang et al.; 2012; Lai et al.; 2016; Zhang et al.; 2018). Therefore, besides the heavy emissions of SO$_2$ and NO$_2$, NH$_3$ emissions from the agriculture activities are also non-negligible.

China is one of the largest agricultural countries in the world. Even though the annual emissions budget of NH$_3$ decreased from 2006 to 2012, the emissions were still high and reached 9.7-12 Tg (Kang et al., 2016; Xu et al., 2016; Zhou et al., 2015), leading to high ambient NH$_3$ concentrations. These massive NH$_3$ levels significantly affect regional air quality and horizontal visibility. Firstly, the major PM$_{2.5}$ components, (NH$_4$)$_2$SO$_4$, (NH$_4$)$_3$H(SO$_4$)$_2$, NH$_4$HSO$_4$, and NH$_4$NO$_3$ were partially or fully produced from the neutralization of H$_2$SO$_4$ and HNO$_3$ by the reaction with NH$_3$ (Tanner et al.; 1981; Brost et al.; 1988; Quan et al.; 2014; Zhao et al.; 2013; Zhang et al.; 2014). Studies also showed that NH$_3$ improves the H$_2$SO$_4$ nucleation by 1-10 times (Benson et al.; 2011), and provides sufficient new particle to alter the number and size distributions. Thus, the NH$_3$ and its secondary product NH$_4^+$ play an important role in the formation of air pollution and haze days. Research has shown that approximately 80% of total anthropogenic NH$_3$ emissions derived from agricultural sources and livestock manure provided a greater contribution than synthetic fertilizer (Kang et al., 2016; Zhou et al., 2016). The Chinese government has undertaken several control strategies to reduce particulate pollution and its precursors, such as catalytic reduction systems in the power sector (Xia et al., 2016), measures to change coal to gas for residential life and heating (Ren et al., 2014), etc. Related observations have shown that the mass burdens of SO$_2$ and NO$_x$ have decreased distinctly in recent years (De Foy et al., 2016; Wang et al., 2015; Zheng et al., 2018). However, no specific measures for agricultural NH$_3$ emissions control have been implemented to date, and the total agricultural NH$_3$ emissions budget did not change substantially from 2010 to 2017 (Zheng et al., 2018).

In addition, accurate information on agricultural NH$_3$ emissions is also important for estimating the NH$_3$ mass burden and its environmental effect. There have been several studies focusing on NH$_3$ emissions...
from agricultural activities in China or East Asia. REAS (Regional Emission inventory in Asia) version 2 established an anthropogenic emissions inventory that included the source of agricultural NH$_3$ (fertilizer application and livestock) (Kurokawa et al.; 2013). This inventory, targeting years from 2000 to 2008, has a 0.25° × 0.25° spatial resolution with monthly variation. MASAGE_NH$_3$ (Magnitude and Seasonality of Agricultural Emissions model for NH$_3$) was used to develop a bottom-up NH$_3$ emissions inventory by using the adjoint of the GEOS-Chem chemical transport model (Paulot et al.; 2014). The inverse of the network data for NH$_4^+$ wet deposition fluxes from 2005-2008 was used to optimize the NH$_3$ emissions in China in this inventory. Fu et al. (2015) used the CMAQ (Community Multiscale Air Quality) model coupled to an agro-ecosystem, which could obtain hourly emissions features by online model calculation, to estimate NH$_3$ emissions in 2011 with high spatial and temporal resolution. These NH$_3$ emissions inventories provided very useful datasets for understanding the distribution features of the NH$_3$ mass burden in China. However, with population migration, economic growth, and the increased consumption of agricultural products, the spatial distribution and strength of agricultural NH$_3$ emissions has significantly changed in China during the last decade (Xu et al., 2017), so that reliable emissions information based on recent years is also necessary for estimating the NH$_3$ mass burden.

Previous studies have investigated the influence of NH$_3$ emissions on aerosol loading in several typical areas of China. Wu et al. (2008) conducted sensitivity studies to assess the impact of livestock-produced NH$_3$ emissions on PM$_{2.5}$ mass concentration in North China by using the MM5/CMAQ modeling system. The results showed that the livestock-produced NH$_3$ provided >20% contributions to nitrate and ammonium, but provided only a small contribution to sulfate. Wang et al. (2011) used the response surface modeling technique to estimate the contribution of NH$_3$ emissions in East China and found that total NH$_3$ emissions contributed 8-11% to PM$_{2.5}$ concentration, and the nonlinear effects were significant while the transition between NH$_3$ rich and poor conditions. Fu et al. (2017) and Zhao et al. (2017) also investigated the impact of NH$_3$ emissions on PM$_{2.5}$ in East China and the Hai River Basin. However, the related studies were few and focused mainly on local regions; furthermore, most of them generally used the brute-force sensitivity method to estimate the NH$_3$ impact based on the chemistry model, which reflected the change in particulate concentration with emissions reduction (Koo et al., 2009).

