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

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Preprint. Discussion started: 27 October 2021

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. Secondary inorganic aerosols (SIA) were the dominant contributor to ambient $PM_{2.5}$ concentrations. 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.

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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 (MEEC, 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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; Zhan et al., 2021).

Following the successful controls on NO_x and SO_2 emissions, 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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.

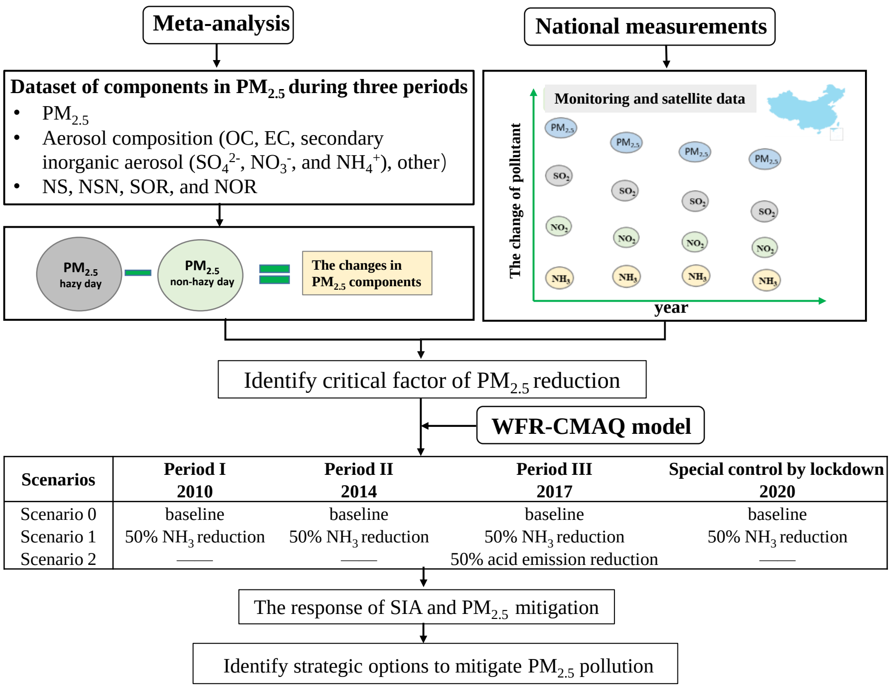

Fig. 1. Integrated assessment framework for Chinese $PM_{2.5}$ mitigation strategic options. OC is organic carbon, EC is elemental carbon, NO_3^- is nitrate, SO_4^{2-} is sulfate, and NH_4^+ is ammonium. NS is the slope of the regression equation between [NH_4^+] and [SO_4^{2-}], NSN is the slope of 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

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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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.

Ninety-eight 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 218 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

Atmospheric Chemistry and Physics Discussions

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:

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

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:

$$RR = \exp\left[\sum \ln RR(i) \times W(i) / \sum W(i)\right] \quad (2)$$

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 variation-related 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.

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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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. (2019). 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. (2018) 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 12km×12km 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 to represent the wintertime when the haze pollution frequently occurred. 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 released in the near future (Liu et al., 2019; Table S4). Zhang et al. (2020) found that societal benefits of halving agricultural NH_3 emissions in China far exceed the abatement costs, with technical mitigation potential of 38-67% for

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

different crops and animal types. 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.

The CMAQ model has been extensively used in air quality studies (Zhang et al., 2019; Backes et al., 2016). The model's performance was evaluated against observation data. Further information about the modelling is given in SI Method 3 and SI Figs. S3 and S4.

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 $PM_{2.5}$. Concentrations of $PM_{2.5}$ showed a downward trend from Period I to Period III on the non-hazy days, decreasing by 19.9% (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).

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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} (MEEC, 2012), indicating that $PM_{2.5}$ mitigation is a significant challenge for China.

