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UNCNET

Urban nitrogen cycles: new economy thinking to master the challenges of climate change

D3/2: A quantitative estimate of the impacts of ammonia emissions on urban PM$_{2.5}$ air quality

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Executive Summary

The North China plain, including megacities such as Beijing and Shijiazhuang, has experienced severe fine particulate matter (PM$_{2.5}$) air pollution in recent years. To mitigate PM$_{2.5}$ air pollution, stringent emission controls have then been implemented through the Five-Year Plan and the Action Plan on Prevention and Control of Air Pollution that mainly control primary PM emissions and the emissions of aerosol precursors (SO$_2$ and NO$_x$). Ammonia (NH$_3$), another important precursor of secondary inorganic aerosols (SIA), also plays a critical role in PM$_{2.5}$ air pollution. NH$_3$ in the atmosphere first reacts with sulfuric acid (H$_2$SO$_4$ as produced from oxidation of SO$_2$) to form ammonium sulfate aerosol, and excessive NH$_3$ then reacts with nitric acid (HNO$_3$ as produced from oxidation of NO$_2$) to form ammonium nitrate aerosol. However, NH$_3$ emissions have not been regulated yet in China. This raises an issue that how effective NH$_3$ emission controls can achieve on urban PM$_{2.5}$ air quality with changing SO$_2$/NO$_x$ emissions.

As part of the task of UNCNET WP3, we investigate the impacts of NH$_3$ emissions on PM$_{2.5}$ air pollution over Beijing-Tianjin-Hebei (BTH) region using a regional air quality model (The Weather Research and Forecasting (WRF) Version 3.6.1 model coupled with Chemistry (WRF-Chem)) combined with our recent developed Chinese agricultural NH$_3$ emission inventory. We conduct a series of model simulations to quantify the impacts of NH$_3$ emissions on urban PM$_{2.5}$ air quality under different NH$_3$ emission reduction conditions as well as under different SO$_2$ and NO$_x$ emission conditions (e.g., considering the 2015-2017 SO$_2$/NO$_x$ emission changes). Obtaining a quantitative estimate of the effectiveness of NH$_3$ emission reductions on PM$_{2.5}$ air pollution regulation will help policy makers to optimize emissions reduction strategies.

We find strong nonlinear responses of PM$_{2.5}$ air pollution to NH$_3$ emission reductions in North China. Under the current NH$_3$ emission condition changes in PM$_{2.5}$ concentrations in North China associated with NH$_3$ emission reductions follow a power exponential function in January. The BTH mean PWC PM$_{2.5}$ concentrations in January would only decrease 1.4-3.8 μg m$^{-3}$ (1.1-2.9% of PM$_{2.5}$) when NH$_3$ emissions in North China were reduced by 20-40%, but the decreases would reach 8.1-26.7 μg m$^{-3}$ (6.2-20.5% of PM$_{2.5}$) with 60-100% NH$_3$ emission reductions. Such nonlinearity reflects a switch of NH$_3$-saturated to NH$_3$-limited condition for SIA, in particular, aerosol nitrate formation. The PM$_{2.5}$ changes in July also show a nonlinear response, but the nonlinearity is much weaker than January.

As SO$_2$ emissions in North China have substantially reduced over 2015-2017, we find that has lowered the efficiency of NH$_3$ emission controls on PM$_{2.5}$ air pollution in both winter and summer. Future reductions of NO$_x$ emissions may partly enhance PM$_{2.5}$ pollution in BTH winter due to the weakened titration effect, and can be offset by jointly controlling NH$_3$ emissions. Our results emphasize the importance of an accurate NH$_3$ emission estimate on the assessment of effectiveness of NH$_3$ emission controls, and also support the need to jointly consider emission reductions of SO$_2$, NO$_x$, and NH$_3$ for mitigating SIA air pollution in the BTH region.
ANNEX 1

The nonlinear response of fine particulate matter pollution to ammonia emission reductions in North China

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The nonlinear response of fine particulate matter pollution to ammonia emission reductions in North China

