Trends in secondary inorganic aerosol pollution in China and its responses to emission controls of precursors in wintertime

Fanlei Meng[1#], Yibo Zhang[2#], Jiahui Kang[1], Mathew R. Heal[3], Stefan Reis[4,3,5], Mengru Wang[6], Lei Liu[7], Kai Wang[1], Shaocai Yu[2*], Pengfei Li[8], Jing Wei[9], Yong Hou[1], Ying Zhang[1], Xuejun Liu[1], Zhenling Cui[1], Wen Xu[1*], Fusuo Zhang[1]

[1]College of Resources and Environmental Sciences, National Academy of Agriculture Green Development, Key Laboratory of Plant–Soil Interactions, Ministry of Education, National Observation and Research Station of Agriculture Green Development (Quzhou, Hebei), China Agricultural University, Beijing 100193, China.

[2]Research Center for Air Pollution and Health, Key Laboratory of Environmental Remediation and Ecological Health, Ministry of Education, College of Environment and Resource Sciences, Zhejiang University, Hangzhou, Zhejiang 310058, P.R. China

[3]School of Chemistry, The University of Edinburgh, David Brewster Road, Edinburgh EH9 3FJ, United Kingdom

[4]UK Centre for Ecology & Hydrology, Penicuik, EH26 0QB, United Kingdom.

[5]University of Exeter Medical School, Knowledge Spa, Truro, TR1 3HD United Kingdom.

[6]Water Systems and Global Change Group, Wageningen University & Research, P.O. Box 47, 6700 AA Wageningen, The Netherlands

[7]College of Earth and Environmental Sciences, Lanzhou University, Lanzhou 730000, China

[8]College of Science and Technology, Hebei Agricultural University, Baoding, Hebei 071000, China

[9]Department of Atmospheric and Oceanic Science, Earth System Science Interdisciplinary Center, University of Maryland, College Park 20740, USA

*Corresponding authors

E-mail addresses: W. Xu (wenxu@cau.edu.cn); S C. Yu (shaocaiyu@zju.edu.cn)

[#] Contributed equally to this work.

ABSTRACT: The Chinese government recently proposed ammonia (NH_3) emissions reductions (but without a specific national target) as a strategic option to mitigate $PM_{2.5}$ pollution. We combined a meta-analysis of nationwide measurements and air quality modelling to identify efficiency gains by striking a balance between controlling NH_3 and acid gas (SO_2 and NO_x) emissions. We found that $PM_{2.5}$ concentrations decreased from 2000 to 2019, but annual mean $PM_{2.5}$ concentrations still exceeded 35 μg m^{-3} at 74% of 1498 monitoring sites in 2015-2019. The concentration of $PM_{2.5}$ and its components were significantly higher (16%-195%) on hazy days than on non-hazy days. Compared with mean values of other components, this difference was more significant for the secondary inorganic ions SO_4^{2-}, NO_3^-, and NH_4^+ (average increase 98%). While sulfate concentrations significantly decreased over the time period, no significant change was observed for nitrate and ammonium concentrations. Model simulations indicate that the effectiveness of a 50% NH_3 emission reduction for controlling SIA concentrations decreased from 2010 to 2017 in four megacity clusters of eastern China, simulated for the month of January under fixed meteorological conditions (2010). Although the effectiveness further declined in 2020 for simulations including the natural experiment of substantial reductions in acid gas emissions during the COVID-19 pandemic, the resulting reductions in SIA concentrations were on average 20.8% lower than that in 2017. In addition, the reduction of SIA concentrations in 2017 was greater for 50% acid gas reductions than for the 50% NH_3 emissions reduction. Our findings indicate that persistent secondary inorganic aerosol pollution in China is limited by acid gases emissions, while an additional control on NH_3 emissions would become more important as reductions of SO_2 and NO_x emissions progress.

Keywords: Air pollution, Particulate matter, Second inorganic aerosols, Anthropogenic emission, Ammonia.

1. Introduction

Over the past two decades, China has experienced severe $PM_{2.5}$ (particulate matter with aerodynamic diameter ≤ 2.5 μm) pollution (Huang et al., 2014; Wang et al., 2016), leading to adverse impacts on human health (Liang et al., 2020) and the environment (Yue et al., 2020). In 2019, elevated $PM_{2.5}$ concentrations accounted for 46% of polluted days in China and $PM_{2.5}$ was officially identified as a key year-round air pollutant (MEEP, 2019). Mitigation of $PM_{2.5}$ pollution is therefore the most pressing current challenge to improve China's air quality.

The Chinese government has put a major focus on particulate air pollution control through a series of policies, regulations, and laws to prevent and control severe air pollution. Before 2010, the Chinese government mainly focused on controlling SO_2 emissions via improvement of energy efficiency, with less attention paid to NO_x abatement (CSC, 2007, 2011, 2016). For example, the 11th Five-Year Plan (FYP) (2006-2010) set a binding goal of a 10% reduction for SO_2 emission (CSC, 2007). The 12th FYP (2011-2015) added NO_x regulation and required 8% and 10% reductions for SO_2 and NO_x emissions, respectively (CSC, 2011) This was followed by further reductions in SO_2 and NO_x emissions of 15% and 10%, respectively, in the 13th FYP (2016-2020) (CSC, 2016). In response to the severe haze events of 2013, the Chinese State Council promulgated the toughest-ever 'Atmospheric Pollution Prevention and Control Action Plan' in September 2013, aiming to reduce ambient $PM_{2.5}$ concentrations by 15-20% in 2017 relative to 2013 levels in metropolitan regions (CSC, 2013). As a result of the implementation of stringent control measures, emissions reductions markedly accelerated from 2013-2017, with decreases of 59% for SO_2, 21% for NO_x, and 33% for primary $PM_{2.5}$ (Zheng et al., 2018). Consequently, significant reductions in annual mean $PM_{2.5}$ concentrations were observed nationwide (Zhang et al., 2019; Yue et al., 2020), in the range 28-40% in the metropolitan regions (CSC, 2018a). To continue its efforts in tackling air pollution, China promulgated the Three-Year Action Plan (TYAP) in 2018 for Winning the Blue-Sky Defense Battle (CSC, 2018b), which required a further 15% reduction in NO_x emissions by 2020 compared to 2018 levels.

Despite a substantial reduction in $PM_{2.5}$ concentrations in China, the proportion of secondary aerosols during severe haze periods is increasing (An et al., 2019), and can comprise up to 70% of $PM_{2.5}$ concentrations (Huang et al., 2014). Secondary inorganic aerosols (SIA, the sum of sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+)) were found to be of equal importance to secondary organic aerosols, with 40-50% contributions to $PM_{2.5}$ in eastern China (Huang et al., 2014; Yang et al., 2011). The acid gases (i.e., NO_x, SO_2), together with NH_3, are crucial precursors of SIA via chemical reactions that form particulate ammonium sulfate, ammonium bisulfate, and ammonium nitrate (Ianniello et al., 2010). In addition to the adverse impacts on human health via fine particulate matter formation (Liang et al., 2020; Kuerban et al., 2020), large amounts of NH_3 and its aerosol-phase products also lead to nitrogen deposition and consequently to environmental degradation (Ortiz-Montalvo et al., 2014; Pan et al., 2015; Xu et al., 2015, 2018; Zhan et al., 2021).

Following the successful controls on NO_x and SO_2 emissions since 2013 in China, some studies found SO_4^{2-} exhibited much larger decline than NO_3^- and NH_4^+ , which lead to a rapid transition from sulfate-driven to nitrate-driven aerosol pollution (Li et al., 2019, 2021; Zhang et al., 2019). Attention is turning to NH_3 emissions as a possible means of further $PM_{2.5}$ control (Bai et al., 2019; Kang et al., 2016), particularly as emissions of NH_3 increased between the 1980s and 2010s. Some studies have found that NH_3 limited the formation of SIA in winter in the eastern United States (Pinder et al., 2007) and Europe (Megaritis et al., 2013). Controls on NH_3 emissions have been proposed in the TYAP, although mandatory measures and binding targets have not yet been set (CSC, 2018b). Nevertheless, this proposal means that China will enter a new phase of $PM_{2.5}$ mitigation, with attention now given to both acid gas and NH_3 emissions. However, in the context of effective control of $PM_{2.5}$ pollution via its SIA component, two key questions arise: 1) what are the responses of the constituents of SIA to implementation of air pollution control policies, and 2) what is the relative efficiency of NH_3 versus acid gas emission controls to reduce SIA pollution?

To fill this evidence gap and provide useful insights for policy-making to improve air quality in China, this study adopts an integrated assessment framework. With respect to the emission control policy summarized above, China's $PM_{2.5}$ control can be divided into three periods: period I (2000–2012), in which $PM_{2.5}$ was not the targeted pollutant; period II (2013–2016), the early stage of targeted $PM_{2.5}$ control policy implementation; and period III (2017–2019), the latter stage with more stringent policies. Therefore, our research framework consists of two parts: (1) assessment of trends in annual mean concentrations of $PM_{2.5}$, its chemical components and SIA gaseous precursors from meta-analyses and observations; (2) quantification of SIA responses to emissions reductions in NH_3 and acid gases using the Weather Research and Forecasting and Community Multiscale Air Quality (WRF/CMAQ) models.

2. Materials and methods

2.1. Research framework

This study developed an integrated assessment framework to analysis the trends of secondary inorganic aerosol and strategic options to reduce SIA and $PM_{2.5}$ pollution in

China (Fig. 1). The difference in $PM_{2.5}$ chemical components between hazy and non-hazy days was first assessed by meta-analysis of published studies. These were interpreted in conjunction with the trends in air concentrations of $PM_{2.5}$ and its secondary inorganic aerosol precursors (SO_2, NO_2, and NH_3) derived from surface measurements and satellite observations. The potential of SIA and $PM_{2.5}$ concentration reductions from precursor emission reductions was then evaluated using the Weather Research and Forecasting and Community Multiscale Air Quality (WRF/CMAQ) models.

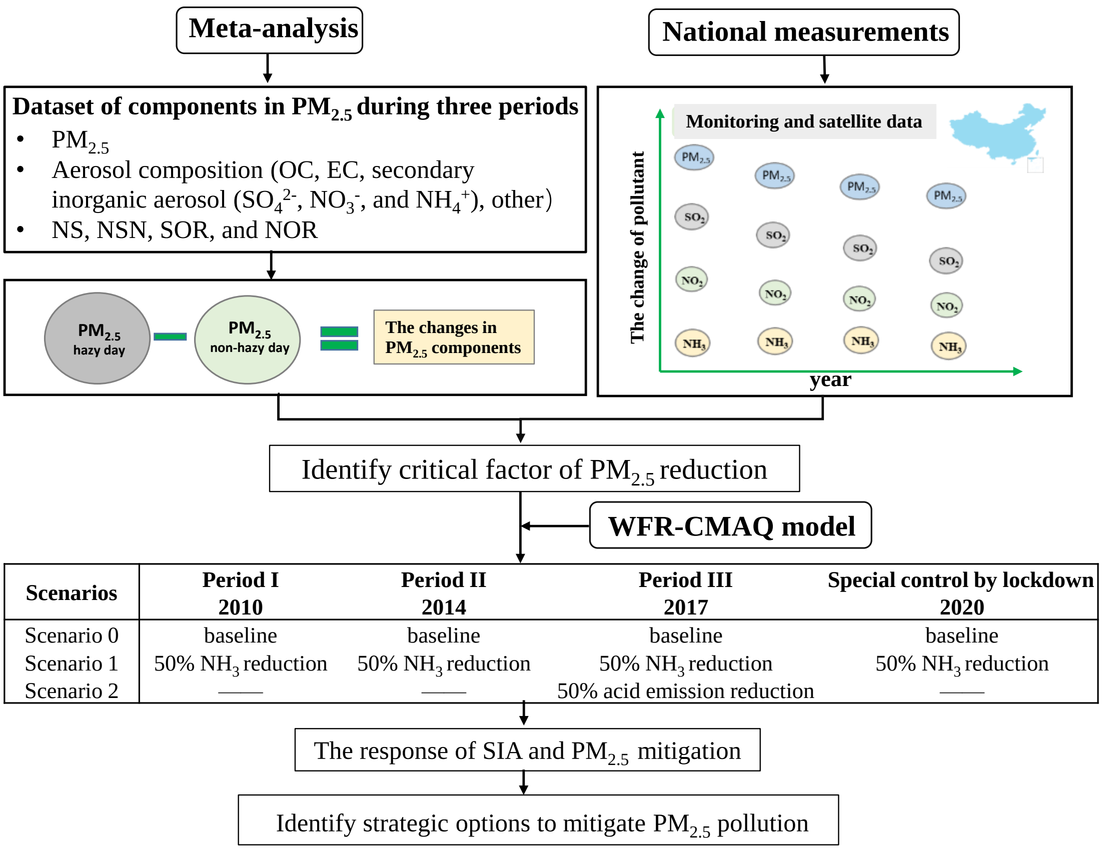

Fig. 1. Integrated assessment framework for Chinese $PM_{2.5}$ mitigation strategic options. OC is organic carbon, EC is elemental carbon, NO_3^- is nitrate, SO_4^{2-} is sulfate, and NH_4^+ is ammonium. NS is the slope of the regression equation between $[NH_4^+]$ and $[SO_4^{2-}]$, NSN is the slope of the regression equation between $[NH_4^+]$ and $[SO_4^{2-} + NO_3^-]$, SOR is sulfur oxidation ratio, and NOR is nitrogen oxidation ratio. SIA is secondary

inorganic aerosols. WRF-CMAQ is Weather Research and Forecasting and Community Multiscale Air Quality models.

