High efficiency of livestock ammonia emission controls on alleviating particulate nitrate during a severe winter haze episode in northern China

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Abstract

Although nitrogen oxide (NO_x) emission controls have been implemented for several years, northern China is still facing high particulate nitrate (NO_3^-) pollution during severe haze events in winter. In this study, the thermodynamic equilibrium model (ISORROPIA-II) and the Weather Research and Forecast model coupled chemistry (WRF-Chem) were used to study the efficiency of NH_3 emission controls on alleviating particulate NO_3^- during a severe winter haze episode. We found that particulate NO_3^- formation in extremely high pollution is almost NH_3-limited, not NO_x-limited often happened in the other days. The improvements in manure management of livestock husbandry could reduce 40% of total NH_3 emissions (currently 100 kiloton per a month) in winter of northern China. Consequently, particulate NO_3^- was reduced by approximately 40% (averagely from 40.8 to 25.7 $\mu g/m^3$). Our results indicate that reducing livestock NH_3 emissions would be highly effective to reduce particulate NO_3^- during severe winter haze events.

1 Introduction

In northern China (including Beijing, Tianjin, Hebei, Shandong, Shanxi and Henan), severe haze pollution events occur frequently during wintertime, with the concentration of $PM_{2.5}$ (particles with an aerodynamic diameter less than 2.5 μm) reaching hundreds of micrograms per cubic meter and SIA (secondary inorganic aerosol) accounting for more than 50% of $PM_{2.5}$ (Zheng et al., 2016;Tan et al., 2018). To mitigate fine particle pollution, the Chinese government has been taking strong measures to control SO_2 emissions (http://www.gov.cn/zwgk/2011-12/20/content_2024895.htm). Since 2007, SO_2 emissions have been reduced by 75% in China (Li et al., 2017). Consequently, the particulate sulfate concentration has also been declining continuously in the past decade (Geng et al., 2017).

Although NO_x emissions in 48 Chinese cities decreased by 21% from 2011 to 2015 (Liu et al., 2017a), unfortunately, no obvious decreasing trend for particulate NO_3^- had been observed in northern China during recent years (Zhang et al., 2015). In October 2015, a severe haze episode was reported in North China Plain (NCP), with the hourly peak concentration of particulate NO_3^- exceeding 70 $\mu g/m^3$ (Zhang et al., 2018b). Even in November 2018, during a heavy haze episode in northern China, the hourly peak concentration of $PM_{2.5}$ still exceeded 289 $\mu g/m^3$, of which particulate NO_3^- accounted for 30% (http://www.mee.gov.cn/xxgk2018/xxgk/xxgk15/201811/t20181116_674022.html).

Another way to alleviate the particulate NO_3^- pollution is to control NH_3 emissions. Previous studies were performed to demonstrate the necessity of NH_3 emissions abatement in reducing $PM_{2.5}$ concentrations in the United States (Pinder et al., 2007;Tsimpidi et al., 2007;Pinder et al., 2008;Wu et al., 2016) and Europe (de Meij et al., 2009;Bessagnet et al., 2014;Backes et al., 2016). Recently, a feature article pointed out that NH_3 could be key to limiting particulate pollution (Plautz, 2018). In contrast with low particulate matter pollution levels in the United States and Europe, what we are facing in northern China is the extremely high particulate NO_3^- pollution especially happened in severe winter haze

events.

Although Fu et al. (2017) proposed that the NH_3 emission controls are urgently required in China, the effectiveness of NH_3 emissions mitigation to alleviate the particulate NO_3^- peaks during severe winter haze episodes was seldom reported. Only Guo et al. (2018b) used a thermodynamic model to estimate the sensitivity of particulate NO_3^- to TA (sum of ammonia and ammonium) during one winter haze episode in Beijing. In their study, the atmospheric chemistry simulations based on NH_3 emission controls scenario were lacking to demonstrate the regional effects.

To alleviate severe particulate NO_3^- pollution in northern China is urgent, the study on the effectiveness by NH_3 emission controls is necessary. In this study, we firstly compile a comprehensive NH_3 emission inventory for northern China in winter of 2015, and estimate the NH_3 emission reductions by improving manure management. Then, the ISORROPIA-II and WRF-Chem models are used to investigate the effectiveness of NH_3 emission reductions on alleviating particulate NO_3^- during a severe haze episode. The molar ratio based on observations is used to explore the efficiency of particulate NO_3^- reductions during the severe haze conditions in wintertime.