PKU-NH$_3$, a comprehensive high-resolution NH$_3$ emissions inventory based on the year 2015, was applied in this study to capture the agricultural NH$_3$ mass concentration in China, and the contribution to PM$_{2.5}$ particles was estimated with an RAMS-CMAQ air quality modeling system, coupled with the online
source tagged module ISAM. Compared with previous studies, this high-resolution agricultural NH$_3$
emissions inventory was more accurate and reflected the latest spatial and temporal distribution features
(Liu et al.; 2019). The major trace gases and aerosol species in 2015 were simulated by the modeling system
and evaluated by several observational data. The contribution to the pollutant concentrations was tagged
and quantified by RAMS-CMAQ-ISAM under the current scenario (Wang et al., 2009). Then, several brute-
force sensitivity tests were conducted to estimate the effect of reducing agricultural NH$_3$ emissions on the
PM$_{2.5}$ mass burden. The results from the source apportionment simulation and brute-force sensitivity tests
in January, April, July, and October are presented here, and the detailed features over seven major populated
areas of China (as shown in Figure 1) are discussed.

2. Methodology

The emissions inventory can be described as follows: First, the NH$_3$ emissions data in China were
provided by the PKU-NH$_3$ emissions inventory (Kang et al., 2016; Zhang et al., 2018). This inventory was
developed on the basis of previous studies (Huang et al., 2012) and improved the horizontal resolution and
accuracy. It was compiled at a 1 km $\times$ 1 km horizontal resolution, with monthly statistical data from 2015.
Some of the most uncertain parameters, the emission factors applied in this inventory, were enhanced by
considering as many native experiment results as possible, with ambient temperature, soil acidity, and
changes in other factors. In addition, this inventory not only included fertilizer and husbandry emissions
from agricultural activities but also collected the emissions data of farmland ecosystems, livestock waste,
biomass burning (forest and grassland fires, crop residue burning, and fuel wood combustion), and other
sources (excrement waste from rural populations, the chemical industry, waste disposal, NH$_3$ escape from
thermal power plants, and traffic sources). Second, the anthropogenic emissions of primary aerosols and
their precursors were obtained from the MIX Asian emission inventory (base year 2012), prepared by the
Model Inter-Comparison Study for Asia (MICS-ASIA III) (Lu et al., 2011; Lei et al., 2011). The
anthropogenic emissions sources of SO$_2$, NO$_x$, volatile organic compounds (VOCs), black carbon (BC),
organic carbon (OC), primary PM$_{2.5}$, and PM$_{10}$ were obtained from the monthly MIX inventory, with a 0.25°
$\times$ 0.25° spatial resolution. The REAS (Regional Emission Inventory in Asia; Version 2; Kurokawa et al.,
2013) and GFED (Global Fire Emissions Database; Version 3; van der Werf et al., 2010) were used to
provide the VOCs, and nitrogen oxides from flight exhaust, lightning, paint, wildfires, savanna burning,
and slash-and-burn agriculture.
The RAMS-CMAQ modeling system was applied to simulate the transformation and transport of pollutants in the atmosphere. The CMAQ regional air quality model (version 5.0.2) released by the US Environmental Protection Agency (Eder et al., 2009; Mathur et al., 2008) was a major component of the RAMS-CMAQ modeling system. In this model, the CB05 (version CB05tucl) chemical mechanism (Whitten, 2010) and the sixth-generation CMAQ aerosol model (AERO6) were used to treat the gas-phase chemical mechanism and the formation and dynamic processes of aerosols. The ISORROPIA model (version 2.1) (Fountoukis and Nenes, 2007) was used to describe the thermodynamic equilibrium of gas-particle transformation. The highly versatile RAMS numerical model, which can well capture the boundary layer and the underlying surface, was applied to provide the meteorological fields for CMAQ (Cotton et al., 2003). The European Centre for Medium-Range Weather Forecasts reanalysis datasets (1° × 1° spatial resolution) were used to supply the background fields and sea surface temperatures. The model domain (Figure 1) was 6654 km × 5440 km, with 64 km² fixed-grid cells, and a rotated polar stereographic map projection covering the entire mainland of China and its surrounding regions was used. The model had 15 vertical layers, and half of them were located in the lowest 2 km to provide a more precise simulation of the atmospheric boundary layer. Several previous studies have demonstrated that the modeling system performs well when simulating the spatial and temporal distribution of China’s major aerosol components (Han et al., 2013, 2014, 2016).

The ISAM is a flexible and efficient online source apportionment implementation, which was used to track multiple pollutants emitted from different geographic regions and source types. Compared with its previous version TSSA (Tagged Species Source Apportionment), the processes of tracking tagged tracer transport and precursor reactions were optimized for balancing the computational requirements and reliable representation of the physical and chemical evolution. To reduce the nonlinear effect during phase transformation and relative chemical interactions, a standalone subroutine “wrapper” approach was applied to the ISAM model to apportion the secondary PM species and their precursor gases during the thermodynamic equilibrium simulation; a hybrid approach, which employed the LU decomposition triangular matrices (Yang et al., 1997), was also developed for describing the gas-phase chemical interactions. In this study, ISAM was coupled with RAMS-CMAQ and was set to trace the transport and chemical reactions of NH₃ from fertilizer and husbandry emissions sectors to quantitatively estimate the contribution of agricultural NH₃ emissions to the PM₂.₅ mass concentration in China.
3. Model evaluation