2.2. Meta-analysis of $PM_{2.5}$ and its chemical components

Meta-analyses can be used to quantify the differences in concentrations of $PM_{2.5}$ and its secondary inorganic aerosol components (NH_4^+, NO_3^-, and SO_4^{2-}) between hazy and non-hazy days and to identify the major pollutants on non-hazy days (Wang et al., 2019b); this provides evidence for effective options on control of precursor emissions (NH_3, NO_2, and SO_2) for reducing occurrences of hazy days. To build a database of atmospheric concentrations of $PM_{2.5}$ and chemical components between hazy and non-hazy days, we conducted a literature survey using the Web of Science and the China National Knowledge Infrastructure for papers published between January 2000 and January 2020. The keywords included: (1) "particulate matter," or "aerosol," or "$PM_{2.5}$" and (2) "China" or "Chinese". Studies were selected based on the following conditions:

(1) Measurements were taken on both hazy and non-hazy days.

(2) $PM_{2.5}$ chemical components were reported.

(3) If hazy days were not defined in the screened articles, the days with $PM_{2.5}$ concentrations > 75 μg m^{-3} (the Chinese Ambient Air Quality Standard Grade II for $PM_{2.5}$ (CSC, 2012)) were treated as hazy days.

(4) If an article reported measurements from different monitoring sites in the same city, e.g. Mao et al. (2018) and Xu et al. (2019), then each measurement was considered an independent study.

(5) If there were measurements in the same city for the same year, e.g. Tao et al. (2016) and Han et al. (2017), then each measurement was treated as an independent study.

One hundred articles were selected based on the above conditions with the lists provided in the Supporting Material dataset. For each selected study, we documented the study sites, study periods, seasons, aerosol types, and aerosol species mass concentrations (in μg m^{-3}) over the entire study period (2000–2019) (the detailed data are provided in the dataset). In total, the number of sites contributing data to the meta-analysis was 267 and their locations are shown in Fig. S1. If relevant data were not directly presented in studies, a GetData Graph Digitizer (Version 2.25, http://www.getdatagraph-digitizer.com) was used to digitize concentrations of $PM_{2.5}$ chemical components from figures. The derivations of other variables such as sulfur and nitrogen oxidation ratios are described in Supplementary Information Method 1.

Effect sizes were developed to normalize the combined studies' outcomes to the same scale. This was done through the use of log response ratios (lnRR) (Nakagawa et al., 2012; Ying et al., 2019). The variations in aerosol species were evaluated as follows:

$$\ln RR = \ln \left(\frac{X_p}{X_n}\right) \tag{1}$$

where X_p and X_n represent the mean values of the studied variables of $PM_{2.5}$ components on hazy and non-hazy days, respectively. The mean response ratio was then estimated as:

$$RR = \exp\left[\sum \ln RR(i) \times W(i) \,/ \sum W(i)\right] \tag{2}$$

where $W(i)$ is the weight given to that observation as described below. Finally, variable-related effects were expressed as percent changes, calculated as (RR−1) ×100%. A 95% confidence interval not overlapping with zero indicates that the difference is significant. A positive or negative percentage value indicates an increase or decrease in the response variables, respectively.

We used inverse sampling variances to weight the observed effect size (RR) in the meta-analysis (Benitez-Lopez et al., 2017). For the measurement sites where standard deviations (SD) or standard errors (SE) were absent in the original study reports, we used the "Bracken, 1992" approach to estimate SD (Bracken et al., 1992). The variationrelated chemical composition of $PM_{2.5}$ was assessed by random effects in meta-analysis. Rosenberg's fail safe-numbers (N_{f_s}) were calculated to assess the robustness of findings on $PM_{2.5}$ to publication bias (Ying et al., 2019) (See Table S1). The results (effects) were considered robust despite the possibility of publication bias if $N_{f_s} > 5 \times n + 10$, where n indicates the number of sites. The statistical analysis of the concentrations of $PM_{2.5}$ and secondary inorganic ions for three periods used a non-parametric statistical method since concentrations were not normally distributed based on the Kruskal-Wallis test (Kruskal and Walls, 1952). For each species, the Kruskal-Wallis one-way analysis of variance (ANOVA) on ranks among three periods was performed with pairwise comparison using Dunn's method (Dunn, 1964).

2.3. Data collection of air pollutant concentrations

To assess the recent annual trends in China of $PM_{2.5}$ and of the SO_2 and NO_2 gaseous precursors to SIA, real-time monitoring data of these pollutants at 1498 monitoring stations in 367 cities during 2015–2019 were obtained from the China National Environmental Monitoring Center (CNEMC) (http://106.37.208.233:20035/). This is an open-access archive of air pollutant measurements from all prefecture-level cities since January 2015. Successful use of data from CNEMC to determine characteristics of air pollution and related health risks in China has been demonstrated previously (Liu et al., 2016; Kuerban et al., 2020). The geography stations are shown in Fig. S1. The annual mean concentrations of the three pollutants at all sites were calculated from the hourly time-series data according to the method of Kuerban et al. (2020). Information about sampling instruments, sampling methods, and data quality controls for $PM_{2.5}$, SO_2, and NO_2 is provided in Supplementary Method 2. Surface NH_3 concentrations over China for the 2008–2016 (the currently available) were extracted from the study of Liu et al. (2019a). Further details are in Supplementary Method 2.

2.4. WRF/CMAQ model simulations

The Weather Research and Forecasting model (WRFv3.8) and the Models-3 community multi-scale air quality (CMAQv5.2) model were used to evaluate the impacts of emission reductions on SIA and $PM_{2.5}$ concentrations over China. The simulations were conducted at a horizontal resolution of 12 km × 12 km. The simulation domain covered the whole of China, part of India and east Asia. In the current study, focus was on the following four regions in China: Beijing-Tianjin-Hebei (BTH), Yangtze River Delta (YRD), Pearl River Delta (PRD), and Sichuan Basin (SCB). The model configurations used in this study were the same as those used in Wu et al. (2018a) and are briefly described here. The WRFv3.8 model was applied to generate meteorological inputs for the CMAQ model using the National Center for Environmental Prediction Final Operational Global Analysis (NCEP-FNL) dataset (Morrison et al., 2009). Default initial and boundary conditions were used in the simulations. The carbon-bond (CB05) gas-phase chemical mechanism and AERO6 aerosol module were selected in the CMAQ configuration (Guenther et al., 2012). Anthropogenic emissions for 2010, 2014 and 2017 were obtained from the Multi-resolution Emission Inventory (http://meicmodel.org) with 0.25 ° × 0.25 ° spatial resolution and aggregated to 12 km×12 km resolution (Zheng et al., 2018; Li et al., 2017). Each simulation was spun-up for six days in advance to eliminate the effects of the initial conditions.

The years 2010, 2014 and 2017 were chosen to represent the anthropogenic emissions associated with the periods I, II, III, respectively. January was selected as the typical simulation month because wintertime haze pollution frequently occurs in this month (Wang et al., 2011; Liu et al., 2019b). January of 2010 was also found to have $PM_{2.5}$ pollution more serious than other months (Geng et al., 2017, 2021). The sensitivity scenarios of emissions in January can therefore help to identify the efficient option to control haze pollution.

The Chinese government has put a major focus on acid gas emission control through a series of policies in the past three periods (Fig. S2). The ratio decreases of anthropogenic emissions SO_2 and NO_x in January for the years 2010, 2014, 2017 and 2020 are presented in SI Tables S2 and S3, respectively. The emissions from surrounding countries were obtained from the Emissions Database for Global Atmospheric Research (EDGAR): HTAPV2. The scenarios and the associated reductions of NH_3, NO_x and SO_2 for selected four years in three periods can be found in Fig. 1.

The sensitivities of SIA and $PM_{2.5}$ to NH_3 emissions reductions were determined from the average $PM_{2.5}$ concentrations in model simulations without and with an additional 50% NH_3 emissions reduction. The choice of 50% additional NH_3 emissions reduction is based on the feasibility and current upper bound of NH_3 emissions reduction expected to be realized in the near future (Liu et al., 2019a; Zhang et al., 2020a; Table S4). For example, Zhang et al. (2020a) found that the mitigation potential of NH_3 emissions from cropland production and livestock production in China can reach up to 52% and 58%, respectively. To eliminate the influences of varying meteorological conditions, all simulations were conducted under the fixed meteorological conditions of 2010.

During the COVID-19 lockdown in China, emissions of primary pollutants were subject to unprecedented reductions due to national restrictions on traffic and industry; in particular, emissions of NO_x and SO_2 reduced by 46% and 24%, respectively, averaged across all Chinese provinces (Huang et al., 2021). We therefore also ran simulations applying the same reductions in NO_x and SO_2 (based on 2017 MEIC) that were actually observed during the COVID-19 lockdown as a case of special control in 2020.

2.5 Model performance

The CMAQ model has been extensively used in air quality studies (Zhang et al., 2019; Backes et al., 2016) and the validity of the chemical regime in the CMAQ model had been confirmed by our previous studies (Zhang et al., 2021a; Wang et al., 2020a, 2021a). In this study, we used surface measurements from previous publications (e.g., (Xiao et al., 2020, 2021; Geng et al., 2019; Xue et al., 2019) and satellite observations to validate the modelling meteorological parameters by WRF model and air concentrations of $PM_{2.5}$ and associated chemical components by CMAQ model. The meteorological measurements used for validating the WRF model performances were obtained from the National Climate Data Center (NCDC) (ftp://ftp.ncdc.noaa.gov/pub/data/noaa/). For validation of the CMAQ model, monthly mean concentrations of $PM_{2.5}$ were obtained from ChinaHighAirPollutants (CHAP, https://weijing-rs.github.io/product.html) database. We also collected ground-based observations from previous publications to validate the modeling concentrations of SO_4^{2-}, NO_3^-, and NH_4^+. The detailed information of the monitoring sites is presented in Table S5. Further information about the modelling is given in Supplementary Method 3 and Figs. S3-S7 and Table S5.

3. Results and discussion

3.1. Characteristics of $PM_{2.5}$ and its chemical components from the meta-analysis and from nationwide observations

The meta-analysis based on all published analyses of $PM_{2.5}$ and chemical component measurements during 2000–2019 reveals the changing characteristics of $PM_{2.5}$. To assess the annual trends in $PM_{2.5}$ and its major chemical components, we made a three-period comparison using the measurements at sites that include both $PM_{2.5}$ and secondary inorganic ions SO_4^{2-}, NO_3^-, and NH_4^+ (Fig. 2). The $PM_{2.5}$ concentrations on both hazy and non-hazy days showed no significant trend from period I to period II based on the Kruskal-Wallis test. This could be explained by the enhanced atmospheric oxidation capacity (Huang et al., 2021), faster deposition of total inorganic nitrate (Zhai et al., 2021) and the changes of atmospheric circulation (Zheng et al., 2015; Li et al., 2020). However, the observed concentrations of $PM_{2.5}$ showed a downward trend from Period I to Period III on the non-hazy days, decreasing by 8.2% (Fig. 2a), despite no significant decreasing trend on the hazy days (Fig. 2a). In addition, the annual mean $PM_{2.5}$ concentrations from the nationwide measurements showed declining trends during 2015-2019 averaged across all China and for each of the BTH, YRD, SCB, and PRD megacity clusters of eastern China (Fig. 3a, d).

These results reflect the effectiveness of the pollution control policies (Fig. S2) implemented by the Chinese government at the national scale. Nevertheless, $PM_{2.5}$ remained at relatively high levels. Over 2015–2019, the annual mean $PM_{2.5}$ concentrations at 74% of the 1498 sites (averaging 51.9 ± 12.4 μg m^{-3}, Fig. 3a) exceeded the Chinese Grade-II Standard (GB 3095–2012) of 35 μg m^{-3} (MEPC, 2012), indicating that $PM_{2.5}$ mitigation is a significant challenge for China.