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Abstract
Recent Chinese air pollution actions have significantly lowered the fine particulate matter (PM$_{2.5}$) levels in North China via controlling emissions of sulfur dioxide (SO$_2$) and nitrogen oxides (NO$_x$) together with other primary aerosols, while emissions of another precursor, ammonia (NH$_3$) have not been regulated. This raises a question that how effective NH$_3$ emission controls can achieve on PM$_{2.5}$ pollution with changing SO$_2$/NO$_x$ emissions. Here we use a regional air quality model to investigate this issue accounting for different NH$_3$ emission reductions and different SO$_2$/NO$_x$ emissions in North China. We find that the PM$_{2.5}$ reduction efficiency of NH$_3$ emission controls is highly sensitive to the NH$_3$ emission condition and reduction strength. The Beijing-Tianjin-Hebei regional population weighted PM$_{2.5}$ concentrations would only decrease 1.4-3.8 μg m$^{-3}$ (1.1-2.9% of PM$_{2.5}$) with 20-40% NH$_3$ emission reductions, but reach 8.1-26.7 μg m$^{-3}$ (6.2-20.5%) with 60-100% NH$_3$ emission reductions in January 2015. The 2015-2017 emission changes (reduction in SO$_2$ emissions) have lowered the efficiency of NH$_3$ emission controls. NO$_x$ emission reductions may enhance wintertime PM$_{2.5}$ pollution due to the weakened titration effect and can be offset by jointly controlling NH$_3$ emissions. Our results emphasize the need to jointly consider NH$_3$ emission controls when designing PM$_{2.5}$ pollution mitigation strategies.

Keywords
ammonia, air pollution, fine particulate matter, PM$_{2.5}$, emission reduction

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1. Introduction

Fine particulate matter (particle with aerodynamic diameters less than or equal to 2.5 μm; also referred as PM$_{2.5}$) not only poses serious harm to human health but also adversely influences atmospheric environment (Li et al 2014; Gao et al 2016; Liao et al 2015). The North China plain has experienced severe PM$_{2.5}$ air pollution in recent years, and drawn worldwide attention (Huang et al 2014; Zhang et al 2015). To abate PM$_{2.5}$ air pollution, the Chinese government has implemented the “Action Plan on Prevention and Control of Air Pollution” in 2013 and “Three-year Action Plan Fighting for a Blue Sky” in 2018 (Zhang et al 2019; Chinese State Council 2013, 2018). The annual mean PM$_{2.5}$ concentration in the Beijing-Tianjin-Hebei (BTH) region has decreased from 106 μg m$^{-3}$ in 2013 to 64 μg m$^{-3}$ in 2017 (MEE 2013; MEE 2017). This value is still much higher than the China’s National Ambient Air Quality Standard (NAAQS) of 35 μg m$^{-3}$, and calls for more stringent emission control measures.

Ammonia (NH$_3$) is a vital alkaline gas in the ambient atmosphere and plays a critical role in nitrogen deposition and haze pollution (Pan et al 2018; Wang et al 2013; Zhang et al 2015). NH$_3$ in the air first reacts with sulfuric acid (H$_2$SO$_4$ as produced from oxidation of SO$_2$) to form ammonium sulfate aerosol, and excessive NH$_3$ then reacts with nitric acid (HNO$_3$ as produced from oxidation of NO$_2$) to form ammonium nitrate aerosol. These secondary inorganic aerosols (SIA, including sulfate, nitrate, and ammonium) account for 30-50% of PM$_{2.5}$ in the eastern China (Zhao et al 2013; Huang et al 2014; Sun et al 2016). Depending on the abundance of NH$_3$ in the air, the formation of SIA can be considered as the NH$_3$-poor condition (when there is no sufficient NH$_3$ to neutralize H$_2$SO$_4$) or the NH$_3$-rich condition (when there is NH$_3$ to further neutralize HNO$_3$) (Seinfeld and Pandis, 2006). When NH$_3$ is too abundant, formation of aerosol nitrate becomes HNO$_3$-limited, and most NH$_3$ remains gaseous in the atmosphere (Xu et al 2019). The availability of NH$_3$ also significantly modulates liquid aerosol pH and then affects the heterogenous chemistry on the aerosol surface (Ge et al 2019).

Air pollution actions in China have implemented a series of emission control measures mainly targeting fuel combustion induced emissions of SO$_2$, NO$_x$ (NO+NO$_2$), and other primary aerosols (Zhang et al 2019). NH$_3$ emissions are dominantly from agricultural activities (i.e., fertilizer application, livestock manure management) (Zhang et al 2018) and have not been regulated yet in China (Fu et al 2017; Zheng et al 2018). The recent “Three-year Action Plan Fighting for a Blue Sky” called for agricultural NH$_3$ emission controls but did not establish a target reduction amount (Chinese State Council, 2018). Atmospheric chemistry modelling studies indicated that controlling agricultural NH$_3$ emissions would significantly decrease aerosol nitrate in North China in particular during severe winter haze events (Xu et al 2019; Han et al 2020), while thermodynamic calculations suggested that a substantial (> 50%) NH$_3$ emission reduction was required to effectively reduce SIA levels under present winter haze conditions in this region (Guo et al 2018; Song et al 2019). The discrepancy can be largely induced by the accuracy of NH$_3$ emission estimates, and the effectiveness of NH$_3$ emission controls on PM$_{2.5}$ under the conditions of rapid SO$_2$ and NO$_x$ emission changes as occurring in North China is still undetermined.