To evaluate the model performances, several observation data were compared with the simulation results. The meteorological factors are important to capture the formation processes and transport of secondary aerosols. Thus, in this paper, the observed meteorological data from surface stations of the Chinese National Meteorological Center are collected to evaluate the performance of the model. The detail information is described in Appendix A. Furthermore, the observed SO$_2$, NO$_2$, and PM$_{2.5}$ released from the Ministry of Environmental Protection of China were applied to evaluate the modeled mass concentration of these pollutants. The observation data at 416 stations, located in 101 model grids (distributed in Beijing, Tianjin, Hebei, Shandong, Shanxi, Henan, Jiangsu, and Anhui), were collected, and the values in same grid were averaged. The scatter plots of comparison are shown in Figure 2, and the statistical parameters between the observations and simulations are listed in Table 1. It can be seen that most of the scatter points broadly gather around the 1:1 solid line. The correlation coefficients in this table are all higher than 0.5, which indicates that the model can capture the regional variation in the measurements. The standard deviations between the observations and simulations were similar in most cases, except for SO$_2$ in January. The largest deviation of the modeled mean, which was higher than that of the observation, was also between the observed and modeled SO$_2$ in January. However, the correlation coefficients reached 0.71 in January, and the performance of the model in other months was relatively good, as shown in Table 1. It can be deduced that the obvious deviation may be a systemic underestimation due to the lack of emission intensity in this month.

The horizontal distributions of modeled monthly NH$_3$ mass concentration in January, April, July, and October in 2015 are shown in Figure 3. Pan et al. (2018) provided the distributions of satellite NH$_3$ total column distribution and the surface NH$_3$ concentrations at several observation sites (as shown in Figure 1 in the aforementioned study). As shown from their results, the highest mass burden was concentrated mainly in the North China Plain (NCP), Central China (CNC), the Yangtz River Delta (YRD), and the Sichan Basin (SCB). The simulation results in this study broadly reflected these distribution features. The NH$_3$ concentrations in these regions reached 10-25 μg m$^{-3}$ in Pan et al. (2018), which also coincided well with the simulation results. However, some obvious deviations appeared in the eastern part of Gansu province. The modeled NH$_3$ in these regions was slightly higher than that of the observations in Pan et al. (2018). Zhang et al. (2018) also showed the NH$_3$ mass concentration in four seasons over China from simulation (horizontal distribution) and ground-based measurements (point values) in Figure 9 of their
study. Aside from the regions mentioned in Pan et al. (2018), the high mass burden of NH$_3$ also appeared in the NEC, as shown by both simulation and observation results in Zhang et al. (2018). Generally, this distribution feature should be reasonable because the Three River Plain located in NEC is an important agriculture base in China, and the NH$_3$ emissions in this region can be strong during spring and summer. The simulation results in this study also supported the seasonal variation of the NH$_3$ mass burden shown in Zhang et al. (2018), which was higher in summer and lower in winter, and the magnitudes of the two were close. Thus, it can be seen that the NH$_3$ concentration modeled by RAMS-CMAQ was reliable and can be applied to the analysis in this study.

4. Results and discussions

The horizontal distributions of modeled monthly PM$_{2.5}$ mass concentrations in January, April, July, and October 2015 are shown in Figure 4. Over the eastern part of China, the heavy PM$_{2.5}$ pollution occurred in January, and the relatively better air quality appeared in July. The large PM$_{2.5}$ mass burden, exceeding 200 µg m$^{-3}$ in January, was mainly concentrated in the NCP, the Yangtze River Valley of CNC, and the SCB, which broadly coincided with the regions covered by a high mass burden of NH$_3$, as shown in Figure 3. In addition, the PM$_{2.5}$ mass burden (50-150 µg m$^{-3}$) was obviously lower in July than in the other months. Since NH$_3$ concerns mainly with secondary inorganic aerosols: sulfate, nitrate, and ammonium (SNA) formation, the analysis hereafter will mainly focus on the SNA. Figure 5 presents the modeled monthly SNA mass concentrations in January, April, July, and October 2015. The mass loading of SNA generally contributed 40-60% of the total PM$_{2.5}$ in the eastern part of China, which was comparable with previous studies (Cao et al., 2017; Chen et al., 2016; Lai et al., 2016; Wang et al., 2016). The distribution pattern and seasonal variation of SNA also followed the features of PM$_{2.5}$, and the high mass concentration of SNA exceeded 100 µg m$^{-3}$ in January.

Then, the contributions of NH$_3$ from multiple agricultural emissions (including fertilizer, husbandry, farmland ecosystems, livestock waste, crop residue burning, and excrement waste from rural populations) to aerosols were calculated using RAMS-CMAQ-ISAM; the monthly average contribution percentage of total agriculture activities (Tagr) in January, April, July, and October are shown in Figure 6. Generally, Tagr NH$_3$ provided a 30-50% contribution to the SNA over most of eastern China in January and October, and a 20-40% contribution in April and July. The relatively lower value appeared mainly in April. The regional and annual average percent contributions of Tagr to sulfate, nitrate, ammonium, SNA, and PM$_{2.5}$ are shown...
in Table 2. As shown in this table, Tagr NH$_3$ provided the major contribution to ammonium, which reached 90%, and a relatively small contribution to nitrate mass burden, which was 5-10%. However, the contribution to sulfate was tiny, and the main reason is that there are various methods of sulfate formation from SO$_2$ other than neutralization by NH$_3$, such as oxidation by H$_2$O$_2$, O$_3$, or peroxyacetic acid.