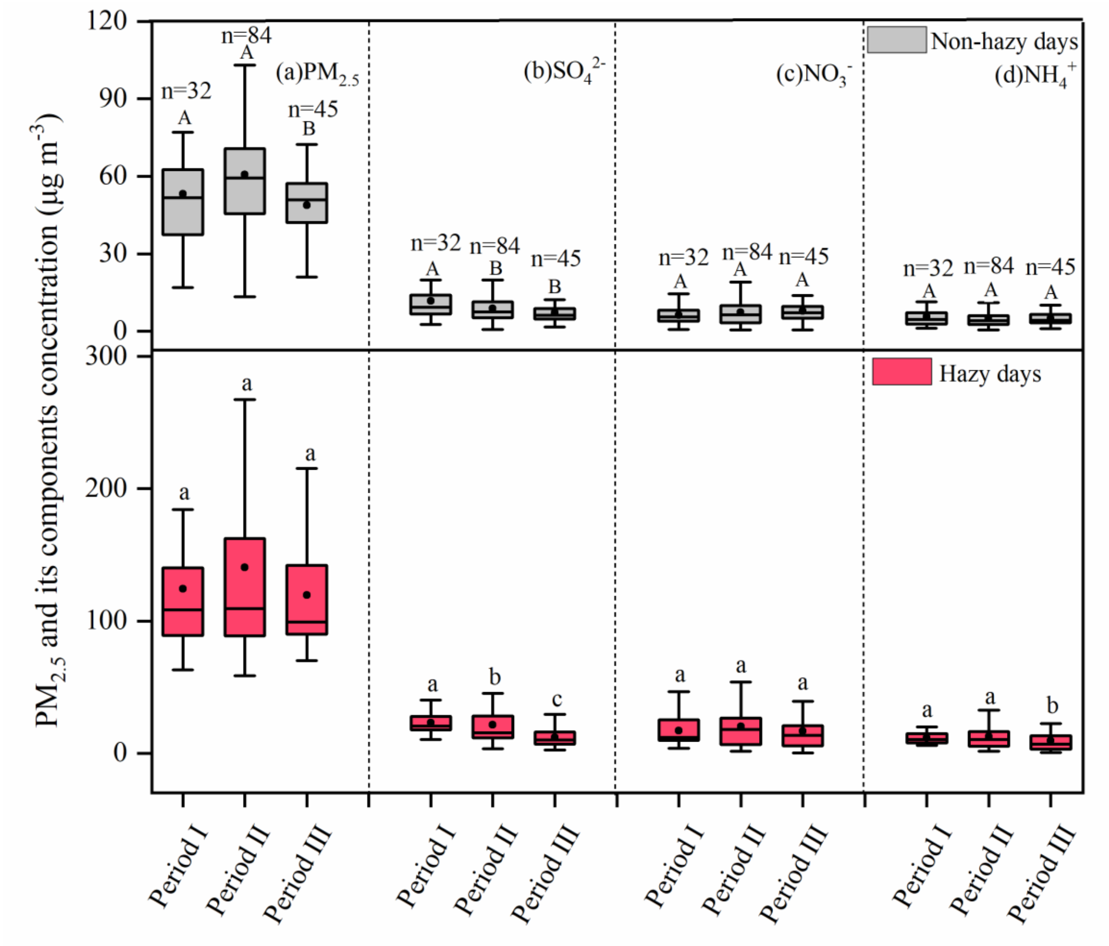

Fig. 2. Comparisons of observed concentrations of (a) $PM_{2.5}$, (b) SO_4^{2-}, (c) NO_3^-, and (d) NH_4^+ between non-hazy and hazy days in Period I (2000–2012), Period II (2013–2016), and Period III (2017–2019). Bars with different letters denote significant differences among the three periods (P <0.05) (upper and lowercase letters for non-hazy and hazy days, respectively). The upper and lower boundaries of the boxes represent the 75th and 25th percentiles; the line within the box represents the median value; the whiskers above and below the boxes represent the 90th and 10th percentiles; the point within the box represents the mean value. Comparison of the pollutants among the three-periods using Kruskal-Wallis and Dunn's test. The n represents independent sites; more detail on this is presented in Section 2.2.

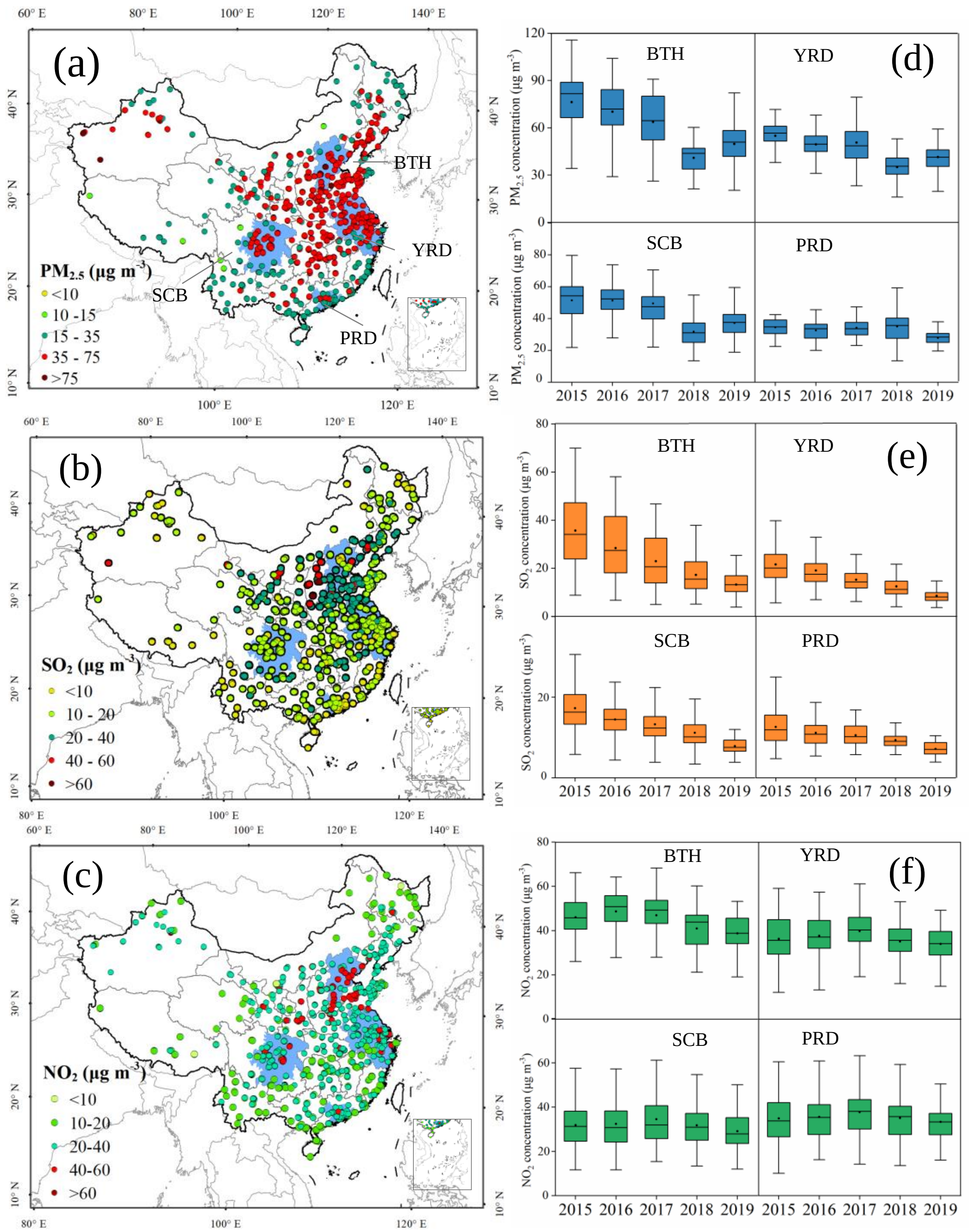

Fig. 3. Left: spatial patterns of annual mean observed concentration of (a) $PM_{2.5}$, (b) SO_2, (c) NO_2 at 1498 sites, averaged for 2015–2019. Right: the annual observed concentrations of (d) $PM_{2.5}$, (e) SO_2, and (f) NO_2 for 2015-2019 in four megacity clusters (BTH: Beijing-Tianjin-Hebei, YRD: Yangtze River Delta, SCB: Sichuan Basin, PRD: Pearl River Delta). The locations of the regions are indicated by the blue shading on the map. The upper and lower boundaries of the boxes represent the 75th and 25th

percentiles; the line within the box represents the median value; the whiskers above and below the boxes represent the 90th and 10th percentiles; the point within the box represents the mean value.

To further explore the underlying drivers of $PM_{2.5}$ pollution, we analyzed the characteristics of $PM_{2.5}$ chemical components and their temporal changes in China. The concentrations of $PM_{2.5}$ and all its chemical components (except F^- and Ca^{2+}) were significantly higher on hazy days than on non-hazy days (Fig. 4A). Compared with other components this difference was more significant for secondary inorganic ions (i.e., SO_4^{2-}, NO_3^-, and NH_4^+). Sulfur oxidation ratio (SOR) and nitrogen oxidation ratio (NOR) were also 58.0% and 94.4% higher on hazy days than on non-hazy days, respectively, implying higher oxidations of gaseous species to sulfate- and nitrate-containing aerosols on the hazy days (Sun et al., 2006; Xu et al., 2017).

To provide quantitative information on differences in $PM_{2.5}$ and its components between hazy days and non-hazy days, we made a comparison using 46 groups of data on simultaneous measurements of $PM_{2.5}$ and chemical components. The 46 groups refer to independent analyses from the literature that compare concentrations of $PM_{2.5}$ and major components (SO_4^{2-}, NO_3^-, NH_4^+, OC, and EC) on hazy and non-hazy days measured across different sets of sites. The "Other" species was calculated by difference between $PM_{2.5}$ and sum of OC, EC, and secondary inorganic ions (SO_4^{2-}, NO_3^- and NH_4^+). As shown in Fig.4B (a), $PM_{2.5}$ concentrations significantly increased (by 136%) on the hazy days (149.2 ± 81.6 μg m^{-3}) relative to those on the non-hazy days (63.2 ± 29.8 μg m^{-3}). By contrast, each component's proportions within $PM_{2.5}$ differed slightly, with 36% and 40% contributions by SIA on non-hazy days and hazy days, respectively (Fig. 4B(b)). This is not surprising because concentrations of $PM_{2.5}$ and SIA both significantly increased on the hazy days (60.1 ± 37.4 μg m^{-3} for SIA) relative to the non-hazy days (22.4 ± 12.1 μg m^{-3} for SIA). Previous studies have found that increased SIA formation is the major influencing factor for haze pollution in wintertime and summertime (mainly in years since 2013) in major Chinese cities in eastern China (Huang et al., 2014; Wang et al., 2019a; Li et al., 2018). Our results extend confirmation of the dominant role of SIA to $PM_{2.5}$ pollution over a large spatial scale in China and to longer temporal scales.

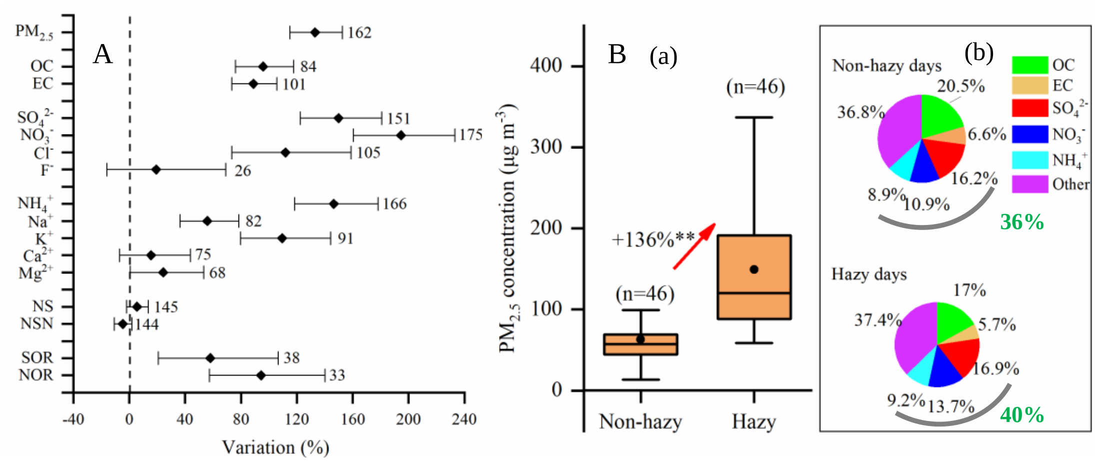

Fig. 4. (A) Variations in $PM_{2.5}$ concentration, aerosol component concentration, NS, NSN, SOR, and NOR from non-hazy to hazy days in China during 2000–2019. (B) (a) Summary of differences in $PM_{2.5}$ concentration between non-hazy and hazy days in China; (b) the average proportions of components of $PM_{2.5}$ on non-hazy and hazy days. NS is the slope of the regression equation between $[NH_4^+]$ and $[SO_4^{2-}]$, NSN is the slope of the regression equation between $[NH_4^+]$ and $[SO_4^{2-} + NO_3^-]$, SOR is sulfur oxidation ratio, and NOR is nitrogen oxidation ratio. The variations are considered significant if the confidence intervals of the effect size do not overlap with zero. ** denotes significant difference (P <0.01) between hazy days and non-hazy days. The upper and lower boundaries of the boxes represent the 75th and 25th percentiles; the line within the box represents the median value; the whiskers above and below the boxes represent the 90th and 10th percentiles; the point within the box represents the mean value. Values adjacent to each confidence interval indicate number of measurement sites. The *n*

represents independent sites; more detail on this is presented in Section 2.2.

The effect values of SIA on the hazy days were significantly higher than those on non-hazy days for all three periods (I, II, and III) (Fig. 5), indicating the persistent prevalence of the SIA pollution problem over the past two decades. Considering changes in concentrations, SO_4^{2-} showed a downward trend from Period I to Period III on the non-hazy days and hazy day, decreasing by 38.6% and 48.3%, respectively (Fig. 2b). These results reflect the effectiveness of the SO_2 pollution control policies (Ronald et al., 2017). In contrast, there were no significant downward trends in concentrations of NO_3^- and NH_4^+ on either hazy or non-hazy days (Fig. 2c, d), but the mean NO_3^- concentration in Period III decreased by 10.5% compared with that in Period II, especially on hazy days (-16.8%). These results could be partly supported by decreased NO_x emissions and tropospheric NO_2 vertical column densities between 2011 and 2019 in China owing to effective NO_x control policies (Zheng et al., 2018; Fan et al., 2021). The lack of significantly downward trends in NH_4^+ concentrations is due to the fact that the total NH_3 emissions in China changed little and remained at high levels between 2000 and 2018, i.e., slightly decreased from 2000 (10.3 Tg) to 2012 (9.3 Tg) (Kang et al., 2016) and then slightly increased between 2013 and 2018 (Liu et al., 2021). The same trends are also found in Quzhou in China, which is a long-term in situ monitoring site (in Quzhou County, North China Plain, operated by our group; the detailed information on Quzhou can be found in Meng et al. (2022) and Feng et al. (2022)) during the period 2012-2020 from previous publications (Xu et al., 2016; Zhang et al., 2021b, noted that data during 2017-2020 are unpublished before) (Fig. S8). Zhang et al. (2020b) found that the clean air actions implemented in 2017 effectively reduced wintertime concentrations of PM_1 (particulate matter with diameter ≤ 1 μm), SO_4^{2-} and

NH_4^+ in Beijing compared with those in 2007, but had no apparent effect on NO_3^-. Li et al. (2021) also found that SO_4^{2-} exhibited a significant decline, However, NO_3^- did not evidently exhibit a decreasing trend in the BTH region.