2 Methods and Materials

2.1 Observational data

Hourly time-resolution aerosol and gas measurements were conducted at the Peking University urban atmosphere environment monitoring station (PKUERS) (39.991N, 116.313E) in Beijing in December 2015 and December 2016. A commercialized semi-continuous In-situ Gas and Aerosol Composition (IGAC) Monitor was used to measure the concentrations of water-soluble ions (e.g., NH_4^+, SO_4^{2-}, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-) in $PM_{2.5}$ and inorganic gases (e.g., NH_3, HNO_3, HCl). Relative humidity (RH) and temperature were observed at 1-min resolution at the same site. The quality assurance and control for the IGAC was described in Liu et al. (2017b). A typical severe haze episode occurred during the 6 to 10 in December 2015, with daily average concentrations of $PM_{2.5}$ exceeding 150 μg/m^3 for three days ($PM_{2.5}$ data are from China National Environmental Monitoring Centre). The average RH and temperature in this haze event were 60.9 ± 11.4% and 276.5 ± 1.4 K. The south wind was dominant with wind speed mostly less than 3 m/s. The average concentrations of particulate NO_3^-, NH_4^+ and SO_4^{2-} were 39.8 ± 14.7 μg/m^3, 27.7 ± 8.6 μg/m^3 and 42.4 ± 16.0 μg/m^3, respectively. The ratios of particulate NO_3^- concentrations to SNA (including sulfate, nitrate and ammonium) were 36.5 ± 4.0%.

2.2 NH_3 emission inventory

A comprehensive NH_3 emission inventory of northern China (including the six provinces mentioned above) in December 2015 at a monthly and 1 km × 1 km resolution is developed based our previous studies (Huang et al., 2012;Kang et al., 2016). Here is a brief introduction to our inventory. More detailed descriptions and validation are in our previous studies. Our NH_3 emission inventory is a bottom-up process-based and statistical model which considers a diverse range of sources, including both agricultural (livestock manure and chemical fertilizer) and non-agricultural sectors (e.g., traffic, biomass burning etc.). According to our inventory, the estimated NH_3 emission amount in northern China

was 100 kiloton in December 2015. The largest source was livestock waste (57 kiloton, 57.0% of the total emissions), following by vehicle (12.2%), chemical industry (8.8%), biomass burning (5.4%), waste disposal (4.0%), synthetic fertilizer applications (2.4%) and other minor sources (9.1%). The proportion of chemical fertilizer is small due to the limited fertilization activity in winter. In the past few years, our inventory has been compared with many studies to prove its reliability. For example, the spatial pattern of NH_3 emissions calculated in our inventory agreed well with the distribution of the NH_3 column concentrations in eastern Asia retrieved from the satellite measurements of Infrared Atmospheric Sounding Interferometer (IASI) (Van Damme et al., 2014). Specially, our estimation of livestock NH_3 emissions in China is comparable to the results of Streets et al. (2003) and Ohara et al. (2007).

Another method for estimating NH_3 emissions is the inverse modeling method, which provides top-down emission estimates through optimizing comparisons of model simulations with measurements. For example, Paulot et al. (2014) used the adjoint of a global chemical transport model (GEOS-Chem) and data of NH_4^+ wet deposition fluxes to optimize NH_3 emissions estimation in China. Zhang et al. (2018a) applied TES satellite observations of NH_3 column concentration and GEOS-Chem to provide top-down constraints on NH_3 emissions in China. Their estimates are 10.2 Tg a^{-1} and 11.7 Tg a^{-1} respectively, which are close to our results (9.8 Tg a^{-1}) (Paulot et al., 2014;Zhang et al., 2018a). The accuracy of this method relies on many factors, such as the accuracy of initial conditions, the emission inventories, meteorological inputs, reaction rate constants, and deposition parameters in the chemical transport model. Errors of these parameters could cause biases in the top-down estimation of NH_3 emissions. In addition, measurements of NH_3 or NH_4^+ used in this method, including surface and satellite date, are usually sparse in spatial coverage and have uncertainties, which will also affect the estimation of NH_3 emissions.

2.3 ISORROPIA-II and WRF-Chem models

The thermodynamic equilibrium model, ISORROPIA-II (Fountoukis and Nenes, 2007), being used to determine the phase state and composition of an NH_4^+- SO_4^{2-} - NO_3^- - K^+ - Ca^{2+} - Mg^{2+} - Na^+ - Cl^- - H_2O aerosol system with its corresponding gas components in thermodynamic equilibrium, was used to investigate the response of particulate NO_3^- to NH_3 emission reductions. Using measurements of water-soluble ions, T and RH from PKUERS as inputs, ISORROPIA-II can avoid the inherent uncertainty in estimates of emission inventories, pollutant transport, and chemical transformation. In this study, ISORROPIA-II was run in the "forward mode" and assuming particles are "metastable" with no solid precipitates, which is due to the relatively high RH range observed during this haze event (RH = 60.9 ± 11.4%).