Here we investigate the issue using a regional air quality model combined with our recent developed Chinese agricultural NH$_3$ emission inventory (Zhang et al 2018). We conduct a series of model simulations to quantify the effectiveness of NH$_3$ emission reductions on PM$_{2.5}$ air pollution regulation under different NH$_3$ emission reduction conditions as well as under different SO$_2$ and NO$_x$ emission conditions (e.g., considering the 2015-2017 SO$_2$/NO$_x$ emission changes).

2. Methodology and data
The Weather Research and Forecasting (WRF) Version 3.6.1 model coupled with Chemistry (WRF-Chem) is employed to simulate meteorological fields and atmospheric chemistry in North China. The modeling framework is configured with two domains (Figure S1) using 161 (east-west) × 171 (south-north) and 150 (east-west) × 159 (south-north) grid cells at 27 km and 9 km horizontal resolutions, respectively. The outer domain covers China and its adjacent areas, and the inner domain covers North China where this study focuses on. The National Center for Environmental Prediction (NCEP) Final (FNL) Analysis data with 1-degree spatial resolution and 6-hour temporal resolution are used for the initial and lateral boundary conditions of meteorology in the model. The meteorological fields are re-initiated every two days using the FNL Analysis data so that they are nearly the same for all our simulations. The chemical initial and boundary conditions are obtained from the outputs of the global chemical transport model MOZART-4 (Emmons et al 2010).

Our simulations use the gas-phase Carbon-Bond Mechanism Z (CBMZ) mechanism (Zaveri and Peters, 1999) coupled with a 4-bin sectional (0.039-0.156, 0.156-0.625, 0.625-2.5, and 2.5-10.0 μm for dry diameter) Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) aerosol scheme (Zaveri et al 2008). We have implemented the heterogeneous sulfate formation reactions on particle surface based on Chen et al (2016) to improve the model simulation of secondary inorganic aerosols, and have increased the anthropogenic OC emissions by a factor of 4 to account for secondary organic aerosols in the model (Sun et al 2012). The new gas-particle partitioning module Adaptive Step Time-Split Euler Method (ASTEM) is used to determine the NH$_3$ and HNO$_3$ gas-aerosol equilibrium (Zaveri et al 2008).

The model physical settings include the Morrison double-moment microphysics scheme (Morrison et al 2009), the Grell-3 cumulus scheme (Grell et al 2002), the RRTM (Rapid Radiative Transfer Model) long-wave radiation scheme (Mlawer et al 1997), the Goddard short-wave radiation scheme (Chou and Suarez, 1994), the YSU (Yonsei University) planetary boundary layer scheme (Hong et al 2006), the Revised MM5 (fifth-generation Mesoscale Model) Monin-Obukhov surface layer scheme, and the Unified Noah land-surface model (Chen and Dudhia, 2001). A single-layer Urban Canopy Model is used to explicitly simulate the urban areas (Kusaka et al 2001). We have further updated the model land use types with the 2015 Terra and Aqua combined MODIS (Moderate Resolution Imaging Spectroradiometer) Land Cover Type (MCD12Q1) Version 6 data product. We use the anthropogenic emissions from the 2015 Multi-resolution Emission Inventory for China (MEIC, http://www.meicmodel.org/) and 2010 MIX inventory for regions outside China (Li et al 2017), except for Chinese agricultural NH$_3$ emissions that are from Zhang et al (2018) with updated statistics for the year 2015. Biogenic emissions are calculated online using the Model of Emissions of Gases and Aerosols from Nature (MEGAN; Guenther et al 2006). Biomass burning emissions use Fire Inventory from the NCAR (FINN; Wiedinmyer et al 2011). Figure S2 shows the spatial distribution of NH$_3$, SO$_2$ and NO$_x$ emissions over North China for January and July 2015, and Table S1 summarizes the emission totals. Our estimates of anthropogenic NH$_3$ emissions in North China are 0.11 Tg month$^{-1}$ in January and 0.25 Tg month$^{-1}$ in July. Compared with the MEIC NH$_3$ emissions, our estimates are about 1% lower in January and 44% higher in July.