Our findings are to some extent supported by the nationwide measurements. Annual mean SO_2 concentrations displayed a clear decreasing trend with a 53% reduction in 2019 relative to 2015 for the four megacity clusters of eastern China (Fig. 3b, e), whereas there were only slight reductions in annual mean NO_2 concentrations (Fig. 3c, f). In contrast, annual mean NH_3 concentrations showed an obvious increasing trend in in both northern and southern regions of China, and especially in the BTH region (Fig. S9).

Overall, the above analyses indicate that SO_4^{2-} concentrations responded positively to air policy implementations at the national scale, but that reducing NO_3^- and NH_4^+ remains a significant challenge. China has a history of around 10-20 years for SO_2 and NO_x emission control and has advocated NH_3 controls despite to date no mandatory measures and binding targets having been set (Fig. S2). Nevertheless, $PM_{2.5}$ pollution, especially SIA such as NO_3^- and NH_4^+, is currently a serious problem (Fig. 4 and 5a, b). Some studies have reported that $PM_{2.5}$ pollution can be effectively reduced if implementing synchronous NH_3 and NO_x/SO_2 controls (Liu et al., 2019b). Therefore, based on the above findings, we propose that NH_3 and NO_x/SO_2 emission mitigation should be simultaneously strengthened to mitigate haze pollution.

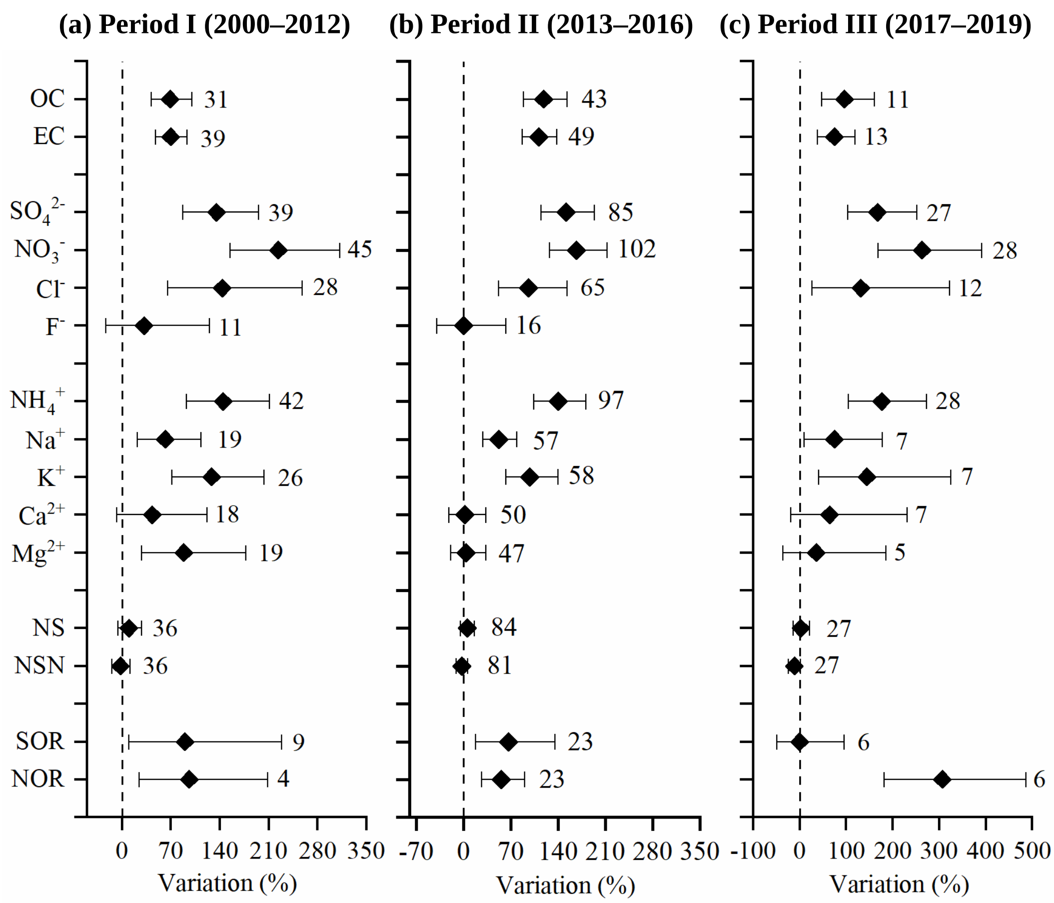

Fig. 5. Variations in $PM_{2.5}$ composition, NS, NSN, SOR, and NOR from non-hazy to hazy days in (a) Period I (2000–2012), (b) Period II (2013–2016), (c) Period III (2017–2019). NS is the slope of the regression equation between [NH_4^+] and [SO_4^{2-}], NSN is the slope of the regression equation between [NH_4^+] and [SO_4^{2-} + NO_3^-], SOR is sulfur oxidation ratio, and NOR is nitrogen oxidation ratio. The variations are statistically significant if the confidence intervals of the effect size do not overlap with zero. Values adjacent to each confidence interval indicate number of measurement sites. The *n* represents independent sites; more detail on this is presented in Section 2.2.

3.2. Sensitivities from model simulations

To further examine the efficiencies of NH_3 and acid gas emission reductions on SIA and $PM_{2.5}$ mitigation, the decreases of mean SIA and $PM_{2.5}$ concentrations with and without additional 50% NH_3 reductions were simulated using the WRF/CMAQ model.

Fig. 6 and Fig. S10 shows that, compared to 2010, SIA and $PM_{2.5}$ concentrations in January in 2017 were significantly decrease in the BTH, YRD, SCB, and PRD megacity clusters, respectively, in the simulations without additional NH_3 emission reductions. Across the four megacity clusters, the reduction in SIA and $PM_{2.5}$ is largest in the SCB region from 2010 to 2017 and smallest in the PRD region.

When simulating the effects of an additional 50% NH_3 emissions reductions in January in each of the years 2010, 2014 and 2017, the SIA concentrations in the megacity clusters (i.e. BTH, YRD, SCB and PRD) decreased by 25.9 ± 0.3%, 24.4 ± 0.3%, and 22.9 ± 0.3%, respectively (Fig. 6 , Fig. S11, and Table S6). The reductions of $PM_{2.5}$ in 2010, 2014 and 2017 were 9.7 ± 0.1%, 9.0 ± 0.1%, and 9.2 ± 0.2% in the megacity clusters, respectively (Figs. S10 and S12). Whilst these results confirm the effectiveness of NH_3 emission controls, it is important to note that the response of SIA concentrations is less sensitive to additional NH_3 emission controls along the timeline of the SO_2 and NO_x anthropogenic emissions reductions associated with the series of clean air actions implemented by the Chinese government from 2010 to 2017 (Zheng et al., 2018). Given the feasibility and current upper bound of NH_3 emission reductions options in the near future (50%) (Liu et al., 2019b), further abatement of SIA concentrations merely by reducing NH_3 emissions is limited in China. In other words, the controls on acid gas emissions should continue to be strengthened beyond their current levels.

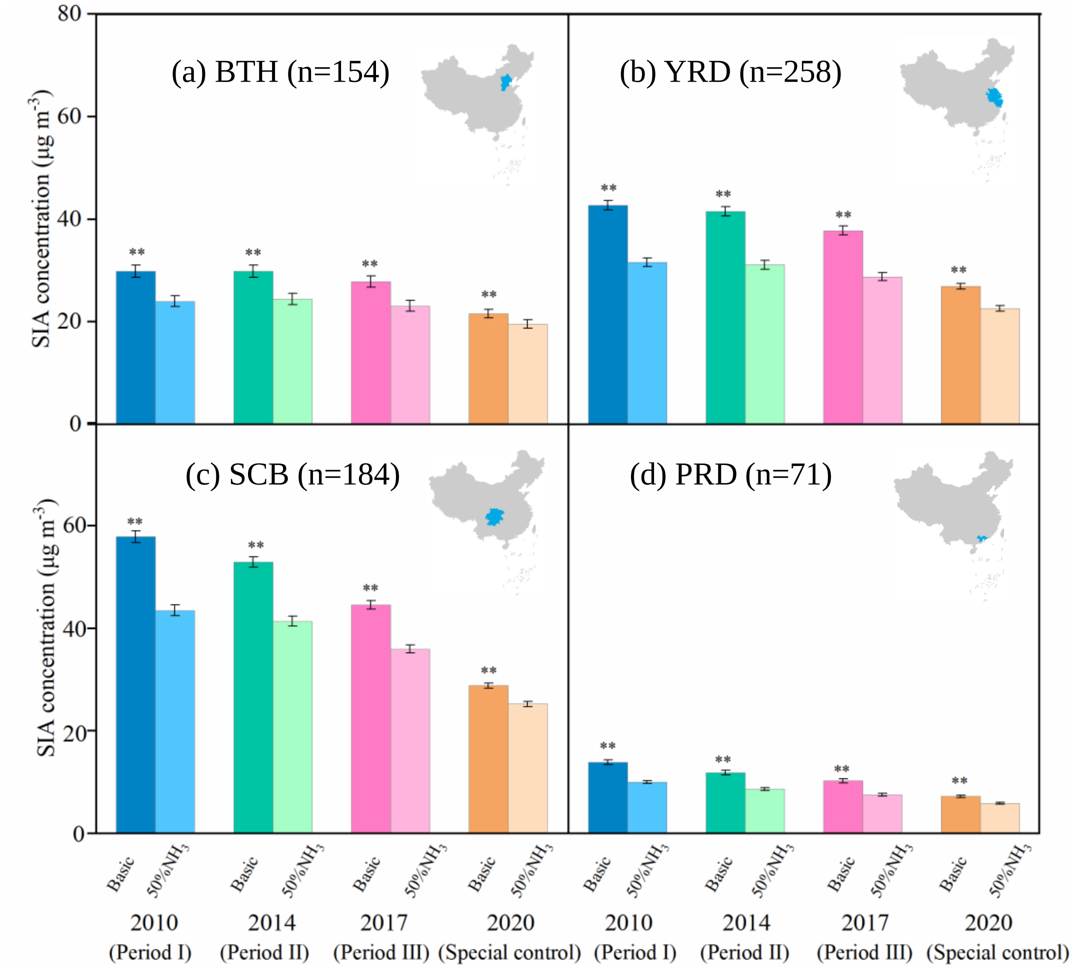

Fig. 6. Simulated SIA concentrations (in μg m^{-3}) without (basic) and with 50% ammonia (NH_3) emissions reductions in January for the years 2010, 2014, 2017 and 2020 in four megacity clusters (BTH: Beijing-Tianjin-Hebei, YRD: Yangtze River Delta, SCB: Sichuan Basin, PRD: Pearl River Delta). Inset maps indicate the location of each region. ** denotes significant difference without and with 50% ammonia emission reductions (P <0.05). n is the number of calculated samples by grid extraction. Error bars are standard errors of means. (Period I (2000–2012), Period II (2013–2016), and Period III (2017–2019); Special control is the restrictions in economic activities and associated emissions during the COVID-19 lockdown period in 2020).

To further verify the above findings, we used the reductions of emissions of acid gases (46% and 23% for NO_x and SO_2, respectively, in the whole China) during the

COVID-lockdown period as a further scenario (Huang et al., 2021). The model simulations suggest that the effectiveness of reductions in SIA and $PM_{2.5}$ concentrations by a 50% NH_3 emission reduction further declined in 2020 (15 ± 0.2% for SIA, and 5.1± 0.2% for $PM_{2.5}$), but the resulting concentrations of them were lower (20.8 ± 0.3% for SIA, and 15.6 ± 0.3% for $PM_{2.5}$) when compared with that in 2017 under the same scenario of an additional 50% NH_3 emissions reduction (and constant meteorological conditions) (Fig. 6 and Table S6), highlighting the importance of concurrently NH_3 mitigation when acid gas emissions are strengthened. To confirm the importance of acid gas emissions, another sensitivity simulation was conducted for 2017, in which the acid gas (NO_x and SO_2) emissions were reduced by 50% (Fig. 7). We found that reductions in SIA concentrations are 13.4 ± 0.5% greater for the 50% reductions in SO_2 and NO_x emissions than for the 50% reductions in NH_3 emissions. These results indicate that to substantially reduce SIA pollution it remains imperative to strengthen emission controls on NO_x and SO_2 even when a 50% reduction in NH_3 emission is targeted and achieved.