We assess the performance of ISORROPIA-II by comparing measured and predicted particulate NO_3^-, NH_4^+ and gaseous HNO_3, NH_3. An error metric, the mean bias (MB), is used to quantify the bias (the description of MB is shown below Figure S1). The predicted particulate NO_3^-, NH_4^+ and NH_3 agree well with the measurements and the value of R^2 are 0.99, 0.94 and 0.84, respectively (Figure S1). The MB is only 1.0 μg/m^3, 0.3 μg/m^3 and -1.8 μg/m^3, respectively. However, the model performs poorly on HNO_3, with an R^2 of only 0.06 and a MB of -1.0 μg/m^3. This is because particulate NO_3^- is predominantly in the particle phase (the mass ratio of particulate NO_3^- to the total nitric acid (TN = NO_3^- + HNO_3)

was 99.2 ± 1.9%), small errors in predicting particulate NO_3^- are amplified in HNO_3 predicting. Since the MB of HNO_3 is much smaller than the observed particulate NO_3^- (39.8 ± 14.7 μg/m^3) and NH_4^+ (27.7 ± 8.6 μg/m^3), this bias have little influence on simulating the efficiency of particulate NO_3^- reductions.

In the real atmosphere, changes in the level of TA (TA = NH_4^+ + NH_3) can affect the lifetime of TN (Pandis and Seinfeld, 1990). This is because the gaseous HNO_3 has a faster deposition rate in the atmosphere than particulate NO_3^-, and reductions in NH_4^+ may prompt particulate NO_3^- partitioning into the gas phase. In such a case, the concentration of TN would not remain constant but decrease. In order to consider these, we use the Weather Research and Forecast Model coupled Chemistry (WRF-Chem) model (ver. 3.6.1) to investigate the effect of NH_3 emission controls on particulate NO_3^- formation in the regional scale. The simulations were performed for the severe haze event during 6 to 10 December 2015. The modeling domain covered the whole northern China with horizontal resolution of 25 km and 24 vertical layers from surface to 50 hPa. The initial meteorological fields and boundary conditions were taken from the 6 h National Centers for Environmental Prediction (NCEP) global final analysis with a 1° × 1° spatial resolution. The inorganic gas-aerosol equilibrium was predicted by Multicomponent Equilibrium Solver for Aerosols (MESA) in WRF-Chem (Zaveri et al., 2005). The Carbon-Bond Mechanism version Z (CBMZ) photochemical mechanism and Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) aerosol model were used in this study (Fast et al., 2006). Anthropogenic emissions from power plants, industrial sites, residential locations, and vehicles were taken from the Multi-resolution Emission Inventory for China (MEIC; available at www.meicmodel.org).

The performance of WRF-Chem is evaluated by comparing measured and simulated NO_3^-, NH_4^+, SO_4^{2-} and TA. Specifically, the observed and simulated values are, respectively: (1) NO_3^-, 39.8 ± 14.7 μg/m^3 versus 39.1 ± 15.6 μg/m^3; (2) NH_4^+, 27.7 ± 8.6 μg/m^3 versus 26.5 ± 11.7 μg/m^3; (3) SO_4^{2-}, 42.4 ± 16.0 μg/m^3 versus 39.7 ± 20.8 μg/m^3 and (4) TA, 34.6 ± 8.5 μg/m^3 versus 32.1 ± 11.0 μg/m^3. The MB of these four species are -0.7, -1.2, -2.7 and -2.5 μg/m^3, respectively. Simulated particulate NO_3^-, NH_4^+, SO_4^{2-} and TA approximately agreed with the measurements (Figure S2). There are still some simulation biases that may affect the simulation of particulate NO_3^- reductions efficiency. This is discussed in detail in Sect 3.3.

3 Results

3.1 High potential reduction of wintertime NH_3 emissions in northern China

Livestock husbandry accounts for the largest proportion of NH_3 emissions in winter of northern China (approximately 60%), which is mainly caused by the poor manure management. There are three main animal-rearing systems in China: free-range, grazing and intensive. On the one hand, the proportion of intensive livestock husbandry in China is only about 40%, far lower than that of developed countries (Harun and Ogneva-Himmelberger., 2013). As a result, the widespread free-range and grazing animal rearing systems contribute more than half of the total livestock NH_3 emissions due to lacking manure collection and treatment (Kang et al., 2016). On the other hand, there were no relevant regulations about storage of manure for intensive farms in China in the past few

decades. This causes most livestock farms also lack necessary measures and facilities for manure collection and storage (Chadwick et al., 2015).