We conduct a series of WRF-Chem simulations as summarized in Table 1. First, the baseline simulation (Base, corresponding to the S1R0 scenario) includes the emissions described above and can be evaluated with observations. Second, a group of sensitivity simulations (S1RN) by reducing anthropogenic NH$_3$ emissions over North China (110°-120°E and 35°-43°N; Figure S1) by 20%, 40%, 60%, 80%, and 100%, respectively (denoted as S1RN scenarios, N = 20/40/60/100). The differences in PM$_{2.5}$ concentrations between S1R0 and S1RN then estimate the effects of NH$_3$ emission reductions. Third, a group of sensitivity simulations (S2RN, N = 0/20/40/60/100), similar to S1RN, but further reduces the North China anthropogenic SO$_2$ emissions by ~40% and anthropogenic NO$_x$ emissions by ~8% to reflect emission changes from 2015 to 2017 (Zheng et al 2018; Figure S3). Fourth, another group of sensitivity simulations, similar to S2RN, but further reduces anthropogenic NO$_x$ emissions in North China by 20% (S3RN, N = 0/20/40/60/100). For all
simulations, a winter month (January) and a summer month (July) are simulated after 3-day spin-up for initialization.

For model evaluation, meteorological observations including 10-m wind direction (WD10), 10-m wind speed (WS10), 2-m air temperature (T2), and 2-m relative humidity (RH2) in January and July 2015 at 36 stations in North China are collected from National Climatic Data Center (NCDC, https://ncdc.noaa.gov/isd/data-access). Hourly observations of surface PM$_{2.5}$ concentrations at 39 stations in North China are obtained from the Ministry of Ecology and Environment (MEE) of China (http://106.37.208.233:2035/).

Monthly NH$_3$ concentrations at seven sites from the Ammonia Monitoring Network in China (AMoN-China; Pan et al. 2018) are used to evaluate our NH$_3$ emission inventory in North China. We use NH$_3$ measurements from AMoN-China conducted during 01-31 January and 15-31 July 2015. We also use measurements of PM$_{2.5}$ components, including sulfate, nitrate, ammonium, organic carbon (OC) and black carbon (BC) in January and July 2015 at Beijing (39.94°N, 116.38°E) and Tianjin (39.09°N, 117.31°E) as obtained by the Institute of Atmospheric Physics (IAP). Hourly model simulated results are sampled at the grids covering the station locations. Correlation coefficient ($R$) and mean bias (MB) between observations and simulations are calculated.

3. Observed and simulated surface pollutant concentrations

Evaluations of model simulated meteorological variables (WD10, WS10, T2, and RH2) are shown in Figure S4. Simulated spatial patterns of meteorological variables are overall in good agreement with observations except for WD10 for which the model results are biased low in North China. Figure 1 shows the time series and spatial distributions of observed and Base simulated PM$_{2.5}$ concentrations over North China in January (Figure 1a-b) and July (Figure 1c-d) 2015. The comparisons of PM$_{2.5}$ components with measurements at Beijing and Tianjin are shown in Figure S5. We find that the WRF-Chem Base simulation in general captures the magnitudes and variations of observed surface PM$_{2.5}$ concentrations in both January and July with correlation coefficients of 0.60-0.85 in January and 0.33-0.66 in July. The MB is small (2.6 μg m$^{-3}$) in January and relatively large in July (-9.1 μg m$^{-3}$). Evaluations with measurements of PM$_{2.5}$ components show that the model simulated SIA concentrations are biased low by 10-40% in July, likely suggesting the implemented heterogeneous sulfate formation (Chen et al. 2016) still needs to be enhanced in summer.

We compare in Figure 2 the spatial distributions of measured and simulated surface NH$_3$ concentrations over North China for 01-31 January (Figure 2a) and 15-31 July (Figure 2c) 2015. Although measured and Base simulated NH$_3$ concentrations show similar spatial variations ($R$ values of 0.93 in January and 0.72 in July), the Base model results are biased high by 38% (simulated 11.6 μg m$^{-3}$ vs. observed 8.4 μg m$^{-3}$) in January and biased low by 30% (15.2 μg m$^{-3}$ vs. 21.5 μg m$^{-3}$) in July. We find that when we decrease/increase anthropogenic NH$_3$ emissions by 20% in January/July, the biases can be nearly corrected in January and reduced to only -12% in July (Figure 2b and 2d). This indicates that our Base NH$_3$ emissions might be overestimated in January and underestimated in July over North China.