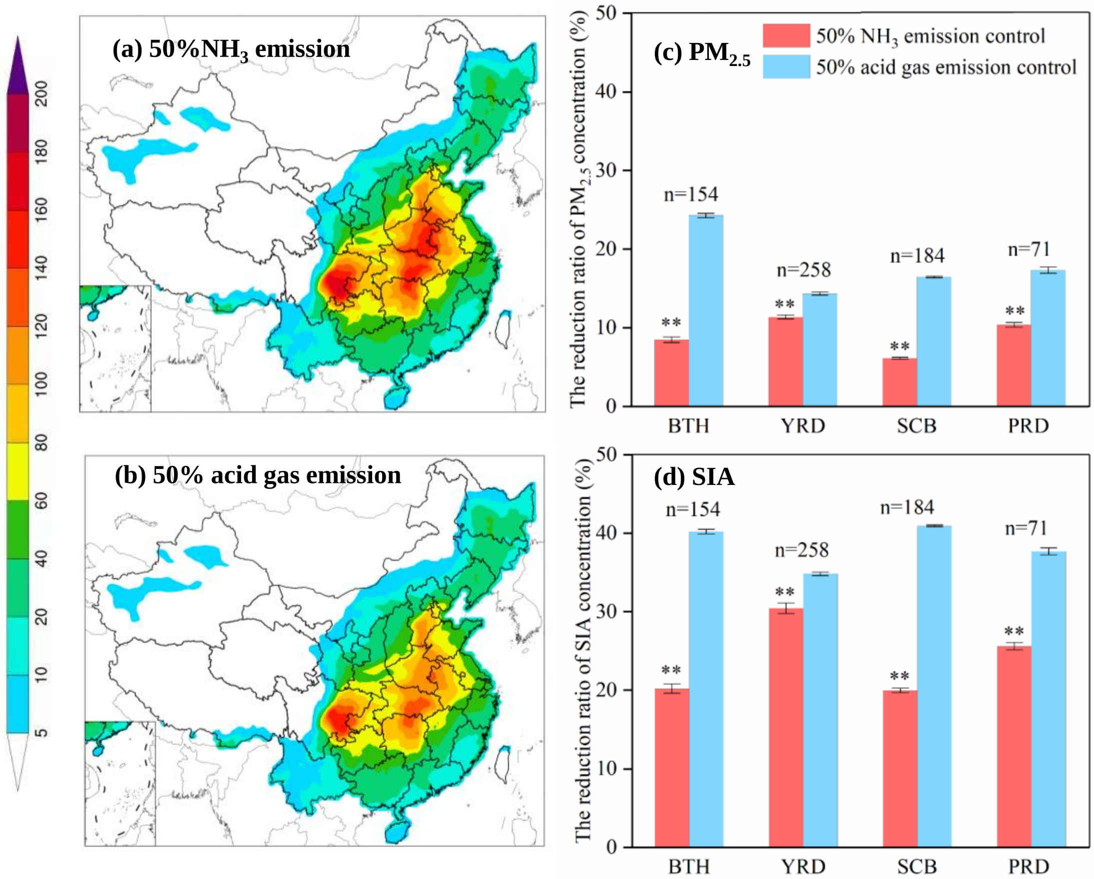

Fig. 7. Left: the spatial distributions of simulated $PM_{2.5}$ concentrations (in μg m^{-3}) in January 2017 with (a) 50% reductions in ammonia (NH_3) emissions and (b) 50% reductions in acid gas (NO_x and SO_2) emissions. Right: the % decreases in $PM_{2.5}$ (c) and SIA (d) concentrations for the simulations with compared to without the NH_3 and acid gas emissions reductions in four megacity clusters (BTH: Beijing-Tianjin-Hebei, YRD: Yangtze River Delta, SCB: Sichuan Basin, PRD: Pearl River Delta). ** denotes significant differences without and with 50% ammonia emission reductions (P <0.05). n is the number of calculated samples by grid extraction. Error bars are standard errors of means.

3.3. Uncertainty analysis and limitations

Some limitations should be noted in interpreting the results of the present study: this study examined period-to-period changes in $PM_{2.5}$ chemical components based on a meta-analysis and the efficiencies of NH_3 and acid gas emission reductions on $PM_{2.5}$ mitigation. Some uncertainties may still exist in meta-analysis of nationwide measurements owing to differences in monitoring, sample handling and analysis methods as well as lack of long-term continuous monitoring sites (Fig. 2). For example, the measurements of $PM_{2.5}$ were mainly taken using the TEOM method, which is associated with under-reading of PM due to some nitrate volatilization at its operational temperature. To test whether the use of data during 2000–2019 could bias annual trends of $PM_{2.5}$ and chemical components, we summarize measurements of $PM_{2.5}$ at a long-term monitoring site (Quzhou County) during the period 2012-2020. The $PM_{2.5}$ and SO_4^{2-} show the decreasing trend. The concentration of NO_3^- and NH_4^+ do not show significant change (Fig. S8). The results are consistent with the trend for the whole of China obtained from the meta-analysis. Considering the uncertainty of $PM_{2.5}$ and its major components between different seasons (winter, summer, etc) and site type (urban, suburban or rural). We have analyzed historic trend in the different season and sites (Figs. S13-S20). We found that concentrations of $PM_{2.5}$ and its major chemical components (SO_4^{2-}, NO_3^-, and NH_4^+) were significantly higher in fall and winter than in spring and summer (Fig. S13). Only the winter season showed significant change trend in the three periods (Figs. S14-S17). The analyses also confirmed that pollution days predominated in winter. We also found that concentrations of $PM_{2.5}$ and its major chemical components were higher at urban than rural sites (Fig. S18). Spatially, the trends of $PM_{2.5}$ and its major components are similar across the whole of China (both of urban and rural) (Fig. S19). Rural areas show the same change trend in hazy days compared with whole of China (Fig. S20).

WRF-CMAQ model performance also has some uncertainty. We performed the validations of WRF and CMAQ models. The simulations of temperature at 2 m above ground (T2), wind speed (WS), and relative humidity (RH) versus observed values at 400 monitoring sites in China are shown in Fig. S7. The meteorological measurements were obtained from the National Climate Data Center (NCDC) (ftp://ftp.ncdc.noaa.gov/pub/data/noaa/). The comparisons showed that the model performed well at predicting meteorological parameters with *R* values of 0.94, 0.64 and 0.82 for T2, WS and RH, respectively. However, the WS was overestimated (22.3% NMB) in most regions of China, which is also reported in previous studies (Gao et al., 2016; Chen et al., 2019). This may be related to the underlying surface parameters set in the WRF model configurations.

In addition, the simulations of $PM_{2.5}$ and associated chemical components by the CMAQ model have potential biases in the spatial pattern, although the CMAQ model has been extensively used in air quality studies (Backes et al., 2016; Zhang et al., 2019) and the validity of the chemical regime in the CMAQ model had been confirmed by our previous studies (Zhang et al., 2021a; Wang et al., 2020a, 2021a). Since nationwide measurements of $PM_{2.5}$ and associated chemical components are lacking in 2010 in China, we undertook our own validation of $PM_{2.5}$ and its components (such as SO_4^{2-}, NO_3^-, and NH_4^+) using a multi-observation dataset that includes those monitoring data and satellite observations at a regional scale that were available.

First, the simulated monthly mean $PM_{2.5}$ concentration in January 2010 was compared with corresponding data obtained from the ChinaHighAirPollutants (CHAP, https://weijing-rs.github.io/product.html) database. The satellite historical $PM_{2.5}$ predictions are reliable (average R^2 = 0.80 and RMSE = 11.26 μg m^{-3}) using cross validation against the in-situ surface observations on a monthly basis (Wei et al., 2020, 2021). The model well captured the spatial distributions of $PM_{2.5}$ concentrations in our studied regions of BTH, YRD, PRD, and SCB (Fig. S3a), with correlation coefficient

(R) between simulated and satellite observed $PM_{2.5}$ concentrations of 0.96, 0.80, 0.60, and 0.85 for BTH, YRD, PRD, and SCB, respectively.

Second, we also collected ground-based observations from previous publications (Xiao et al., 2020, 2021; Geng et al., 2019; Xue et al., 2019) to validate the modeling concentrations of SO_4^{2-}, NO_3^-, and NH_4^+. Detailed information about the monitoring sites is presented in Table S5. The distributions of the simulated monthly mean concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ in January 2010 over China is compared with collected surface measurements are shown in Fig. S4a, b, and c, respectively, with their linear regression analysis presented in Fig. S4d. The model showed underestimation in simulating SO_4^{2-} and NO_3^- in the BTH region, which might be caused by the uncertainty in the emission inventory. The lack of heterogeneous pathways for SO_4^{2-} formation in the CMAQ model might also be an important reason for the negative bias between simulations and measurements (Yu et al., 2005; Cheng et al., 2016). The model overestimated NO_3^- concentration in the SCB region, but can capture the spatial distribution of NO_3^- in other regions. The overestimation of NO_3^- has been a common problem in regional chemical transport models such as CMAQ, GEOS-CHEM and CAMx (Yu et al., 2005; Fountoukis et al., 2011; Zhang et al., 2012; Wang et al., 2013), due to the difficulties in correctly capturing the gas and aerosol-phase nitrate partitioning (Yu et al., 2005). The modeling of NH_4^+ concentrations show good agreement with the observed values. Generally, the evaluation results indicate that the model reasonably predicted concentrations of SO_4^{2-}, NO_3^-, and NH_4^+ in $PM_{2.5}$.

Third, we performed a comparison of the time-series of the observed and simulated hourly $PM_{2.5}$ and its precursors (SO_2 and NO_2) during January 2010. The model well captures the temporal variations of the $PM_{2.5}$ in Beijing, with an NMB value of 0.05 μg m^{-3}, NME of 28%, and R of 0.92 (Fig. 5a). The predicted daily concentrations of NO_2

and SO_2 during January 2010 also show good agreement with the ground measurements in Beijing, with NMB and *R* values of 0.12 μg m^{-3} and 0.89 for NO_2, and -0.04, 0.95 for SO_2, respectively (Fig. 5b). The variations of daily $PM_{2.5}$ concentrations between simulation and observation at 4 monitoring sites (Shangdianzi, Chengdu, Institute of Atmospheric Physics, Chinese Academy of Sciences (IAP-CAS), and Tianjin) from 14 to 30 January 2010 also matched well, with NMB values ranging from -0.05 to 0.12 μg m^{-3}, and *R* values exceeding 0.89 (Fig. S5c).

We also compared the simulated and observed concentrations of $PM_{2.5}$, NO_2, and SO_2 in China in pre-COVID period (1–26 January 2020) and during the COVID-lockdown period (27 January–26 February) with actual meteorological conditions. As shown in Fig. S6, both the simulations and observations suggested that the $PM_{2.5}$ and NO_2 concentrations substantially decreased during the COVID-lockdown, mainly due to the sharp reduction in vehicle emissions (Huang et al., 2021; Wang et al., 2021b). For SO_2, the concentrations decreased very little and even increased at some monitoring sites. The model underestimated the concentrations of $PM_{2.5}$, NO_2, and SO_2, with NMB values of -21.4%, -22.1%, and -9.6%, respectively. We also newly evaluated the model performance in actual meteorological conditions for $PM_{2.5}$ concentrations in January 2014 and 2017, respectively. As shown in the Figure S21, the model well captured the spatial distribution of $PM_{2.5}$ concentration in China with MB (NMB) values of 23.2 μg m^{-3} (15.4%) and 26.8 μg m^{-3} (-26.7%) for 2014 and 2017, respectively. The simulated $PM_{2.5}$ concentrations compared well against the observations, with R values of 0.82 and 0.65, respectively

3.4. Implication and outlook

Improving air quality is a significant challenge for China and the world. A key target in China is for all cities to attain annual mean $PM_{2.5}$ concentrations of 35 μg m^{-3} or below by 2035 (Xing et al., 2021). However, this study has shown that 74% of 1498 nationwide measurement sites have exceeded this limit value in recent years (averaged across 2015-2019). Our results indicated that acid gas emissions still need to be a focus of control measures, alongside reductions in NH_3 emissions, in order to reduce SIA (or $PM_{2.5}$) formation. Model simulations for the month of January underpin the finding that the relative effectiveness of NH_3 emission control decreased over the period from 2010 to 2017. However, simulating the substantial emission reductions in acid gases due to the lockdown during the COVID-19 pandemic, with fossil fuel-related emissions reduced to unprecedented levels, indicated the importance of ammonia emission abatement for $PM_{2.5}$ air quality improvements when SO_2 and NO_x emissions have already reached comparatively low levels. Therefore, a strategic and integrated approach to simultaneously undertaking acid gas emissions and NH_3 mitigation is essential to substantially reduce $PM_{2.5}$ concentrations. However, the mitigation of acid gas and NH_3 emissions pose different challenges due to different sources they originate from.

The implementation of further reduction of acid gas emissions is challenging. The prevention and control of air pollution in China originally focused on the control of acid gas emissions (Fig. S2). The controls have developed from desulfurization and denitrification technologies in the early stages to advanced end-of-pipe control technologies. By 2018, over 90% of coal-fired power plants had installed end-of-pipe control technologies (CEC, 2020). The potential for further reductions in acid gas emissions by end-of-pipe technology might therefore be limited. Instead, addressing total energy consumption and the promotion of a transition to clean energy through a de-carbonization of energy production is expected to be an inevitable requirement for further reducing $PM_{2.5}$ concentrations (Xing et al., 2021). In the context of improving air quality and mitigating climate change, China is adopting a portfolio of low-carbon policies to meet its Nationally Determined Contribution pledged in the Paris Agreement. Studies show that if energy structure adjusts and energy conservation measures are implemented, SO_2 and NO_x will be further reduced by 34% and 25% in Co-Benefit Energy scenario compared to the Nationally Determined Contribution scenario in 2035 (Xing et al., 2021). Although it has been reported that excessive acid gas emission controls may increase the oxidizing capacity of the atmosphere and increase other pollution, $PM_{2.5}$ concentrations have consistently decreased with previous acid gas control (Huang et al., 2021). In addition, under the influence of low-carbon policies, other pollutant emissions will also be controlled. Opportunities and challenges coexist in the control of acid gas emissions.