Due to the current poor manure management in China, the improved manure management may have great potential for NH_3 emission reductions from livestock husbandry (Wang et al., 2017). The improved manure management mainly includes three phases: in-house handling, storage and land application (Chadwick et al., 2011). For winter, the emission reduction measures mainly focus on in-house handling and storage, since land application mainly occurs in spring and summer. According to previous studies, for in-house handling, regularly washing the floor and using slatted floor or deep litter to replace solid floor could both reduce NH_3 emissions by more than 50% (Groenestein and VanFaassen, 1996;Monteny and Erisman, 1998;Gilhespy et al., 2009;Hou et al., 2015). For storage, covering slurry and manure could reduce NH_3 emissions by about 50%-70% (Balsari. et al., 2006;Petersen et al., 2013;Hou et al., 2015;Wang et al., 2017).

Based on the above research results, the livestock NH_3 emission reductions strategies applied in this study include the following steps. Firstly, the proportion of intensive livestock production was raised from 40% to 80% in our NH_3 emission inventory model. In our model, the animals in free-range and grazing animal rearing systems are assumed to live outdoors for half a day, and the improved manure management is only effective for indoor animals. Therefore, increasing the proportion of intensive livestock production is conducive to better manure management (Hristov et al., 2011). Secondly, the ratios of NH_3 emission reductions mentioned above were multiplied by NH_3 emission factors in two phases of manure management: 50% reduction at in-house handling and 60% (average value of 50% and 70%) reduction at storage. With these measures, we estimate that the NH_3 emission factors for the livestock in China could be comparable to those in Europe and the USA (shown in Table S1). Meanwhile, our NH_3 emission model predicted that the livestock NH_3 emissions were reduced by 60% (from 57 to 23 kiloton), causing approximately 40% reduction in total NH_3 emissions. Spatially, NH_3 emissions decreased significantly in Hebei, Henan and Shandong, where the livestock NH_3 emissions accounted for a large proportion of the total (shown in Figure S3).

3.2. Simulations of NO_3^- reduction due to NH_3 emission controls

In the ISORROPIA-II simulation, 40% reduction of TA was used to reflect the effects of reducing NH_3 emissions by 40%. This approach has been used in many previous studies (Blanchard and Hidy, 2003;Vayenas et al., 2005). However, in the real atmosphere, the reductions of NH_3 emission are not always equal to the reductions of TA due to the regional transmission. Their differences are discussed in the WRF-Chem simulation.

In this haze event (from 6 to 10 December, 2015), the mean concentration of particulate NO_3^- decreased from 40.8 to 25.7 $\mu g/m^3$ (a 37% reduction). In addition, the peak hourly concentration of NO_3^- decreased from 81.9 to 30.7 $\mu g/m^3$ (a 63% reduction) (shown in Figure 1). The fundamental thermodynamic processes of TA reductions on decreasing particulate NO_3^- are explained below. Firstly, we found that NH_3 was quite available to react with HNO_3 in the thermodynamic equilibrium system, because NH_3 was 6.6 ± 3.8 $\mu g/m^3$ while HNO_3 was only 0.4 ± 1.1 $\mu g/m^3$. Secondly, almost all of particulate NO_3^- condensed into aerosol phase (the mass ratio of particulate NO_3^- to TN was 99.2 ± 1.9%) under such low temperature conditions (276.5 ± 1.4 K). Thirdly, the NH_3-HNO_3 partial

pressure production (Kp) was as low as about 0.1 ppb^2 (calculated from ISORROPIA-II outputs, depending not only on temperature and RH but also sulfate concentration). The value of K_P would remain constant, if the temperature, RH and sulfate concentration remained unchanged. In general, NH_4NO_3 was not easy to volatilize into gas phase under these circumstances.