To further illustrate the effect of NH$_3$ emission changes on surface concentrations, we also show in Figure 2 changes in BTH regional mean gaseous NH$_3$, aerosol ammonium (NH$_4^+$), and total reduced nitrogen (NH$_3$ = NH$_3$+NH$_4^+$) as we gradually reduce anthropogenic NH$_3$ emissions in North China (i.e., S1RN scenarios). When we begin to decrease NH$_3$ emissions (reductions < 40%), surface NH$_3$ concentrations decrease rapidly, while NH$_4^+$ concentrations decrease much slower, reflecting saturated NH$_3$ conditions with current emissions in particular for the January month. Under large emission reductions (> 60%), changes in aerosol NH$_4^+$ concentrations become faster than gaseous
NH₃ concentrations. Changes in the two species balance each other, leading to a close-to-linear response of the NH₃ concentrations to NH₃ emission reductions in North China. This is consistent with previous studies that suggest atmospheric NH₃ is a better indicator of NH₃ emissions than NH₃ or NH₄⁺ alone in the US (Pinder et al. 2006; Zhang et al. 2012).

4. **Response of PM₂.₅ pollution to NH₃ emission reductions**

The sensitivity simulations with perturbed NH₃ emissions allow us to assess the responses of air pollution to NH₃ emission reductions. Figure 3 shows changes in surface PM₂.₅ concentrations as we gradually reducing NH₃ emissions in North China in January 2015. To describe the saturation of atmospheric NH₃, we follow previous studies (Song et al. 2018; Xu et al. 2019) and define the excess NH₃ (in unit of μg m⁻³) as the differences in NH₃ and required NH₃ to meet ionic equilibrium using the formula below:

\[ \text{Excess NH}_3 = \text{Total NH}_x - \text{required NH}_3 \]  \hspace{1cm} (1)

\[ \text{Total NH}_x = 17 \times \left( \frac{[\text{NH}_3^+]}{18} + \frac{[\text{NH}_2]}{22.4} \right) \]  \hspace{1cm} (2)

\[ \text{required NH}_3 = 17 \times \left( \frac{[\text{SO}_4^{2-}]}{48} + \frac{[\text{NO}_3^-]}{62} + \frac{[\text{Cl}^-]}{35.5} + \frac{[\text{HNO}_3]}{22.4} + \frac{[\text{HCl}]}{22.4} - \frac{[\text{Na}^+]}{23} \right) \]  \hspace{1cm} (3)

where \([\text{NH}_3^+], [\text{SO}_4^{2-}], [\text{NO}_3^-], [\text{Cl}^-], \) and \([\text{Na}^+]\) are the mass concentrations (in unit of μg m⁻³) of these ions, and \([\text{NH}_3], [\text{HNO}_3],\) and \([\text{HCl}]\) are gas mixing ratios (ppb).

As shown in Figure 3, changes in the January mean PM₂.₅ concentration become much more distinct with stronger NH₃ emission reductions in North China. The first 20% NH₃ emission reduction would only decrease PM₂.₅ in Beijing by 1.6 μg m⁻³ and by 1.4 μg m⁻³ in BTH. The values increase to 8.3 μg m⁻³ in Beijing and 7.0 μg m⁻³ in BTH with 60% NH₃ emission reductions, and 20.8 μg m⁻³ in Beijing and 20.4 μg m⁻³ in BTH when all NH₃ emissions are turned off. The largest PM₂.₅ responses shift towards the southern Hebei province where PM₂.₅ concentrations are particularly high (Figure 1a). Such nonlinear responses can be largely explained by the derived excess NH₃ concentrations in each scenario. As also shown in Figure 3, NH₃ is highly saturated in the southern Hebei province in the Base condition and scenarios with small NH₃ emission reductions, and thus the SIA portion of PM₂.₅ are insensitive to NH₃ emissions. We find similar results for July but with lower PM₂.₅ decreases under strong NH₃ emission reductions than those in January (Figure S6). Figure 4 summarizes the changes in BTH mean PM₂.₅ and its components as driven by NH₃ emission changes in North China for January and July 2015. The decreases of PM₂.₅ concentration associated with NH₃ emission reductions follow a power exponential function in January leading to small PM₂.₅ changes under small NH₃ emission reductions. The responses in July are closer to a linear function. BTH mean PM₂.₅ in July would be decreased by 1.6/5.3/11.1 μg m⁻³ with 20%/60%/100% NH₃ emission reductions in North China. The PM₂.₅ components in both months show that aerosol sulfate has minor changes and aerosol nitrate can be substantially decreased with reducing NH₃ emissions, as also pointed out by Han et al. (2020). We find stronger PM₂.₅ responses in heavy pollution episodes in both months. As shown in Figure 4, for the highest 5% PM₂.₅ concentrations, their values can be decreased by 4.5/24.2/64.4 μg m⁻³ when NH₃ emissions in North China are reduced by 20%/60%/100% in January. By contrast, the cleanest 5% PM₂.₅ concentrations have nearly no change associated with NH₃ emission reductions.
13.2 μg m⁻³ (14.4-32.0% of PWC) in July, illustrating PM_{2.5} air quality improvements we can achieve by the NH₃ emission controls under 2015 emission conditions. The analyses above have emphasized strong nonlinear responses of PM_{2.5} concentrations to NH₃ emission changes in North China. To better quantify their effectiveness, we further calculate the NH₃ emission control efficiency based on the sensitivity simulations as $\beta_1 = \frac{\Delta PWC}{\Delta E}$, where $\frac{\Delta PWC}{PWC}$ is the relative change of PWC and $\frac{\Delta E}{E}$ is the relative change of NH₃ emissions in North China, denoting the relative response of PWC in percentage to 1% reduction in NH₃ emissions under each NH₃ emission scenario. We also calculate the absolute efficiency $\beta_2 = \frac{PWC}{\Delta E}$, describing changes in PM_{2.5} per unit mass change in NH₃ emissions as shown in Figure S7. We find for the 2015 emission condition, the BTH mean $\beta_1$ efficiencies in January increase from 0.055 %/% in the Base condition to 0.48 %/% (a factor of 8.7 higher) when NH₃ emissions are reduced by 80%. The calculated $\beta_1$ efficiencies in July also indicate a nonlinear response, yet much weaker than January, with values of 0.22 %/% for the Base condition and 200% higher (0.65 %/%) when NH₃ emissions are 80% lower.