In contrast to acid gas emissions, NH_3 emissions predominantly come from agricultural sources. Although the Chinese government has recognized the importance of NH_3 emissions controls in curbing $PM_{2.5}$ pollution, NH_3 emissions reductions have only been proposed recently as a strategic option and no specific nationwide targets have yet been implemented (CSC, 2018b). The efficient implementation of NH_3 reduction options is a major challenge because NH_3 emissions are closely related to food production, and smallholder farming is still the dominant form of agricultural production in China. The implementation of NH_3 emissions reduction technologies is subject to investment in technology, knowledge and infrastructure, and most farmers are unwilling or economically unable to undertake additional expenditures that cannot generate financial returns (Gu et al., 2011; Wu et al., 2018b). Therefore, economically feasible options for NH_3 emission controls need to be developed and implemented nationwide.

We propose the following three requirements that need to be met to achieve effective reductions of SIA concentrations and hence of $PM_{2.5}$ concentrations in China.

First, binding targets to reduce both NH_3 and acid gas emissions should be set. The targets should be designed to meet the $PM_{2.5}$ standard, and NH_3 concentrations should be incorporated into the monitoring system as a government assessment indicator. In this study, we find large differences in $PM_{2.5}$ concentration reductions from NH_3 emissions reduction in the four megacity regions investigated. At a local scale (i.e., city or county), the limiting factors may vary within a region (Wang et al., 2011). Thus, local-specific environmental targets should be considered in policy-making.

Second, further strengthening of the controls on acid gas emissions are still needed, especially under the influence of low-carbon policies, to promote emission reductions and the adjustment of energy structures and conservation. Ultra-low emissions should be requirements in the whole production process, including point source emissions, diffuse source emissions, and clean transportation (Xing et al., 2021; Wang et al., 2021a). The assessment of the impact of ultra-low emissions is provided in Table S7. In terms of energy structure, it is a requirement to eliminate outdated production capacity and promote low-carbon new energy generation technologies.

Third, a requirement to promote feasible NH_3 reduction options throughout the whole food production chain, for both crop and animal production. Options include the following. 1) Reduction of nitrogen input at source achieved, for example, through balanced fertilization based on crop needs instead of over-fertilization, and promotion of low-protein feed in animal breeding. 2) Mitigation of NH_3 emissions in food production via, for example, improved fertilization techniques (such as enhanced-efficiency fertilizer (urease inhibitor products), fertilizer deep application, fertilization-irrigation technologies (Zhan et al., 2021), and coverage of solid and slurry manure. 3) Encouragement for the recycling of manure back to croplands, and reduction in manure discarding and long-distance transportation of manure fertilizer. Options for NH_3 emissions control are provided in Table S4. Although the focus here has been on methods to mitigate NH_3 emissions, it is of course critical simultaneously to minimize N losses in other chemical forms such as nitrous oxide gas emissions and aqueous nitrate leaching (Shang et al., 2019; Wang et al., 2020b).

4. Conclusions

The present study developed an integrated assessment framework using meta-analysis of published literature results, analysis of national monitoring data, and chemical transport modelling to provide insight into the effectiveness of SIA precursor emissions controls in mitigating poor $PM_{2.5}$ air quality in China. We found that $PM_{2.5}$ concentration significantly decreased in 2000-2019 due to acid gas control policies, but $PM_{2.5}$ pollution still severe. Compared with other components, this difference was more significant higher (average increase 98%) for secondary inorganic ions (i.e., SO_4^{2-}, NO_3^-, and NH_4^+) on hazy days than on-hazy days. This is mainly caused by the persistent SIA pollution during the same period. with sulfate concentrations significantly decreased and no significant changes observed for nitrate and ammonium concentrations. The reductions of SIA concentrations in January in megacity clusters of eastern China by additional 50% NH_3 emission controls decreased from 25.9 ± 0.3% in 2010 to 22.9 ± 0.3% in 2017, and to 15 ± 0.2% in the COVID lockdown in 2020 for simulations representing reduced acid gas emissions to unprecedented levels, but the SIA concentrations decreased by 20.8 ± 0.3% in 2020 compared with that in 2017 under the same scenario of an additional 50% NH_3 emissions reduction. In addition, the reduction of SIA concentration in 2017 was 13.4 ± 0.5% greater for 50% acid gas (SO_2 and NO_x) reductions than for the NH_3 emissions reduction. These results indicate that acid gas emissions need to be further controlled concertedly with NH_3 reductions to substantially reduce $PM_{2.5}$ pollution in China.

Overall, this study provides new insight into the responses of SIA concentrations in China to past air pollution control policies and the potential balance of benefits in including NH_3 emissions reductions with acid gas emissions controls to curb SIA pollution. The outcomes from this study may also help other countries seeking feasible strategies to mitigate $PM_{2.5}$ pollution.

Data availability

All data in this study are available from the from the corresponding authors (Wen Xu, wenxu@cau.edu.cn; Shaocai Yu, shaocaiyu@zju.edu.cn) upon request.

Author contributions

W.X., S.Y., and F.Z. designed the study. F.M., Y.Z., W.X., and J.K. performed the research. F.M., Y.Z., W.X., and J.K. analyzed the data and interpreted the results. Y.Z. conducted the model simulations. L.L. provided satellite-derived surface NH_3 concentration. F.M., W.X., Y.Z., and M.R.H. wrote the paper, S. R., M.W., K.W., J.K., Y.Z., Y.H., P.L., J.W., Z.C., X.L., M.R.H., S.Y. and F.Z. contributed to the discussion and revision of the paper.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This study was supported by National Natural Science Foundation of China (42175137, 21577126 and 41561144004), China Scholarship Council (201913043), the National Key Research and Development Program of China (2021YFD1700900), the Department of Science and Technology of China (2016YFC0202702, 2018YFC0213506 and 2018YFC0213503), National Research Program for Key Issues in Air Pollution Control in China (DQGG0107), and the High-level Team Project of China Agricultural University. SR's contribution was supported by the Natural Environment Research Council award number NE/R000131/1 as part of the SUNRISE program delivering National Capability. We would like to thank Prof. Yuepeng Pan and Dr. Yangyang Zhang for their help on validating the modeling results.

References

An, Z. S., Huang, R. J., Zhang, R.Y., Tie, X. X., Li, G. H., Cao, J. J., Zhou, W. J., Shi, Z. G ., Han, Y. M ., Gu, Z. L., and Ji, Y. M.: Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes, Proc. Natl. Acad. Sci. U. S. A., 116, 8657-8666. https://doi.org/10.1073/pnas.1900125116, 2019.

Backes, A., Aulinger, A., Bieser, J., Matthias, V., and Quante, M.: Ammonia emissions in Europe, part II: How ammonia emission abatement strategies affect secondary aerosols, Atmos. Environ., 126, 153-161, https://doi.org/10.1016/j.atmosenv.2015.11.039, 2016.

Bai, Z., Winiwarter, W., Klimont, Z., Velthof, G., Misselbrook, T., Zhao, Z., Jin, X., Oenema, O., Hu, C., and Ma, L.: Further improvement of air quality in China needs clear ammonia mitigation target, Environ. Sci. Technol., 53, 10542-10544, https://doi.org/ 10.1021/acs.est.9b04725, 2019.

Benitez-Lopez, A., Alkemade, R., Schipper, A. M., Ingram, D. J., Verweij, P. A., Eikelboom, J. A. J., and Huijbregts, M. A. J.: The impact of hunting on tropical mammal and bird populations, Science, 356, 180-183, https://doi.org/10.1126/science.aaj1891, 2017.

Bracken, M. B.: Statistical methods for analysis of effects of treatment in overviews of randomized trials. In: J.C. Sinclair, M.B. Bracken (Eds.) Effective care of the newborn infant, Oxford University Press, 1992.

Chen, Z.Y., Chen, D.L., Wen, W., Zhuang, Y., Kwan, M.P., Chen, B., Zhao, B., Yang, L., Gao, B.B., Li, R.Y., and Xu, B.: Evaluating the "2+26" regional strategy for air quality improvement during two air pollution alerts in Beijing: Variations in $PM_{2.5}$ concentrations, source apportionment, and the relative contribution of local emission and regional transport, Atmos. Chem. Phys., 19, 6879-6891. https://doi.org/10.5194/acp-19-6879-2019, 2019.

Cheng, Y.F., Zheng, G.A., Wei, C., Mu, Q., Zheng, B., Wang, Z.B., Gao, M., Zhang, Q., He, K.B., Carmichael, G., Poschl, U., and Su, H.: Reactive nitrogen chemistry in aerosol water as a source of sulfate during haze events in China, Sci. Adv. 2(12). https://doi.org/10.1126/sciadv.1601530, 2016.

China Electricity Council.: China Power Industry Annual Development Report 2019, https://www.cec.org.cn/yaowenkuaidi/2019-06-14/191782.html, 2020.

CSC (China State Council): The 11th Five-Year plan on energy saving and emissions reduction, http://www.gov.cn/zhengce/content/2008-03/28/content_4877.htm, 2007.

CSC (China State Council): The 12th Five-Year plan on energy saving and emissions reduction. http://www.gov.cn/zwgk/2011-12/20/content_2024895.htm, 2011.

CSC (China State Council): Action Plan on Prevention and Control of Air Pollution, China State Council, Beijing, China. http://www.gov.cn/zwgk/2013-

09/12/content_2486773.htm, 2013.

CSC (China State Council): The 13th Five-Year plan on energy saving and emissions reduction. http://www.gov.cn/zhengce/content/2016-12/05/content_5143290.htm, 2016.

CSC (China State Council): Air quality targets set by the Action Plan have been fully realized, http://www.gov.cn/xinwen/2018-02/01/content_5262720.htm, 2018a.

CSC (China State Council): Notice of the state council on issuing the three-year action plan for winning the Blue Sky defense battle. http://www.gov.cn/zhengce/content/2018-07/03/content_5303158.htm, 2018b.

Dunn, O.J.: Multiple comparisons using rank sums. Technometrics, 6, 241-252, 1964.

Fountoukis, C., Racherla, P. N., Denier van der Gon, H. A. C., Polymeneas, P., Charalampidis, P. E., Pilinis, C., Wiedensohler, A., Dall'Osto, M., O'Dowd, C., and Pandis, S. N.: Evaluation of a three-dimensional chemical transport model (PMCAMx) in the European domain during the EUCAARI May 2008 campaign, Atmos. Chem. Phys., 11, 10331–10347, https://doi.org/10.5194/acp- 11-10331-2011, 2011.

Fan, C., Li, Z., Li, Y., Dong, J., van der A, R., and de Leeuw, G.: Variability of NO_2 concentrations over China and effect on air quality derived from satellite and ground-based observations, Atmos. Chem. Phys., 21, 7723-7748, https://doi.org/10.5194/acp-21- 7723-2021, 2021.

Feng, S. J., Xu, W., Cheng, M. M., Ma, Y. X., Wu, L. B., Kang, J. H., Wang, K., Tang, A. H., Collett Jr., J. L., Fang, Y. T., Goulding, K., Liu, X. J., and Zhang, F. S.: Overlooked nonagricultural and wintertime agricultural NH_3 emissions in Quzhou County, North China Plain: Evidence from ^{15}N-stable isotopes, Environ. Sci. Technol. Lett., 9, 127-133, https://doi.org/10.1021/acs.estlett.1c00935, 2022.

Gao, M., Carmichael, G. R., Wang, Y., Saide, P. E., Yu, M., Xin, J., Liu, Z., and Wang, Z.: Modeling study of the 2010 regional haze event in the North China Plain, Atmos. Chem. Phys., 16, 1673–1691, https://doi.org/10.5194/acp-16-1673-2016, 2016.

Geng, G., Xiao, Q., Zheng, Y., Tong, D., Zhang, Y., Zhang, X., Zhang, Q., He, K., and Liu, Y.: Impact of China's air pollution prevention and control action plan on $PM_{2.5}$ chemical composition over eastern China, Sci China Earth Sci., 62, 1872-1884, https://doi.org/10.1007/s11430-018-9353-x, 2019.

Geng, G., Xiao, Q., Liu, S., Liu, X., Cheng, J., Zheng, Y., Xue, T., Tong, D., Zheng, B., Peng, Y., and Huang, X.: Tracking air pollution in China: Near real-time PM2. 5 retrievals from multisource data fusion, Environ. Sci. Technol., *55*, 12106-12115, https://doi.org/10.1021/acs.est.1c01863, 2021.

Geng, G., Zhang, Q., Tong, D., Li, M., Zheng, Y., Wang, S., and He, K.: Chemical composition of ambient PM2. 5 over China and relationship to precursor emissions during 2005–2012, Atmos. Chem. Phys., 17, 9187–9203, https://doi.org/10.5194/acp-17-9187-2017, 2017.

Gu, B. J., Zhu, Y. M., Chang, J., Peng, C. H., Liu, D., Min, Y., Luo, W. D., Howarth, R. W., and Ge, Y.: The role of technology and policy in mitigating regional nitrogen pollution, Environ. Res. Lett., 6, 1, https://doi.org/10.1088/1748-9326/6/1/014011, 2011.

Guenther, A. B., Jiang, X., Heald, CL., Sakulyanontvittaya, T., Duhl, T., Emmons, L. K., and Wang, X.: The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, Geosci. Model Dev., 5, 1471-1492. https://doi.org/10.5194/gmd-5-1471-2012, 2012.

Han, Y., Wu, Y. F., Don, H. Y., and Chen, F.: Characteristics of $PM_{2.5}$ and its chemical composition during the Asia-Pacific Economic Cooperation Summit in Beijing-Tianjin-Hebei Region and surrounding cities, Environ. Sci. Technol., 40, 134-138 (in Chinese with English abstract), 2017.