Tagr NH$_3$ provided a 28-37% contribution to the SNA mass concentration, and the spatial features of the Tagr NH$_3$ contribution to the PM$_{2.5}$ mass concentration were similar to the features of SNA. Generally, it provided an approximately 14-18% contribution to the total PM$_{2.5}$ mass concentration in these places, and the largest annual average contribution appeared in CNC (17.5%).

In addition, the brute-force method (zero-out sensitivity test), which can capture the effect of emissions changes on aerosol mass burden, was applied to investigate the impact of the removal of Tagr NH$_3$ emissions. Unlike online source apportionment, the brute-force method mainly reflects the disparity of the chemical balance caused by the emissions change, which could significantly alter secondary pollutant formation. Several sensitivity tests were conducted, and the results are shown in Figure 7 and Table 3.

Figure 7 presents the mass burden variation of SNA associated with Tagr NH$_3$ removal. From Figure 7, it can be seen that the reduction patterns of the aerosol broadly followed those of their mass burden. The significant reduction of SNA mainly appeared in the high concentration regions, and generally exceeded 25 µg m$^{-3}$. Table 3 shows the percentage of the variation of sulfate, nitrate, ammonium, SNA, and PM$_{2.5}$. Compared with Table 2, it can be seen that the variation percent of SNA and PM$_{2.5}$, which reached 40-51% and 23-35%, respectively, were approximately two times higher than those of the contribution percent, and this significant distinction was mainly caused by the variation of nitrate: the contribution of Tagr NH$_3$ to nitrate was generally below 10%, as shown in Table 2, but the reduction of nitrate associated with removing Tagr NH$_3$ emissions could exceed 95%, as shown in Table 3. This difference between the results of ISAM and brute-force was expected as a result of high nonlinearity in the NO$_x$ chemistry. The nitrate formation could become more sensitive when the “rich NH$_3$” environment shifts to a “poor NH$_3$” environment, which means the decrease of the nitrate mass burden would accelerate with the NH$_3$ emissions reduction. Therefore, it can be deduced that the contribution of NH$_3$ to nitrate should be significantly lower under a “rich NH$_3$” environment than that under a “poor NH$_3$” environment. A similar phenomenon was also reported in previous studies (Wang et al., 2011; Xu et al., 2016). To prove this point, further brute-force sensitivity tests were conducted. The variations of sulfate, nitrate, ammonium, and SNA mass burden associated with the reduction of NH$_3$ emissions (80%, 50%, 40%, 30%, 20%, and 10% TA NH$_3$ emission,
respectively) is shown in Figure 8. It can be seen that the decrease in nitrate mass concentration was more rapid than that of ammonium, and the trend became slightly faster with the reduction of NH$_3$ emissions (signifying the transition from a “rich NH$_3$” to a “poor NH$_3$” environment) in the regions with a high mass burden of NH$_3$: BTH, NEC, SCB, and SDP. Furthermore, this acceleration stopped while 20% of NH$_3$ emissions remained.

5. Conclusions

The emission budget of agriculture NH$_3$ was huge and played an important role on the regional particle pollution in China. As a precursor of the secondary aerosol, reasonably estimate the nonlinear processes of secondary aerosol formation should be the key point for capturing the contribution of NH$_3$ to particle pollution. In this study, the air quality modeling system RAMS-CMAQ was applied to simulate spatial-temporal distribution of trace gas and aerosols in 2015. In addition, the PKU-NH$_3$ emission inventory which compiled on 1km $\times$ 1km horizontal resolution with monthly based data was applied to accurately capture the agriculture NH$_3$ emission features in China. Then, the source apportionment module ISAM was coupled into this modeling system to quantitatively estimate the contribution of agriculture NH$_3$ to PM$_{2.5}$ mass burden. The brute-force sensitivity tests were also conducted for discussing the impact of the agriculture NH$_3$ emission reduction. The meteorological factors and mass concentration of NH$_3$, SO$_2$, NO$_2$, and PM$_{2.5}$ from simulation were evaluated and showed well agreement with the observation data. Some interesting results were explored and summarized as follow:

1. The high mass burden of NH$_3$ could exceeded 10 $\mu$g m$^{-3}$, and mainly appeared in the NCP, CNC, YRD, and SCB. These regions were highly coincidence with the regions that heavy particle pollution covered in China. Therefore, it can be deduced that the influence of agriculture NH$_3$ on the PM$_{2.5}$ mass concentration should be significant.

2. The results from ISAM simulation shows that the Tagr NH$_3$ provided 14-18% contribution to the PM$_{2.5}$ in the most part of east China, and the largest annual average contribution appeared in CNC (17.5%). Specific to the SNA components, the annually and regional average contribution of Tagr NH$_3$ to ammonium, nitrate, sulfate was 87.6%, 10.1%, and 2.2% in China. The agriculture NH$_3$ emission provided major contribution to the ammonium formation, but tiny contribution to the sulfate due to the various other ways of sulfate formation.

3. The brute-force sensitive test could reflect the effect of changing Tagr NH$_3$ emission on PM$_{2.5}$ mass
burden. The results indicated that the reduction percent of PM$_{2.5}$ mass burden due to removal Tagr NH$_3$ emission could reach 23-35% in the most part of east China, which was approximately two times higher than the contribution. The reduction percent of nitrate that reached exceed 95% was the main reason caused this significant different. In addition, the further analysis proved that the ambient NH$_3$ mass burden could obviously affects its contribution to the SNA formation: the NH$_3$ contribution to nitrate should be lower under "rich NH$_3$" and higher under "poor NH$_3$". Therefore, the influence of NH$_3$ would enhance with the decreasing of ambient NH$_3$ mass concentration.