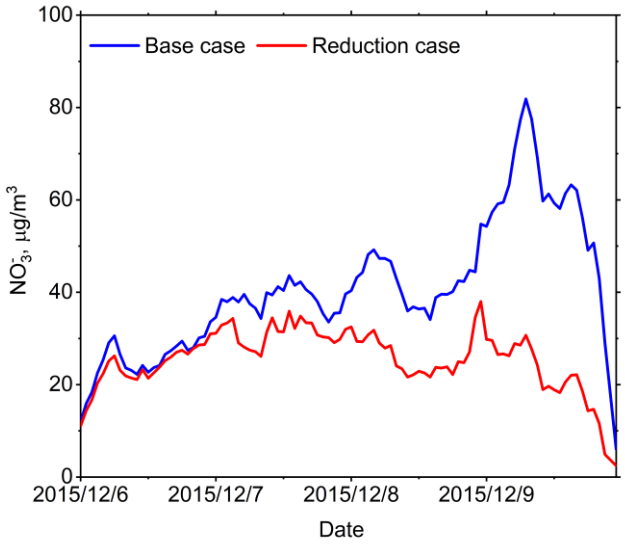

Figure 1. A comparison of particulate nitrate (NO_3^-) between the base (blue line) and emission reductions cases (red line) simulated by the ISORROPIA-II model in this severe haze episode.

When TA was reduced by 40%, the average mass concentration of gaseous NH_3 decreased from 6.6 to 0.01 μg/m^3 (from 8.8 ppb to 0.05 ppb). In order to keep the value of K_P constant in the thermodynamic equilibrium state, the reductions of NH_3 increased HNO_3, which shifted the particulate NO_3^- partitioning toward the gas phase. Hence, when NH_3 in gas phase was almost completely depleted, HNO_3 increased from 0.4 to 15.5 μg/m^3 (from 0.1 ppb to 5.6 ppb), leading to a reduction of particulate NO_3^- from 40.8 to 25.7 μg/m^3 (a 37.0 % reduction). Meanwhile, NH_4^+ also decreased from 27.9 to 20.6 μg/m^3 and there was almost no change in sulfate level (decreased from 39.7 to 39.3 μg/m^3), with only trace amount of NH_4HSO_4 produced. This indicated that the reduction of particulate NH_4^+ and NO_3^- was mainly due to the reduction of NH_4NO_3. The sum of particulate NO_3^- and NH_4^+ decreased from 68.7 to 46.3 μg/m^3 (a 32.6% reduction).

We also conducted WRF-Chem simulations to quantify the impacts of NH_3 emission controls on particulate NO_3^- regionally. A 60% reduction in livestock NH_3 emissions was used as an emission reductions scheme and Figure 2 shows the spatial distribution of particulate NO_3^- under the base case and the emission reductions case. The spatial distribution of particulate NO_3^- was mainly concentrated in most parts of Henan (HN) and Hebei (HB), with the average concentration over 30 μg/m^3 (included in the black box shown in Figure 2a). The highest particulate NO_3^- concentrations, more than 60 μg/m^3, were mainly located in central south of Hebei and northern Henan. In the emission

reductions case, the mean concentration of particulate NO_3^- decreased from 30.6 to 18.5 μg/m^3 (a 39.4% reduction) in the range of the black box. Meanwhile, the particulate NH_4^+ decreased from 16.3 to 11.7 μg/m^3 (a 28.1% reduction). The sum of particulate NO_3^- and NH_4^+ decreased from 46.9 to 30.2 μg/m^3 (a 35.6% reduction). Besides, the sulfate concentration slightly changed from 19.7 to 17.6 μg/m^3, and $PM_{2.5}$ concentration dropped from 143.4 to 125.4 μg/m^3. The largest reductions in particulate NO_3^- were mainly located in the central north of Henan and central Hebei, where the percentage reduction was generally more than 60% (shown in Figure 2b). In some areas with high particulate NO_3^- concentrations, particulate NO_3^- had been effectively reduced by more than 30 μg/m^3 (shown in Figure 2c). In these regions, severe haze events occurred frequently due to their large emissions of air pollutants, including NH_3 (Wang et al., 2014;Zhao et al., 2017). In addition, TN was reduced by 34.1% (from 31.8 μg/m^3 to 21.0 μg/m^3), which was in line with the assumption in Sect 2.3. Correspondingly, TA decreased by 40.7% (from 17.2 μg/m^3 to 10.2 μg/m^3), very close to the reductions of NH_3 emission (40%). This indicates that it is reasonable to use TA reductions to represent NH_3 emission reductions in the ISORROPIA-II simulation.