5. Effects of NOₓ and SO₂ emission changes

We now quantify the influence of NOₓ and SO₂ emission reductions on NH₃ emissions control efficiency. This can be estimated by comparing the S1RN with S2RN and S3RN scenarios. As described above, S1RN scenarios reflect NH₃ emission reductions for the 2015 emission condition, S2RN scenarios reflect the 2017 condition, and S3RN scenarios further consider 20% NOₓ emission reduction. The differences of S2R0 minus Base and S3R0 minus S2R0 then estimate, respectively, the impacts of 2015-2017 SO₂/NOₓ emission changes and further 20% NOₓ emission reductions. The 2015-2017 emission changes (~40% reduction in SO₂ emissions and ~8% reduction in NOₓ emissions) have led to decreases in BTH PWC PM_{2.5} (in both months (2.7 μg m⁻³ in January and 4.0 μg m⁻³ in July), mainly driven by the SO₂ emission reductions (Figure S8). With further 20% NOₓ emission reductions, the BTH PWC would decrease by 1.9 μg m⁻³ in July, but increase by 1.0 μg m⁻³ in January (Figure S8). Reducing North China NOₓ emissions alone in winter would increase ozone levels due to decreases in its titration and further enhance the formation of secondary aerosols, as recently found during the COVID-19 pandemic (Huang et al 2020).

Figure 5 shows the changes in BTH PWC and $\beta_1$ efficiency of NH₃ emission reduction in the S1RN, S2RN, and S3RN scenarios for January and July. We can see that the effects of 2015-2017 SO₂/NOₓ emission reductions on BTH PWC improvements (4.6 in January and 4.9 in July) are comparable to 40-60% NH₃ emission reduction in 2015. The maximum BTH PWC reductions as can be achieved by NH₃ emission controls are 26.7 μg m⁻³ in January and 13.2 μg m⁻³ in July for the S1RN scenarios, and 27.6 μg m⁻³ in January and 9.4 μg m⁻³ in July for the S3RN scenarios. The much larger changes in NH₃ emission reduction in 2015 (13.2 vs. 9.4 μg m⁻³) than January are mainly driven by the different responses of PM_{2.5} to the 20% NOₓ emission reduction. We can see that the impacts of the further 20% emission reduction on BTH PWC (as contributed by decreases in aerosol nitrate due to the NOₓ emission reduction) in July become smaller with decreasing NH₃ emissions. Changes in SO₂ and NOₓ emissions can thus affect the efficiency of NH₃ emission reduction on PM_{2.5} pollution. As shown in Figure 5, the 2015-2017 emission changes have generally decreased $\beta_1$ efficiencies, for no NH₃ emission reduction scenarios, from 0.055 %/% to 0.038 %/% (30% reduction) in January and from 0.22 %/% to 0.19 %/% (14% reduction) in July. SO₂ emission controls generally decrease the formation of ammonium sulfate aerosol, causing NH₃ in the air being saturated and thus suppressing the effectiveness of NH₃ emission controls. The additional 20% NOₓ emission reduction would further suppress $\beta_1$ efficiencies in July but increase them in January, reflecting the enhanced nitrate formation due to NOₓ emission reduction in BTH winter as...
discussed above. Our results indicate that NH$_3$ emission controls at an earlier stage will be more effective for PM$_{2.5}$ air pollution regulation, and a joint NO$_x$ and NH$_3$ emission control in winter will be more effective than controlling NO$_x$ alone.