It is suggested that the influence of NH$_3$ on the PM$_{2.5}$ mass burden is complex because of the nonlinearity of secondary aerosol formation. Significant deviation exists between the results from ISAM and the brute-force method; therefore, these two kinds of results should be distinguished and applied to explain different issues: the contribution under the current scenario and the effect due to emissions reduction, respectively. The modeling system is a versatile tool that allows us to investigate this valuable information to choose more efficient strategies for reducing the impact of agricultural NH$_3$ and improving air quality.

**Acknowledgments**

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA19040204), and the National Natural Science Foundation of China (41830109).
Appendix A

The daily average temperature, relative humidity, wind speed and maximum wind direction in January and July 2015 were compared with the surface shared data from the Chinese National Meteorological Center (http://data.cma.cn/) in 9 stations. The comparison results are shown in Figure A1-A4. These stations are located in the East China where the high NH$_3$ emission regions. Generally, the modeled temperature was in good agreement with the observed data, and can reflect the large fluctuation and seasonal variation of relative humidity as well, except that some of the extreme high or low values appeared abruptly. As shown in Figure A3, most of the daily average wind speed was lower than 3 m s$^{-1}$ at Zhengzhou, Jinan, Miyun, and Baoding station (all located in the North China Plain), which means the diffusion condition was not good due to the stable weather. Otherwise, the relatively strong wind appeared at Nanjing, Chaoyang, Nanning, and Tianjin. The modeled wind speed generally reproduced all these features. The direct comparison between observed and modeled wind direction which can be easily influenced by the surrounding surface features is difficult. Nevertheless, the prevailing wind direction in different seasons can be captured by the simulation results for all stations.
Reference

Babar, Z. B.; Park, J.; Lim, H. Influence of NH$_3$ on secondary organic aerosols from the ozonolysis and photooxidation of α-pinene in a flow reactor. *Atmos. Environ.* 2017, 164, 71-84, DOI: 10.1016/j.atmosenv.2017.05.034

Ball, S. M.; Hanson, D. R.; Eisele, F. L.; McMurry, P. H. Laboratory studies of particle nucleation: Initial results for H$_2$SO$_4$, H$_2$O, and NH$_3$ vapors. *J. Geophys. Res.* 1999, 104, 23709-23718, DOI: 10.1029/1999JD900411

Benson, D. R.; Yu, J. H.; Markovich, A.; Lee, S. H. Ternary homogeneous nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O under conditions relevant to the lower troposphere. *Atmos. Chem. Phys.* 2011, 11, 4755-4766, DOI: 10.5194/acp-11-4755-2011

Brost, R. A.; Delany, A. C.; Huebert, B. J. Numerical modeling of concentrations and fluxes of HNO$_3$, NH$_3$, and NH$_4$NO$_3$ near the ground. *J. Geophys. Res.* 1988, 93, 7137-7152, DOI: 10.1029/JD093iD06p07137

Cao, Z.; Zhou, X.; Ma, Y.; Wang, L.; Wu, R.; Chen, B.; Wang, W. The concentrations, formations, relationships and modeling of sulfate, nitrate and ammonium (SNA) aerosols over China. *Aerosol Air Qual. Res.* 2017, 17, 84-97, DOI: 10.4209/aaqr.2016.01.0020

Chen, Y.; Schleicher, N.; Cen, K.; Liu, X.; Yu, Y.; Zibat, V.; Dietze, V.; Fricker, M.; Kaminski, U.; Chen, Y.; Chai, F.; Norra, S. Evaluation of impact factors on PM$_{2.5}$ based on long-term chemical components analyses in the megacity Beijing, China. *Chemosphere* 2016, 155, 234-242, DOI: 10.1016/j.chemosphere.2016.04.052

Chang, J. The role of H$_2$O and NH$_3$ on the formation of NH$_4$NO$_3$ aerosol particles and De-NOx under the corona discharge treatment of combustion flue gases. *J. Aerosol Sci.* 1989, 20, 1087-1090, DOI: 10.1016/0021-8502(89)90768-4

Cotton, W.; Piekle, R.; Walko, G.; Liston, G.; Tremback, C.; Jiang, H.; McAnelly, R.; Harrington, J.; Nicholls, M.; Carrio, G., McFadden, J. RAMS 2001: current status and future directions, Meteorol. *Atmos. Phys.* 2003, 82, 5-29, DOI: 10.1007/s00703-001-0584-9

DeFoy, B.; Lu, Z.; and Streets, D. G. Satellite NO$_2$ retrievals suggest China has exceeded its NO$_x$ reduction goals from the twelfth five-year plan. *Sci. Rep.* 2016, 6, 35912, DOI: 10.1038/srep35912

Eder, B.; Yu S. A performance evaluation of the 2004 release of Models-3 CMAQ. *Atmos. Environ.* 2006, 40, 4811-4824, DOI: 10.1016/j.atmosenv.2005.08.045

Fountoukis, C.; Nenes, A. ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K$^+$-Ca$^{2+}$-Mg$^{2+}$-NH$_4^+$-Na$^+$-SO$_4^{2-}$-NO$_3^-$-Cl$^-$-$\mathrm{H}_2$O aerosols. *Atmos. Chem. Phys.* 2007, 7, 4639-4659, DOI: 10.5194/acp-7-4639-2007