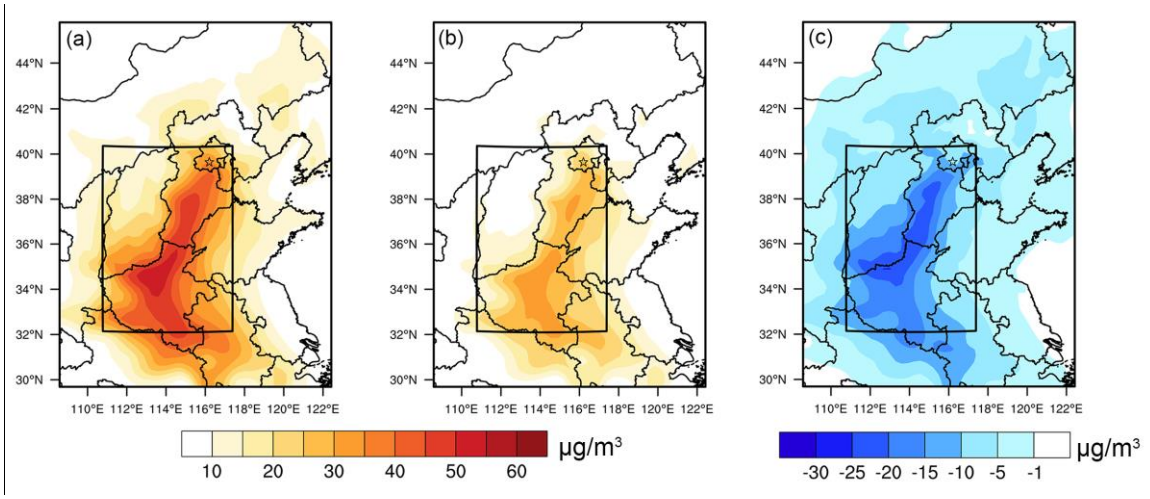

Figure 2. Spatial distribution of particulate NO_3^- concentrations in northern China predicted by WRF-Chem from 6 to 10 December, 2015, for **(a)** the base case, **(b)** the emission reductions case and **(c)** the difference between the base case and the emission reductions case. The scope of this study focuses on the black box, including Beijing (BJ), Tianjin (TJ), Hebei (HB), Shanxi (SX), Shandong (SD) and Henan (HN).

3.3 The particulate NO_3^- reduction efficiency during the wintertime

The sensitivity of particulate NO_3^- to NH_3 is often determined by the availability of ambient NH_3, which can be represented by the observable indicator (Seinfeld and Pandis, 2006). In this study, we use the observed molar ratio (R) of TA to the sum of sulfate, total chlorine and TN minus Na^+, K^+, Ca^{2+} and Mg^{2+} to represent the availability of ambient NH_3 and predict the sensitivity of the particulate NO_3^- to changes in TN and TA.

$$R = \frac{TA}{2SO_4^{2-} + NO_3^- + HNO_3(g) + Cl^- + HCl(g) - 2Ca^{2+} - Na^+ - K^+ - 2Mg^{2+}} \quad (1)$$

The accuracy of R was examined by constructing the isopleths of particulate NO_3^- concentrations as a function of TN and TA (shown in Figure 3). The NO_3^- concentration was constructed by varying the input concentrations of TA and TN from 0 to 200 μg/m^3 in increments of 10 μg/m^3 independently in ISORROPIA-II, while using the observed average value for the other components. Over a range of temperatures (273–283 K) and RHs (30–90%), the dashed line of R = 1 divides each isopleth into two regions with tiny bias, which indicates that R can be used to qualitatively predict the response of the particulate NO_3^- to changes in concentrations of TN and TA.