6. Conclusions

In summary, we have shown strong nonlinear responses of PM$_{2.5}$ air pollution to NH$_3$ emission reductions in North China. Using three sets of model simulations testing NH$_3$ emission reductions under different SO$_2$/NO$_x$ emission conditions, we find that under the current NH$_3$ emission condition changes in PM$_{2.5}$ concentrations in North China associated with NH$_3$ emission reductions follow a power exponential function in January. The BTH January monthly mean PWC PM$_{2.5}$ concentrations would only decrease 1.4-3.8 μg m$^{-3}$ (1.1-2.9% of PM$_{2.5}$) when NH$_3$ emissions in North China were reduced by 20-40%, but the decreases would reach 8.1-26.7 μg m$^{-3}$ (6.2-20.5% of PM$_{2.5}$) with 60-100% NH$_3$ emission reductions. Such nonlinearity reflects a switch of NH$_3$-saturated to NH$_3$-limited condition for SIA, in particular, aerosol nitrate formation. The PM$_{2.5}$ changes in July also show a nonlinear response, but the nonlinearity is much weaker than January. As SO$_2$ emissions in North China have substantially reduced over 2015-2017, we find that has lowered the efficiency of NH$_3$ emission controls on PM$_{2.5}$ air pollution in both winter and summer. Future reductions of NO$_x$ emissions may partly enhance PM$_{2.5}$ pollution in BTH winter due to the weakened titration effect, and can be offset by jointly controlling NH$_3$ emissions. Our results emphasize the importance of an accurate NH$_3$ emission estimate on the assessment of effectiveness of NH$_3$ emission controls, and also support the need to jointly consider emission reductions of SO$_2$, NO$_x$, and NH$_3$ for mitigating SIA air pollution.

Figure 1. Observed and WRF-Chem Base simulated surface PM$_{2.5}$ concentrations over North China in January and July 2015. The left panels show time series of hourly observations (black dots) and model results (blue lines) by averaging 39 stations in North China. The right panels show space distributions of observed (circles) and simulated (contours) monthly mean concentrations. Regional monthly mean observed values (OBS) and corresponding model results (MOD), and their correlation coefficients (temporally and spatially) are shown inset.
Figure 2. Observed and simulated surface NH$_3$ concentrations in North China for the periods of 01-31 January (top panels) and 15-31 July (bottom panels) 2015. The left panels show comparison of measurements (circles) with the Base simulation, and central panels show comparisons with sensitivity simulations (with NH$_3$ emissions in North China reduced by 20% for January and increased by 20% for July). Regional mean observed values (OBS) and corresponding model results (MOD), and their correlation coefficients are shown inset. The right panels show changes in Beijing-Tianjin-Hebei (BTH) mean gaseous NH$_3$ (blue lines), aerosol ammonium (NH$_4^+$, red lines), and total reduced nitrogen (NH$_x$ = NH$_3$+NH$_4^+$, black lines) when NH$_3$ emissions in North China are decreased for January and July 2015.

Figure 3. (Top panels) January mean changes in surface PM$_{2.5}$ concentrations due to NH$_3$ emission reductions in North China estimated as the differences between the Base simulation and S1RN scenarios with NH$_3$ emissions reduced by N% ($N = 20/40/60/80/100$). (Bottom panels) Excess NH$_3$ concentrations in January as estimated by the formula described in the text for the Base simulation and S1RN scenarios ($N = 20/40/60/80$). Regional mean values in Beijing and in BTH are shown inset.
Figure 4. Effectiveness of NH$_3$ emission reductions in North China on BTH regional mean surface PM$_{2.5}$ pollution in January (top panels) and July (bottom panels) 2015. The left panels show BTH geometric mean PM$_{2.5}$ (orange lines), sulfate (red shading), ammonium (green shading), and nitrate (blue shading) levels. The central panels show reductions in monthly mean (black lines), minimum (blue dashed lines), and maximum (red dashed lines) PM$_{2.5}$ concentrations. The right panels show changes in population-weighted PM$_{2.5}$ (PWC) together with sulfate, ammonium, and nitrate contributions. Numbers inset are their values (ug m$^{-3}$) in the Base simulation.