Fu, X.; Wang, S.; Xing, J.; Zhang, X.; Wang, T.; Hao, J. Increasing Ammonia Concentrations Reduce the Effectiveness of Particle Pollution Control Achieved via SO$_2$ and NO$_x$ Emissions Reduction in East China. *Environ. Sci. Technol.* 2017, 4, 221-227, DOI: 10.1021/acs.estlett.7b00143

Huang, X.; Song, Y.; Li, J.; Huo, Q.; Cai, X.; Zhu, T.; Hu, M.; Zhang, H. A high-resolution ammonia emission inventory in China. *Global Biogeochem. Cy.* 2012, 26, 1030-1044, DOI: 10.1029/2011GB004161

Kang, Y.; Liu, M.; Song, Y.; Huang, X.; Yao, H.; Cai, X.; Zhang, H.; Kang, L.; Liu, X.; Yan, X.; He, H.; Zhang, Q.; Shao, M.; Zhu, T. High-resolution ammonia emissions inventories in China from 1980 to 2012. *Atmos. Chem. Phys.* 2016, 16, 2043-2058, DOI: 10.5194/acpd-15-26959-2015

Koo, B.; Wilson, G.; Morris, R.; Dunker, A.; Yarwood, G. Comparison of Source Apportionment and Sensitivity Analysis in a Particulate Matter Air Quality Model. *Environ. Sci. Technol.* 2009, 43, 6669-6675

Kurokawa, J.; Ohara, T.; Morikawa, T.; Hanayama, S.; Maenhout, G.; Fukui, T.; Kawashima, K.; Akimoto, H. Emissions of air pollutants and greenhouse gases over Asian regions during 2000-2008: Regional Emission inventory in ASIA (REAS) version 2. *Atmos. Chem. Phys.* 2013, 13, 11019-11058, DOI: 10.5194/acp-13-11019-2013

Kulmala, M.; Korhonen, P.; Napari, I.; Karlsson, A.; Berresheim, H.; O’Dowd, C. D. Aerosol formation during PARFORCE: Ternary nucleation of H$_2$SO$_4$, NH$_3$, and H$_2$O. *J. Geophys. Res.* 2002, 107, DOI: 10.1029/2001JD000900.

Lai, S.; Zhao, Y.; Ding, A.; Zhang, Y.; Song, T.; Zheng, J.; Ho, K. F.; Lee, S.; Zhong, L. Characterization of PM$_{2.5}$ and the major chemical components during a 1-year campaign in rural Guangzhou. *Southern China, Atmos. Res.* 2016, 167,
Wang, S.; Xing, J.; Jang, C.; Zhu, Y.; Fu, J.; Hao, J. Impact Assessment of Ammonia Emissions on Inorganic Aerosols in East China Using Response Surface Modeling Technique. *Environ. Sci. Technol.* 2011, 45, 9293-9300, DOI: 10.1021/es2022347

Wang, Z.; Chien, C.; Tonnesen, G. Development of a tagged species source apportionment algorithm to characterize three-dimensional transport and transformation of precursors and secondary pollutants. *J. Geophys. Res.* 2009, 114, DOI: 10.1029/2008JD010846;

Whitten, G.; Heo, G.; Kimura, Y.; McDonald-Buller, E.; Allen, D.; Carter, W. P.; Yarwood, G. A new condensed toluene mechanism for Carbon Bond: CB05-TU. *Atmos. Environ.* 2010, 44, 5346-5355, DOI: 10.1016/j.atmosenv.2009.12.029

Wu, S.; Hu, J.; Zhang, Y.; Aneja, V. P. Modeling atmospheric transport and fate of ammonia in North Carolina-Part II: Effect of ammonia emissions on fine particulate matter formation. *Atmos. Environ.* 2008, 42, 3437-3451, DOI: 10.1016/j.atmosenv.2007.04.022

Xia, Y.; Zhao, Y.; and Nielsen, C. P. Benefits of China’s efforts in gaseous pollutant control indicated by the bottom-up emissions and satellite observations 2000-2014. *Atmos. Environ.* 2016, 136, 43-53, DOI: 10.1016/j.atmosenv.2016.04.013

Xu, P.; Liao, Y. J.; Lin, Y. H.; Zhao, C. X.; Yan, C. H.; Cao, M. N.; Wang, G. S.; Luan, S. J. High-resolution inventory of ammonia emissions from agricultural fertilizer in China from 1978 to 2008. *Atmos. Chem. Phys.* 2016, 16, 1207-1218, DOI: 10.5194/acp-16-25299-2015

Yang, Y.; Wilkinson, J.; Russell. A. Fast, Direct Sensitivity Analysis of Multi-Dimensional Photochemical Models. *Environ. Sci. Technol.* 1997, 31, 2859-2868, DOI: 10.1021/es970117w

Zhao, Z.; Bai, Z.; Winiwarter, W.; Kiesewetter, G.; Heyes, C.; Ma, L. Mitigating ammonia emission from agriculture reduces PM$_{2.5}$ pollution in the Hai River Basin in China. *Sci. Total Environ.* 2017, 609, 1152-1160, DOI: 10.1016/j.scitotenv.2017.07.240