Huang, R. J., Zhang, Y. L., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., Daellenbach, K. R., Slowik, J. G., Platt, S. M., Canonaco, F., Zotter, P., Wolf, R., Pieber, S. M., Bruns, E. A., Crippa, M., Ciarelli, G., Piazzalunga, A., Schwikowski, M., Abbaszade, G., Schnelle-Kreis, J., Zimmermann, R., An, Z. S., Szidat, S., Baltensperger, U., El Haddad, I., and Prevot, A. S.: High secondary aerosol contribution to particulate pollution during haze events in China, Nature, 514, 218-222. https://doi.org/10.1038/nature13774, 2014.

Huang, X., Ding, A.J, Gao, J., Zheng, B., Zhou, D.R., Qi, X. M., Tang, R., Wang, J. P., Ren, C. H., Nie, W., Chi, X. G., Xu, Z., Chen, L. D., Li, Y. Y., Che, F., Pang, N. N., Wang, H. K., Tong, D., Qin, W., Cheng, W., Liu, W. J., Fu, Q. Y., Liu, B. X., Chai, F. H., Davis, S. J., Zhang, Q., and He, K. B.: Enhanced secondary pollution offset reduction of primary emissions during COVID-19 lockdown in China, Natl. Sci. Rev., 8, 137, https://doi.org/10.1093/nsr/nwaa137, 2021.

Ianniello, A., Spataro, F., Esposito, G., Allegrini, I ., Rantica, E ., Ancora, MP., Hu, M., and Zhu, T.: Occurrence of gas phase ammonia in the area of Beijing (China). Atmos. Chem. Phys,. 10, 9487-9503, https://doi.org/10.5194/acp-10-9487-2010, 2010.

Kang, Y. N., Liu, M. X., Song, Y., Huang, X ., Yao, H ., Cai, X. H., Zhang, H. S., Kang, L., Liu, X. J., Yan, X. Y., He, H., Zhang, Q., Shao, M., and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, Atmos. Chem. Phys., 16, 2043-2058, https://doi.org/10.5194/acp-16-2043-2016, 2016.

Kruskal, W.H. and Wallis, W.A.: Use of ranks in one-criterion variance analysis. Journal of the American statistical Association, 47, 583-621, https://doi.org/ 10.1080/01621459.1952.10483441, 1952.

Kuerban, M., Waili, Y., Fan, F., Liu, Y., Qin, W., Dore, A. J., Dore, A. J., Xu, W., and Zhang, F. S.: Spatio-temporal patterns of air pollution in China from 2015 to 2018 and implications for health risks, Environ. Pollut., 258, 113659, https://doi.org/ 10.1016/j.envpol.2019.113659, 2020.

Li, H., Cheng, J., Zhang, Q., Zheng, B., Zhang, Y., Zheng, G., and He, K.: Rapid transition in winter aerosol composition in Beijing from 2014 to 2017: response to clean air actions, Atmos. Chem. Phys., 19, 11485–11499, https://doi.org/10.5194/acp-19-11485-2019, 2019.

Li, H. Y., Zhang, Q., Zheng, B., Chen, C. R., Wu, N. N., Guo, H. Y., Zhang, Y. X., Zheng, Y. X., Li, X., and He, K. B.: Nitrate-driven urban haze pollution during summertime over the North China Plain, Atmos. Chem. Phys., 18, 5293-5306, https://doi.org/ 10.5194/acp-18-5293-2018, 2018.

Li, K., Jacob, D. J., Shen, L., Lu, X., De Smedt, I., and Liao, H.: Increases in surface ozone pollution in China from 2013 to 2019: anthropogenic and meteorological influences, Atmos. Chem. Phys., 20, 11423–11433, https://doi.org/10.5194/acp-20-11423-2020, 2020.

Li, M., Liu, H., Geng, G., Geng, G. N., Hong, C. P., Liu, F., Song, Y., Tong, D., Zheng, B., Cui, H. Y., Man, H. Y., Zhang, Q., and He, K. B.: Anthropogenic emission inventories in China: a review, Natl. Sci. Rev., 4, 834-866. https://doi.org/10.1093/nsr/nwx150, 2017.

Li, X., Bei, N., Hu, B., Wu, J., Pan, Y., Wen, T., Liu, Z., Liu, L., Wang, R., and Li, G.: Mitigating NO_X emissions does not help alleviate wintertime particulate pollution in Beijing-Tianjin-Hebei, China, Environ. Pollut., 279(X), https:// 10.1016/j.envpol.2021.11693, 2021.

Liang, F. C., Xiao, Q. Y., Huang, K. Y., Yang, X. L., Liu, F. C ., Li, J. X., Lu, X. F., Liu, Y., and Gu, D. F.: The 17-y spatiotemporal trend of $PM_{2.5}$ and its mortality burden in China, Proc. Natl. Acad. Sci. U. S. A., 117, 25601-25608, https://doi.org/10.1073/pnas.1919641117, 2020.

Liu, J., Han, Y. Q., Tang, X., Zhu, J., and Zhu, T.: Estimating adult mortality attributable to $PM_{2.5}$ exposure in China with assimilated $PM_{2.5}$ concentrations based on a ground monitoring network, Sci. Total. Environ., 568, 1253-1262, https://doi.org/10.1016/j.scitotenv.2016.05.165, 2016.

Liu, L., Zhang, X. Y., Wong, A. Y. H., Xu, W., Liu, X. J., Li, Y., Mi, H., Lu, X. H., Zhao, L. M., Wang, Z., Wu, X. D., and Wei, J.: Estimating global surface ammonia concentrations inferred from satellite retrievals, Atmos. Chem. Phys., 19, 12051-12066, https://doi.org/10.5194/acp-19-12051-2019, 2019a.

Liu, M. X., Huang, X., Song, Y., Tang, J., Cao, J. J., Zhang, X. Y., Zhang, Q., Wang, S. X., Xu, T. T., Kang, L., Cai, X. H., Zhang, H. S., Yang, F. M., Wang, H. B., Yu, J. Z., Lau, A. K. H., He, L. Y., Huang, X. F., Duan, L., Ding, A. J., Xue, L. K., Gao, J., Liu, B., and Zhu, T.: Ammonia emission control in China would mitigate haze pollution and nitrogen deposition, but worsen acid rain, Proc. Natl. Acad. Sci. U. S. A., 116, 7760-7765, https://doi.org/10.1073/pnas.1814880116, 2019b.

Liu, X.J., Sha, Z.P., Song, Y., Dong, H.M., Pan, Y.P., Gao, Z.L., Li, Y.E., Ma, L., Dong, W.X., Hu, C.S., Wang, W.L., Wang, Y., Geng, H., Zheng, Y.H., and Gu, M.N.: China's atmospheric ammonia emission characteristics, mitigation options and policy recommendations, Res. Environ. Sci., 34, 149-157, https://10.13198/j.issn.1001-6929.2020.11.12, 2021.

Mao, S. S., Chen, T, Fu, J. M., Liang, J. L., An, X. X.,Luo, X. X., Zhang, D. W., and

Liu, B. X.: Characteristic analysis for the thick winter air pollution accidents in Beijing based on the online observations, Journal of Safety and Environment. 1, 1009-6094 (in Chinese with English abstract), 2018.

MEEP. The Ministry of Ecology and Environment of the People's Republic of China, China Ecological Environment Bulletin. http://www.mee.gov.cn/hjzl/sthjzk/zghjzkgb/, 2019.

Megaritis, A., Fountoukis, C., Charalampidis, P. E., Pilinis, C., and Pandis, S. N.: Response of fine particulate matter concentrations to changes of emissions and temperature in Europe, Atmos. Chem. Phys., 13, 3423-3443, https://doi.org/10.5194/acp-13-3423-2013, 2013.

Meng, F. L., Wang, M. R., Strokal, M., Kroeze, C., Ma, L., Li, Y. N., Zhang, Q., Wei, Z. B., Hou, Y., Liu, X. J., Xu, W., and Zhang, F. S.: Nitrogen losses from food production in the North China Plain: A case study for Quzhou, Sci. Total. Environ., 816, 151557, https://doi.org/10.1016/j.scitotenv.2021.151557, 2022.

MEPC. Ministry of Environment Protection of China, Ambient air quality standards (GB3095–2012). http://www.mep. gov.cn/, 2012.

Morrison, H., Thompson, G., and Tatarskii, V.: Impact of cloud microphysics on the development of trailing stratiform precipitation in a simulated squall line: comparison of one- and two-moment schemes, Mon. Weather. Rev., 137, 991-1007. https://doi.org/10.1175/2008MWR2556.1, 2012 .

Nakagawa, S. and Santos, E. S. A.: Methodological issues and advances in biological meta-analysis, Evol. Ecol., 26, 1253-1274. https://doi.org/10.1007/s10682-012-9555-5, 2012.

Ortiz-Montalvo, D. Häkkinen, S. A. K., Schwier, A. N., Lim, Y. B., Faye McNeill, V., and Turpin, B. J.: Ammonium addition (and aerosol pH) has a dramatic impact on the volatility and yield of glyoxal secondary organic aerosol, Environ. Sci. Technol., 48, 255-262, https://doi.org/10.1021/es4035667, 2014.

Pan, Y. P., Wang, Y. S., Tang, G. Q., and Wu, D.: Wet and dry deposition of atmospheric nitrogen at ten sites in Northern China, Atmos. Chem. Phys., 12, 6515–6535, doi:10.5194/acp-12-6515-2012, 2012.

Pinder, R. W., Adams, P. J., and Pandis, S. N.: Ammonia emission controls as a cost-effective strategy for reducing atmospheric particulate matter in the eastern United States, Environ. Sci. Technol., 41, 380-386, https://doi.org/10.1021/es060379a, 2007.

Ronald, J. V., Mijling, B., Ding, J. Y., Koukouli, M. E., Liu, F., Li, Q., Mao, H. Q., and Theys, N.: Cleaning up the air: effectiveness of air quality policy for SO_2 and NO_x emissions in China, Atmos. Chem. Phys., 17, 1775-1789, https://doi.org/10.5194/acp-17-1775-2017, 2017.

Shang, Z.Y., Zhou, F., Smith, P., Saikawa, E., Ciais, P., Chang, J.F., Tian, H.Q., Del Grosso, S.L., Ito, A., Chen, M.P., Wang, Q.H., Bo, Y., Cui, X.Q., Castaldi, S., Juszczak, P., Kasimire, A., Magliulo, V., Medinets, S., Medinets, V., Rees, R. M., Wohlfahrt,G., and Sabbatini, S: Weakened growth of cropland-N_2O emissions in China accociated with nationwide policy interventions, Glob. Change. Biol., 25, 3706-3719, https://doi.org/10.1111/gcb.14741, 2021.

Sun, Y. L., Zhuang, G. S., Tang, A. H., Wang, Y., and An, Z. S.: Chemical characteristics of $PM_{2.5}$ and PM_{10} in haze-fog episodes in Beijing, Environ. Sci. Technol., 40, 3148-3155, https://doi.org/10.1021/es051533g, 2006.

Tao, J., Gao, J., Zhang, L. M., Wang, H., Qiu, X. H., Zhang, Z. S., Wu, Y. F., Chai, F. H., and Wang, S. L: Chemical and optical characteristics of atmospheric aerosols in Beijing during the Asia-Pacific Economic Cooperation China 2014, Atmos.

Environ., 144, 8-16, https://doi.org/10.1016/j.atmosenv.2016.08.067, 2016.

Wang S.: How to promote ultra-low emissions during the 14th Five-Year Plan? China. Environment. News. http://epaper.cenews.com.cn/html/2021-04/30/node_7.htm, 2021a.

Wang, G. H., Zhang, R. Y., Gomez, M. E., Yang, L. X., Zamora, M. L., Hu, M., Lin, Y., Peng, J. F., Guo, S., Meng, J. J., Li, J. J., Cheng, C. L., Hu, T. F., Ren, Y. Q., Wang, Y. S., Gao, J., Cao, J. J., An, Z. S., Zhou, W. J., Li, G. H., Wang, J. Y., Tian, P. F., Marrero-Ortiz, W., Secrest, J., Du, Z. F., Zheng, J., Shang, D. J., Zeng, L. M., Shao, M., Wang, W. G., Huang, Y., Wang, Y., Zhu, Y. J., Li, Y. X., Hu, J. X., Pan, B., Cai, L., Cheng, Y. T., Ji, Y. M., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from London Fog to Chinese haze, Proc. Natl. Acad. Sci. U. S. A., 113, 13630-13635, https://doi.org/10.1073/pnas.1616540113, 2016.

Wang, L., Chen, X., Zhang, Y., Li, M., Li, P., Jiang, L., Xia, Y., Li, Z., Li, J., Wang, L., Hou, T., Liu, W., Rosenfeld, D., Zhu, T., Zhang, Y., Chen, J., Wang, S., Huang, Y., Seinfeld, J. H., and Yu, S.: Switching to electric vehicles can lead to significant reductions of $PM_{2.5}$ and NO_2 across China, One Earth, 4, 1037–1048, https://doi.org/ 10.1016/j.oneear.2021.06.008, 2021b.

Wang, L., Yu, S., Li, P., Chen, X., Li, Z., Zhang, Y., Li, M., Mehmood, K., Liu, W., Chai, T., Zhu, Y., Rosenfeld, D., and Seinfeld, J. H.: Significant wintertime $PM_{2.5}$ mitigation in the Yangtze River Delta, China, from 2016 to 2019: observational constraints on anthropogenic emission controls, Atmos. Chem. Phys., 2, 14787–14800, https://doi.org/ 10.5194/acp-20-14787-2020, 2020a.