Figure 5. Changes in BTH PWC (left panels) and NH$_3$ emission reduction efficiency (right panels) in the S1RN scenarios (black lines; the 2015 emission condition), S2RN scenarios (green lines; the 2017 emission condition), and S3RN scenarios (orange lines, the 2017 emission condition with NO$_x$ emission further reduced by 20%) in January (top panels) and July (bottom panels). BTH PWC
Changes are relative to the Base simulated results (i.e., S1R0). PWC values for S1R0, S2R0, and S3R0 are given inset.

**Table 1. Emission settings in the WRF-Chem simulation scenarios.**

<table>
<thead>
<tr>
<th>Simulation scenario</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base</td>
<td>The 2015 emission conditions, also referred as S1R0</td>
</tr>
<tr>
<td>S1RN ((N = 20/40/60/100))</td>
<td>NH(_3) emission is reduced by 20%, 40%, 60%, 80% and 100%, respectively.</td>
</tr>
<tr>
<td>S2RN ((N = 0/20/40/60/100))</td>
<td>Similar to S1RN, but further reduces the NO(_x) and SO(_2) emissions from the levels of 2015 to those of 2017 in North China.</td>
</tr>
<tr>
<td>S3RN ((N = 0/20/40/60/100))</td>
<td>Similar to S2RN, but further reduces NO(_x) emissions by 20% in North China.</td>
</tr>
</tbody>
</table>

**References**

Chen D et al 2016 Simulations of sulfate–nitrate–ammonium (SNA) aerosols during the extreme haze events over northern China in October 2014 Atmos. Chem. Phys. 16 10707-24


Emmons L K et al 2010 Description and evaluation of the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4) Geosci. Model Dev. 3 43-67

Fu X et al 2017 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. Lett. 4 221-7


Ge B et al 2019 Role of Ammonia on the Feedback Between AWC and Inorganic Aerosol Formation During Heavy Pollution in the North China Plain Earth. Space. Sci. 6 1675-93


Guo H et al 2018 Effectiveness of ammonia reduction on control of fine particle nitrate Atmos. Chem. Phys. 18 12241-56

Han X et al 2020 Numerical analysis of agricultural emissions impacts on PM2.5 in China using a high-resolution ammonia emission inventory Atmos. Chem. Phys. 20 9979-96


Huang R J et al 2014 High secondary aerosol contribution to particulate pollution during haze events in China Nature **514** 218-22


Li M et al 2017 MIX: a mosaic Asian anthropogenic emission inventory under the international collaboration framework of the MICS-Asia and HTAP Atmos. Chem. Phys. **17** 935-63


Pinder R W et al 2006 Temporally resolved ammonia emission inventories: Current estimates, evaluation tools, and measurement needs J. Geophys. Res.-Atmos. **111**

Seinfeld J H and Pandis S N 2006 Atmospheric Chemistry and Physics: From Air Pollution to Climate Change (New York: Wiley)

Song S et al 2018 Fine-particle pH for Beijing winter haze as inferred from different thermodynamic equilibrium models Atmos. Chem. Phys. **18** 7423-38


Sun Y et al 2012 Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor Atmos. Environ. **51** 250-9


Wiedinmyer C et al 2011 The Fire INventory from NCAR (FINN): A high resolution global model to estimate the emissions from open burning Geosci. Model Dev. **4** 625-41

Xu Z et al 2019 High efficiency of livestock ammonia emission controls in alleviating particulate nitrate during a severe winter haze episode in northern China Atmos. Chem. Phys. **19** 5605-13
Zaveri R A et al 1999 A new lumped structure photochemical mechanism for large-scale applications J. Geophys. Res.-Atmos. 104 30387-415
Zaveri R A et al 2008 Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) J. Geophys. Res. 113
Zhang L et al 2015 Source attribution of particulate matter pollution over North China with the adjoint method Environ. Res. Lett. 10 084011
Zhang L et al 2018 Agricultural ammonia emissions in China: reconciling bottom-up and top-down estimates Atmos. Chem. Phys. 18 339-55
Zhang Q et al 2019 Drivers of improved PM$_{2.5}$ air quality in China from 2013 to 2017 Proc. Natl Acad. Sci. USA 116 24463-9
Zhao P S et al 2013 Characteristics of concentrations and chemical compositions for PM$_{2.5}$ in the region of Beijing, Tianjin, and Hebei, China Atmos. Chem. Phys. 13 4631-44
Zheng B et al 2018 Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions Atmos. Chem. Phys. 18 14095-111