Zhao, X. J.; Zhao, P. S.; Xu, J.; Meng, W.; Pu, W. W.; Dong, F.; He, D.; Shi, Q. F. Analysis of a winter regional haze event and Its formation mechanism in the North China Plain. *Atmos. Chem. Phys.* 2013, 13, 5685–5696, DOI: 10.5194/acp-13-5685-2013

Zhong, J. K.; Sun, Y.; Liu, Z. R.; Ji, D. S.; Hu, B.; Liu, Q.; Wang, Y. S. Characterization of submicron aerosols during a month of serious pollution in Beijing, 2013. *Atmos. Chem. Phys.* 2014, 14, 2887–2903, DOI: 10.5194/acp-14-2887-2014

Zhang, K.; Ma, Y.; Xin, J.; Liu, Z.; Ma, Y.; Gao, D.; Wu, J.; Zhang, W.; Wang, Y.; Shen, P. The aerosol optical properties and PM$_{2.5}$ components over the world's largest industrial zone in Tangshan, North China. *Atmos. Res.* 2018, 201, 226-234, DOI: 10.1016/j.atmosres.2017.10.025

Zhang, L.; Chen, Y.; Zhao, Y.; Henze, D.; Zhu, L.; Song, Y.; Paulot, F.; Liu, X.; Pan, Y.; Lin, Y.; Huang, B. Agricultural ammonia emissions in China: reconciling bottom-up and top-down estimates. *Atmos. Chem. Phys.* 2018, 18, 339-355, DOI: 10.5194/acp-18-339-2018

Pan, Y.; Tian, S.; Zhao, Y.; Zhang, L.; Zhu, X.; Gao, J.; Huang, W.; Zhou, Y.; Song, Y.; Zhang, Q.; Wang, Y. Identifying ammonia hotspots in China using a national observation network. *Environ. Sci. Technol.* 2018, doi: 10.1021/acs.est.7b05235, DOI: 10.1021/acs.est.7b05235

Zhang, X.; Wang, Y.; Niu, Y.; Zhang, X.; Gong, S.; Zhang, Y.; Sun, J. Atmospheric aerosol compositions in China: spatial/temporal variability, chemical signature, regional haze distribution and comparisons with global aerosols. *Atmos. Chem. Phys.* 2012, 12, 779-799, DOI: 10.5194/acp-12-779-2012

Zhong, F.; Ciais, P.; Hayashi, K.; Galloway, J.; Kim, D.; Yang, J.; Li, S.; Liu, B.; Shang, Z.; Gao, S. Re-estimating NH$_3$ emissions from Chinese cropland by a new nonlinear model. *Environ. Sci. Technol.* 2016, 50, 564-572, DOI: 10.1021/acs.est.5b03156
Zhou, Y.; Cheng, S.; Lang, J.; Chen, D.; Zhao, B.; Liu, C.; Xu, R.; Li, T. A comprehensive ammonia emission inventory with high-resolution and its evaluation in the Beijing–Tianjin–Hebei (BTH) region, China. *Atmos. Environ.* 2015, 106, 305-317, DOI: 10.1016/j.atmosenv.2015.01.069

Xu, P.; Koloutsou-Vakakis, S.; Rood, M.; Luan, S. Projections of NH$_3$ emissions from manure generated by livestock production in China to 2030 under six mitigation scenarios. *Sci. Total Environ.* 2017, 31, 78-86, DOI: 10.1016/j.scitotenv.2017.06.258

Zheng, B.; Tong, D.; Li, M.; Liu, F.; Hong, C.; Geng, G.; Li, H.; Li, X.; Peng, L.; Qi, J.; Yan, L.; Zhang, Y.; Zhao, H.; Zheng, Y.; He, K.; Zhang, Q. Trends in China’s anthropogenic emissions since 2010 as the consequence of clean air actions. *Atmos. Chem. Phys.* 2018, 18, 14095-14111, DOI: 10.5194/acp-18-14095-2018

Kurokawa, J.; Ohara, T.; Morikawa, T.; Hanayama, S.; Janssens-Maenhout, G.; Fukui, T.; Kawashima, K.; Akimoto, H. Emissions of air pollutants and greenhouse gases over Asian regions during 2000-2008: Regional Emission inventory in ASia (REAS) version 2. *Atmos. Chem. Phys.* 2013, 13, 11019-11058, DOI: 10.5194/acp-13-11019-2013