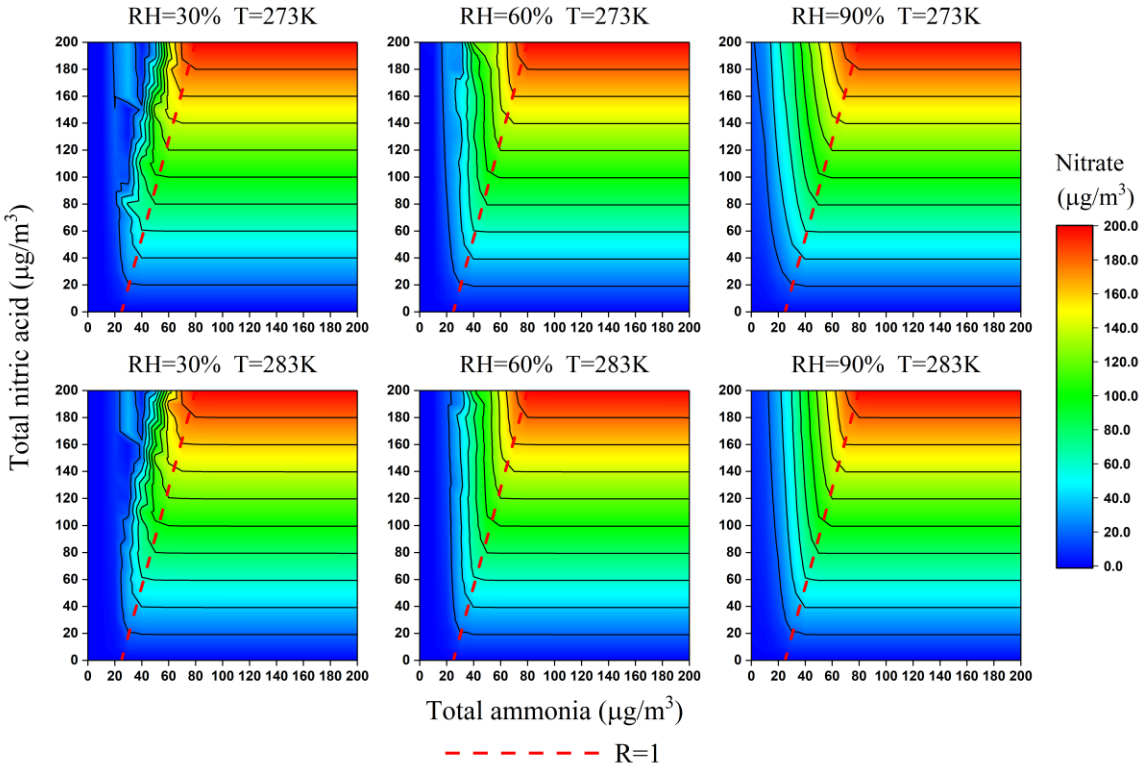

Figure 3. Isopleths of the particulate NO_3^- concentration (μg/m^3) as a function of TN and TA under average severe haze conditions in winter. The concentration of SO_4^{2-}, Cl^-, K^+, Ca^{2+}, Na^+, and Mg^{2+} was 60.2, 9.3, 0.56, 0.04, 0.75, and 0.03 μg/m^3, respectively. Values are averages from all severe hazes during the observation period.

In the right side of the dashed line (R > 1), particulate NO_3^- formation is HNO_3-limited. The NH_3 is surplus and almost all particulate NO_3^- exists in the aerosol phase. The TA reductions mainly reduce NH_3, with negligible effects on particulate NO_3^-. By contrast, particulate NO_3^- formation is NH_3-limited in the left of the dashed line (R < 1). There is less NH_3 present in the gas phase, and TA reductions could reduce particulate NO_3^- efficiently. For example, when the concentrations of TN and TA are 100 and 50 μg/m^3 (RH = 60 % and T =273 K), the concentration of particulate NO_3^- is about 100 μg/m^3 and the value of R is close to one (typical observational values during the severe haze in this study). In such cases, if TA were reduced by 50% to 25 μg/m^3, the particulate NO_3^- would be significantly reduced from 100 to 20 μg/m^3, an 80% reduction.

Under the typical winter conditions in northern China, the value of R was generally greater than one and gradually declining with the increase in SNA concentrations (shown in Figure 4a). When the concentration of SNA is greater than 150 μg/m^3, the values of R become close to and frequently lower than one. This indicated that particulate NO_3^- formation would easily become NH_3-limited under severe haze conditions when NH_3 emissions were reduced. In general, particulate NO_3^- will be reduced effectively by a 40% reduction of NH_3 emissions in the condition that the value of R is less than 1.4 (shown in Figure S4). This situation accounts for 68.1% of the entire December (shown in Figure 4b). It should also be noted that the particulate NO_3^- is insensitive to a 40% reduction in NH_3 emissions when the value of R is greater than 1.4 (shown in Figure S4). This situation mainly occurs in relatively clean days (the concentration of SNA is less than 75 μg/m^3), accounting for only 31.9% of the entire December (shown in Figure 4a and 4b). Overall, reducing 40% of NH_3 emissions could effectively reduce the levels of particulate NO_3^- under typical severe winter haze conditions in northern China.