Wang, Q.H., Zhou, F., Shang, Z.Y., Ciais, P., Winiwarter, W., Jackson, R. B., Tubiello, F,N., Janssens-Maenhout, G., Tian, H. Q., Cui, X. Q., Canadell, J.G., Piao, S. L., and Tao, S.: Data-driven estimates of global nitrous oxide emissions from cropland, Natl. Sci. Rev., 7, 441-452, https://doi.org/10.1093/nsr/nwz087, 2020b.

Wang, S. X, Xing, J., Jang, C., Jang, C. R., Zhu, Y., Fu, J. S., and Hao, J. M.: Impact assessment of ammonia emissions on inorganic aerosols in East China using response surface modeling technique, Environ. Sci. Technol., 45, 9293-9300, https://doi.org/10.1021/es2022347, 2011.

Wang, Y. H., Wang, Y. S., Wang, L.L., Petaja, T., Zha, Q.Z., Gong, C.S., Li, S.X., Pan, Y. P., Hu, B., Xin, J. Y., and Kulmala, M.: Increased inorganic aerosol fraction contributes to air pollution and haze in China, Atmos. Chem. Phys., 19, 5881-5888. https:// 10.5194/acp-19-5881-2019, 2019a.

Wang, Y., Zhang, Q. Q., He, K.B., Zhang, Q., and Chai, L.: Sulfate-nitrate-ammonium aerosols over China: Response to 2000-2015 emission changes of sulfur dioxide, nitrogen oxides, and ammonia, Atmos. Chem. Phys., 13, 2635–2652. https://doi.org/10.5194/acp-13-2635-2013, 2013.

Wang, Y.C., Chen, J., Wang, Q.Y., Qin, Q.D., Ye, J.H., Han, Y.M., Li, L., Zhen, W., Zhi, Q., Zhang, Y.X., and Cao, J.J.: Increased secondary aerosol contribution and possible processing on polluted winter days in China, Environ. Int, 127. https://doi.org/10.1016/j.envint.2019.03.021, 2019b.

Wei, J., Li, Z. Q., Cribb, M., Huang, W., Xue, W.H., Sun, L., Guo, J. P., Peng, Y. R., Li, J., and Lyapustin, A.: Improved 1 km resolution $PM_{2.5}$ estimates across China using enhanced space–time extremely randomized trees, Atmos. Chem. Phys., 20, 3273-3289. https://doi.org/10.5194/acp-20-3273-2020, 2020.

Wei, J., Li, Z. Q., Lyapustin, A., Sun, L., Peng, Y. R., Xue, W. H., Su, T. N., and Cribb, M.: Reconstructing 1-km-resolution high-quality $PM_{2.5}$ data records from 2000 to 2018 in China: spatiotemporal variations and policy implications, Remote. Sens.

Environ., 252, 112136, https://doi.org/10.1016/j.rse.2020.112136, 2021.

Wu, Y. J., Wang, P., Yu, S. C., Wang, L. Q., Li, P. F., Li, Z., Mehmood, K., Liu, W. P., Wu, J., Lichtfouse, E., Rosenfeld, D., and Seinfeld, J. H.: Residential emissions predicted as a major source of fine particulate matter in winter over the Yangtze River Delta, China, Environ. Chem. Lett., 16, 1117-1127. https://doi.org/10.1007/s10311-018-0735-6, 2018a.

Wu, Y. Y., Xi, X. C., Tang, X., Luo, D. M., Gu, B. J., Lam, S. K., Vitousek, P. M., and Chen, D. L.: Policy distortions, farm size, and the overuse of agricultural chemicals in China, Proc. Natl. Acad. Sci. U. S. A., 115, 7010-7015. https://doi.org/10.1073/pnas.1806645115, 2018b.

Xiao, Q.Y, Geng, G.N., Liang, F.C., Wang, X., Lv, Z., Lei, Y., Huang, X,M., Zhang, Q., Liu, Y., and He, K.B: Changes in spatial patterns of $PM_{2.5}$ pollution in China 2000–2018: Impact of clean air policies, Environ. Int., 141, 105776, https://doi.org/10.1016/j.envint.2020.105776, 2020.

Xiao, Q.Y., Zheng, Y.X., Geng, G.N., Chen, C.H., Huang, X.M., Che, H.Z., Zhang, X.Y., He, K.B., and Zhang, Q.: Separating emission and meteorological contribution to $PM_{2.5}$ trends over East China during 2000–2018, Atmos. Chem. Phys., 21, 9475-9496, https://doi.org/10.5194/acp-21-9475-2021, 2021.

Xing, J., Liu, X., Wang, S. X., Wang, T., Ding, D., Yu, S., Shindell, D., Ou, Y ., Morawska, L., Li, S. W., Ren, L., Zhang, Y. Q., Loughlin, D., Zheng, H. T., Zhao, B., Liu, S. C., Smith, K. R., and Hao, J. M.: The quest for improved air quality may push China to continue its CO_2 reduction beyond the Paris Commitment, Proc. Natl. Acad. Sci. U. S. A., 117, 29535-29542, https://doi.org/10.1073/pnas.2013297117, 2021.

Xu, Q. C., Wang, S. X., Jiang, J. K., Bhattarai, N., Li, X. X., Chang, X., Qiu, X. H., Zheng, M., Hua, Y., and Hao, J. M.: Nitrate dominates the chemical composition of $PM_{2.5}$ during haze event in Beijing, China, Sci. Total. Environ., 689, 1293-1303, https://doi.org/10.1016/j.scitotenv.2019.06.294, 2019.

Xu, W., Wu, Q.H., Liu, X.J., Tang, A.H., Dore, A.J., and Heal, M.R.: Characteristics of ammonia, acid gases, and $PM_{2.5}$ for three typical land-use types in the North China Plain, Environ Sci Pollut R., 23, 1158-1172. https://doi.org/10.1007/s11356-015-5648-3, 2016.

Xu, W., Luo, X. S., Pan, Y. P., Zhang, L., Tang, A. H., Shen, J. L., Zhang, Y., Li, K. H., Wu, Q. H., Yang, D. W., Zhang, Y. Y., Xue, J., Li, W. Q., Li, Q. Q., Tang, L., Lu, S. H., Liang, T., Tong, Y. A., Liu, P., Zhang, Q., Xiong, Z. Q., Shi, X. J., Wu, L. H., Shi, W. Q., Tian, K., Zhong, X. H., Shi, K., Tang, Q. Y., Zhang, L. J., Huang, J. L., He, C. E., Kuang, F. H., Zhu, B., Liu, H., Jin, X., Xin, Y. J., Shi, X. K., Du, E. Z., Dore, A. J., Tang, S., Collett Jr., J. L., Goulding, K., Sun, Y. X., Ren, J., Zhang, F. S., and Liu, X. J.: Quantifying atmospheric nitrogen deposition through a nationwide monitoring network across China, Atmos. Chem. Phys., 15, 12345–12360, https://doi.org/10.5194/acp-15-12345- 2015, 2015

Xu, W., Song, W., Zhang, Y. Y., Liu, X. J., Zhang, L., Zhao, Y. H., Liu, D. Y., Tang, A. H., Yang, D. W., Wang, D. D., Wen, Z., Pan, Y. P., Fowler, D., Collett, J. L., Erisman, J. W., Goulding, K., Li, Y., and Zhang, F. S.: Air quality improvement in a megacity: implications from 2015 Beijing Parade Blue pollution control actions, Atmos. Chem. Phys., 17, 31-46, https://doi.org/10.5194/acp-17-31-2017, 2017.

Xu, W., Liu, L., Cheng, M.M., Zhao, Y.H., Zhang, L., Pan, Y.P., Zhang, X.M., Gu, B.J., Li, Y., Zhang, X.Y., Shen, J.L., Lu, L., Luo, X.S., Zhao, Y., Feng, Z.Z., Collett Jr., J.L., Zhang, F.S., and Liu, X.J.: Spatial-temporal patterns of inorganic nitrogen air concentrations and deposition in eastern China. Atmos. Chem. Phys. 18, 10931–

10954, https://doi.org/10.5194/acp-18-10931-2018, 2018.

Xue, T., Liu, J., Zhang, Q., Geng, G.N., Zheng, Y.X., Tong, D., Liu, Z., Guan, D.B., Bo, Y., Zhu, T., He, K.B., and Hao, J.M.: Rapid improvement of $PM_{2.5}$ pollution and associated health benefits in China during 2013–2017, Sci. China Earth Sci., 62, 1847-1856, https://doi.org/10.1007/s11430-018-9348-2, 2019.

Yang, F., Tan, J., Zhao, Q., Du, Z ., He, K ., Ma, Y., Duan, F., Chen, G., and Zhao, Q.: Characteristics of $PM_{2.5}$ speciation in representative megacities and across China. Atmos. Chem. Phys., 11, 5207-5219, https://doi.org/10.5194/acp-11-5207-2011, 2011.

Ying, H., Yin, Y. L., Zheng, H. F., Wang, Y. C., Zhang, Q. S., Xue, Y. F., Stefanovski, D., Cui, Z. L., and Dou, Z. X.: Newer and select maize, wheat, and rice varieties can help mitigate N footprint while producing more grain, Glob. Change. Biol., 12, 4273-4281, https://doi.org/10.1111/gcb.14798, 2019.

Yu, S.C., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., and Robarge, W.: An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO_3^-, J Geophys Res-Atmos., 110(D7). https://doi.org/10.1029/2004JD004718, 2005.

Yue, H. B., He, C. Y., Huang, Q. X ., Yin, D., and Bryan, B. A.: Stronger policy required to substantially reduce deaths from $PM_{2.5}$ pollution in China, Nat. Commun., 11, 1462, https://doi.org/10.1038/s41467-020-15319-4, 2020.

Zhai, S., Jacob, D.J., Wang, X., Liu, Z., Wen, T., Shah, V., Li, K., Moch, J.M., Bates, K.H., Song, S. and Shen, L.: Control of particulate nitrate air pollution in China, Nat. Geosci., 14, 389-395. https://doi.org/10.1038/s41561-021-00726-z, 2021.

Zhan, X.Y., Adalibieke, W., Cui, X.Q., Winiwarter, W., Reis, S., Zhang, L., Bai, Z.H., Wang, Q.H., Huang, W.C., and Zhou, F.: Improved estimates of ammonia emissions from global croplands, Environ. Sci. Technol., 55, 1329-1338, https://doi.org/10.1021/acs.est.0c05149, 2021.

Zhang, L., Jacob, D. J., Knipping, E. M., Kumar, N., Munger, J. W., Carouge, C. C., van Donkelaar, A., Wang, Y. X., and Chen, D: Nitrogen deposition to the United States: distribution, sources, and processes, Atmos. Chem. Phys., 12, 4539–4554, https://doi.org/10.5194/acp-12-4539-2012, 2012.

Zhang, Q., Zheng, Y. X., Tong, D., Shao, M., Wang, S. X., Zhang, Y. H., Xu, X. D., Wang, J. N., He, H., Liu, W. Q., Ding, Y. H., Lei, Y., Li, J. H., Wang, Z. F., Zhang, X. Y., Wang, Y. S., Cheng, J., Liu, Y ., Shi, Q. R., Yan, L., Geng, G. N., Hong, C. P., Li, M., Liu, F., Zheng, B., Cao, J. J., Ding, A. J., Gao, J., Fu, Q. Y., Huo, J. T., Liu, B. X., Liu, Z. R., Yang, F. M., He, K. B., and Hao, J. M.: Drivers of improved $PM_{2.5}$ air quality in China from 2013 to 2017, Proc. Natl. Acad. Sci. U. S. A., 49, 24463-24469, https://doi.org/10.1073/pnas.1907956116, 2019.

Zhang, X. M., Gu, B. J., van Grinsven, H., Lam, S.K., Liang, X., Bai, M., and Chen, D.L.: Societal benefits of halving agricultural ammonia emissions in China far exceed the abatement costs. Nat. Commun., 11, 4357, https://doi.org/10.1038/s41467-020-18196-z, 2020a.

Zhang, Y., Vu, T. V., Sun, J., He, J., Shen, X., Lin, W., Zhang, X., Zhang, J., Gao, W., Wang, Y., Fu, T., Ma, Y., Li, W., and Shi, Z.: Significant changes in chemistry of fine particles in wintertime Beijing from 2007 to 2017: Impact of clean air actions, Environ. Sci. Technol., 54, 1344-1352, https://doi.org/10.1021/acs.est.9b04678, 2020b.

Zhang, Y., Chen, X., Yu, S., Wang, L., Li, Z., Li, M., Liu, W., Li, P., Rosenfeld, D., and Seinfeld, J. H: City-level air quality improvement in the Beijing-Tianjin-Hebei region from 2016/17 to 2017/18 heating seasons: Attributions and process analysis, Environ. Pollut., 274, https://doi.org/10.1016/j.envpol.2021.116523, 2021a.

Zhang, Y., Liu, X., Zhang, L., Tang, A., Goulding, K., and Collett Jr, J.L.: Evolution of secondary inorganic aerosols amidst improving $PM_{2.5}$ air quality in the North China Plain, Environ. Pollut., 281, 117027, https://doi.org/10.1016/j.envpol.2021.117027, 2021b.

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

Zheng, G. J., Duan, F. K., Su, H., Ma, Y. L., Cheng, Y., Zheng, B., Zhang, Q., Huang, T., Kimoto, T., Chang, D., Pöschl, U., Cheng, Y. F., and He, K. B.: Exploring the severe winter haze in Beijing: the impact of synoptic weather, regional transport and heterogeneous reactions, Atmos. Chem. Phys., 15, 2969–2983, https://doi.org/10.5194/acp-15-2969-2015, 2015.