Fu, X.; Wang, S.; Ran, L.; Pleim, J.; Cooter, E.; Bash, J.; Benson, V.; Hao, J. Estimating NH$_3$ emissions from agricultural fertilizer application in China using the bi-directional CMAQ model coupled to an agro-ecosystem model. *Atmos. Chem. Phys.* 2015, 15, 6637-6649, DOI: 10.5194/acp-15-6637-2015
Figure 1. Model domain used in this study and the geographic locations of Northeast China, Beijing-Tianjin-Hebei, Shandong Province, Yangtze River Delta, Central China, Sichuan Basin, and Pearl River Delta. The location of observation data was also shown in the model domain.
Figure 2. The scatter plots between the modeled and the observed monthly SO$_2$, NO$_2$, and PM$_{2.5}$ in 2015. The solid lines are 1:1 and the dashed lines are 2:1 or 1:2.
Figure 3. The horizontal distributions of the modeled monthly NH$_3$ mass concentration in January, April, July, and October in 2015.
Figure 4. The horizontal distributions of the modeled monthly PM$_{2.5}$ mass concentration in January, April, July, and October in 2015.
Figure 5. The horizontal distributions of the modeled monthly SNA mass concentration in January, April, July, and October in 2015.
Figure 6. The horizontal distributions of the contribution percentage of NH$_3$ emissions to SNA mass concentration (%) in January and July.
Figure 7. The horizontal distributions of SNA mass concentration (μg m$^{-3}$) variation associated with agriculture NH$_3$ removal in January and July.
Figure 8. The variation (%) of sulfate, nitrate, ammonium, and SNA mass burden associated with the NH$_3$ emission reduction (%).
Figure A1. Observed and modeled daily average temperatures (K) in January and July 2015.
Figure A2. Same as Figure A1 but for relative humidity (%)
Figure A3. Same as Figure A1 but for wind speed (m s$^{-1}$)
Figure A4.Same as Figure A1 but for daily maximum wind direction (degree)
Table 1. Statistical summary of the comparisons of the monthly average PM$_{2.5}$ between simulation and observation

|  | $N^a$ | $M^b$ | $O^c$ | $\sigma_m^d$ | $\sigma_o^e$ | $R^f$ | $FB^g$ | $NMB^h$ |
|---|---|---|---|---|---|---|---|---|
| **PM$_{2.5}$** | | | | | | | | |
| Jan | 101 | 128.3 | 100.1 | 34.9 | 28.3 | 0.60 | 0.2 | 28.2 |
| Apr | 101 | 74.9 | 58.4 | 15.4 | 15.2 | 0.67 | 0.3 | 28.3 |
| Jul | 100 | 58.6 | 50.3 | 17.6 | 16.0 | 0.52 | 0.1 | 16.6 |
| Oct | 100 | 81.0 | 54.8 | 23.1 | 19.7 | 0.52 | 0.4 | 47.9 |
| **NO$_2$** | | | | | | | | |
| Jan | 101 | 42.5 | 51.7 | 19.4 | 16.2 | 0.65 | -0.2 | -17.8 |
| Apr | 101 | 27.8 | 35.0 | 15.7 | 11.5 | 0.57 | -0.3 | -20.5 |
| Jul | 100 | 24.3 | 26.5 | 13.2 | 9.2 | 0.50 | -0.2 | -8.4 |
| Oct | 100 | 33.2 | 42.0 | 16.4 | 14.9 | 0.53 | -0.3 | -20.9 |
| **SO$_2$** | | | | | | | | |
| Jan | 101 | 39.9 | 69.1 | 18.7 | 42.4 | 0.71 | -0.5 | -42.2 |
| Apr | 101 | 22.9 | 31.2 | 10.1 | 12.7 | 0.51 | -0.3 | -26.6 |
| Jul | 100 | 17.8 | 20.3 | 10.9 | 10.4 | 0.46 | -0.2 | -12.5 |
| Oct | 100 | 27.0 | 31.5 | 12.3 | 16.7 | 0.63 | -0.1 | -14.4 |

$^a$ Number of samples  
$^b$ Total mean of observation  
$^c$ Total mean of simulation  
$^d$ Standard deviation of observation  
$^e$ Standard deviation of simulation  
$^f$ Correlation coefficient between daily observation and simulation  
$^g$ Fractional Bias  
$^h$ Normalized Mean Bias
Table 2. The regional percent (%) of T contribution to sulfate, nitrate, ammonium, and SNA mass concentration.

| Region | Sulfate | Nitrate | Ammonium | SNA | PM$_{2.5}$ |
|--------|---------|---------|----------|-----|------------|
| BTH    | 1.1     | 8.0     | 83.3     | 31.9| 15.5       |
| NEC    | 1.0     | 5.6     | 83.7     | 28.1| 14.3       |
| YRD    | 1.0     | 7.4     | 85.7     | 29.2| 15.3       |
| PRD    | 0.9     | 5.8     | 90.6     | 33.5| 14.2       |
| SCB    | 0.7     | 5.1     | 93.9     | 32.6| 13.0       |
| CNC    | 0.9     | 6.0     | 92.8     | 36.6| 17.5       |
| SDP    | 0.9     | 7.1     | 80.5     | 30.1| 15.1       |
| China  | 2.2     | 10.1    | 87.6     | 29.0| 16.0       |
Table 3. The variation percent (%) of sulfate, nitrate, ammonium, and SNA mass concentration associated with agriculture NH$_3$ removal.

| Region | Sulfate | Nitrate | Ammonium | SNA | PM$_{2.5}$ |
|--------|---------|---------|----------|-----|-----------|
| BTH    | 0.7     | 99.8    | 94.7     | 49.4| 34.4      |
| NEC    | 0.7     | 96.9    | 92.5     | 48.9| 31.1      |
| YRD    | 5.0     | 99.2    | 96.1     | 48.8| 31.6      |
| PRD    | 2.0     | 99.2    | 97.2     | 40.3| 23.4      |
| SCB    | 2.6     | 96.7    | 85.9     | 49.8| 25.9      |
| CNC    | 1.9     | 99.2    | 92.3     | 50.9| 32.3      |
| SDP    | 2.7     | 99.5    | 93.4     | 46.6| 34.0      |
| China  | 1.6     | 98.8    | 93.8     | 45.7| 25.2      |