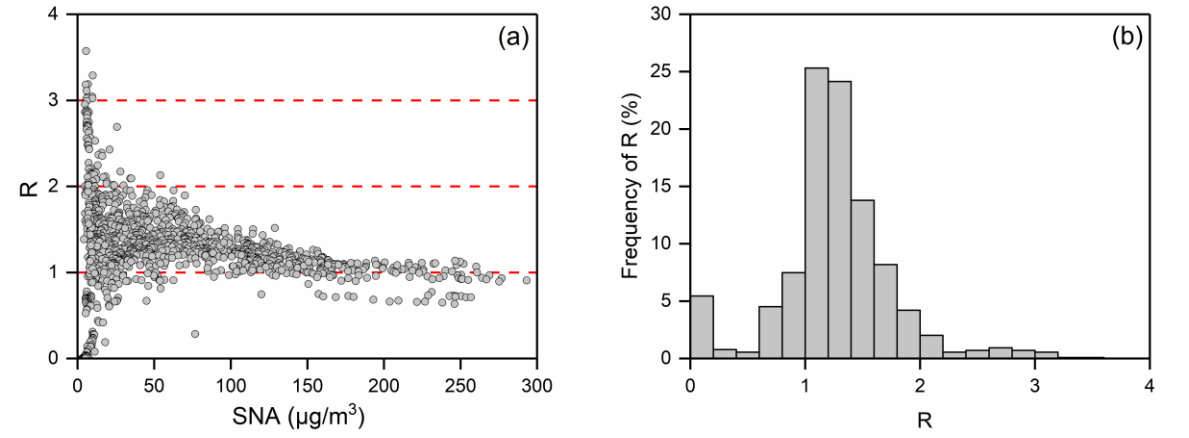

Figure 4. (a) The observed molar ratio (R) and the concentrations of SNA in PKUERS in December 2015 and December 2016. (b) The frequency of R during the same period.

The observed R provides a simple method to rapidly estimate the efficiency of NH_3 emission reductions on the particulate NO_3^- reductions, which can avoid the shortage of the air quality model, especially the uncertain estimates of meteorology. However, it also needs to be examined in more detail for specific pollution and meteorological conditions. Therefore, the observed indicator and air quality models should be used in a complementary way to assess the effectiveness of NH_3 emission controls strategies.

Based on the above analysis, the influence of WRF-Chem simulation biases on particulate NO_3^- reduction efficiency simulation mainly depends on the simulation bias of R. During the simulation case, the average simulated value of R is 1.3, which is equivalent to the observed value (1.3). Since WRF-Chem has a good estimation of the availability of ambient NH_3, its estimation of the efficiency of particulate NO_3^- reductions is reliable.

It is noteworthy that the efficiency of particulate NO_3^- reductions by NH_3 emission controls in northern China during severe winter hazes may be higher than that in the United States and Europe. Compared with our results (40% NH_3 emission reductions lead to about

40% particulate NO_3^- reductions), in the United States and Europe, NH_3 emissions often need to be reduced by more than 70% before particulate NO_3^- begin to decrease (Pozzer et al., 2017;Guo et al., 2018a). This is mainly because the strict emission controls of SO_2 and NO_x in these areas lead to a more ammonia-rich environment, which makes particulate NO_3^- insensitive to NH_3 emission reductions.

4 Conclusions

In this study, we found that during severe winter haze episodes, the particulate NO_3^- formation is NH_3-limited, resulting in its high sensitivity to NH_3 emission reductions. Meanwhile, livestock NH_3 emission controls is a very efficient way to alleviate particulate NO_3^- pollution during severe winter hazes. The estimations showed that the improvements in manure management of livestock husbandry could effectively reduce total NH_3 emissions by 40% (from 100 kiloton to 60 kiloton) in winter of northern China. It would lead to a reduction of particulate NO_3^- by about 40% (averagely from 40.8 to 25.7 $\mu g/m^3$) during severe haze conditions.

NO_x emission controls could be a more direct and effective way to reduce the particulate NO_3^- than NH_3 emission reductions. However, in northern China, the target of NO_x emission reductions is only about 25% in the 13th Five-Year Plan (2016-2020) (http://www.gov.cn/zhengce/content/2017-01/05/content_5156789.htm). Due to the dominance of free-range animal rearing systems and the lack of emission controls policies, livestock NH_3 emission reductions in China could be practicable. In order to control $PM_{2.5}$ pollution more effectively in northern China, measures to improve manure management in livestock urgently need to be implemented.

Author contribution

Y.S, S.W and M.Z initiated the investigation. C.Y, T.Z and M.Z conducted the aerosol and gas measurements. Z.X, T.W and M.L performed the modelling analyses. Z.X, S.W, L.Z, C.Y and M.Z wrote and edited the manuscript. M.Z, T.X, T.W, Y.S, Y.P, M.H and T.Z contributed to discussions of the results and the manuscript.

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