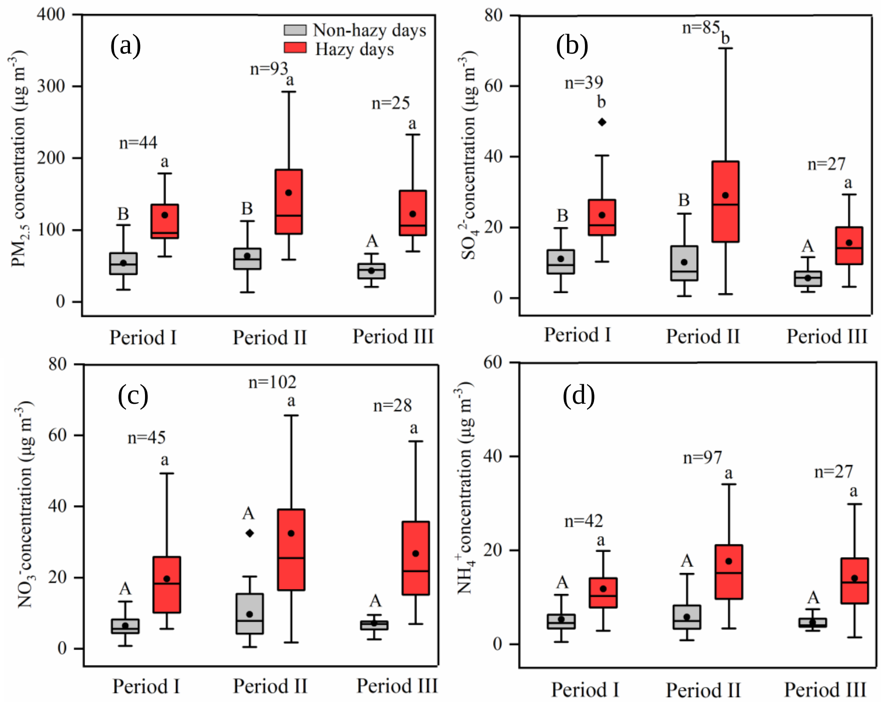

Fig. 2. Comparisons of concentrations of (a) $PM_{2.5}$, (b) SO_4^{2-}, (c) NO_3^-, and (d) NH_4^+ between non-hazy and hazy days in Period I (2000–2012), Period II (2013–2016), and Period III (2017–2019). Bars with different letters denote significant differences among the three periods (P <0.05) (upper 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

represents the mean value.

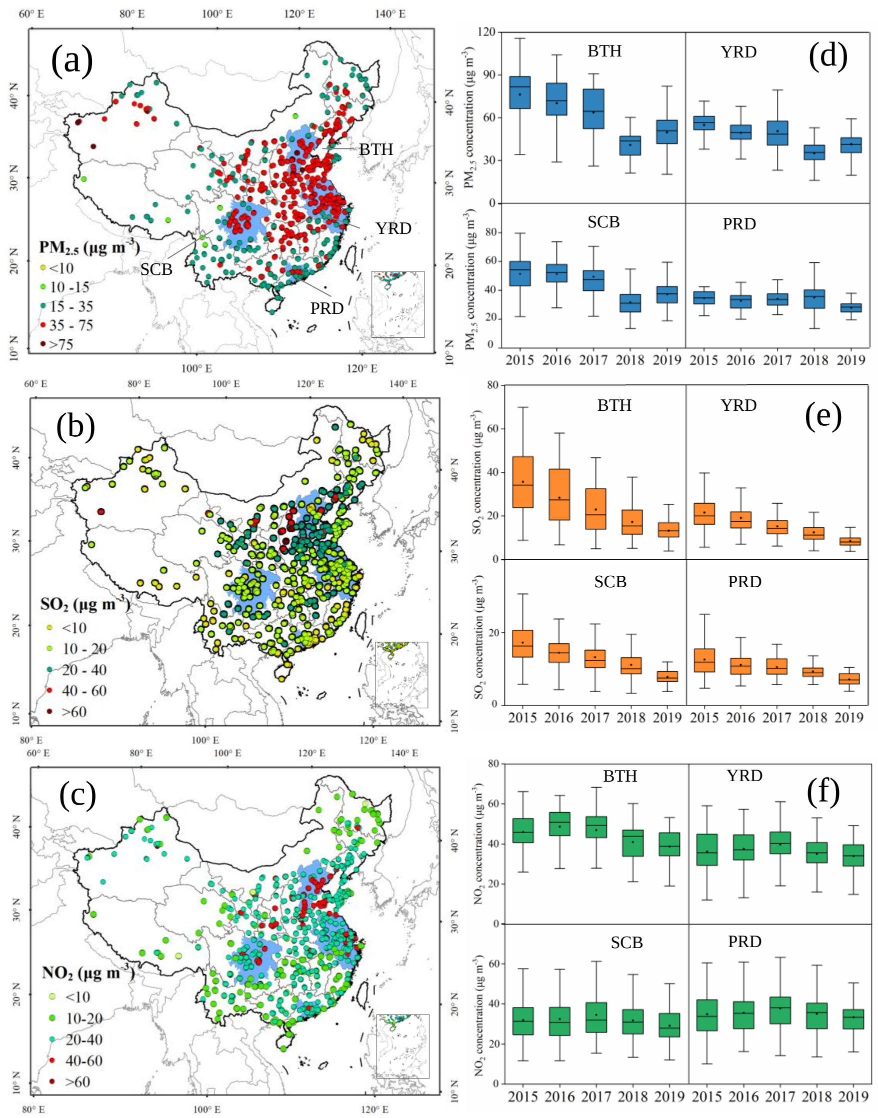

Fig. 3. Left: spatial patterns of annual mean concentration of (a) $PM_{2.5}$, (b) SO_2, (c) NO_2 at 1498 sites, averaged for 2015–2019. Right: the annual concentrations of (d) $PM_{2.5}$, (e) SO_2, and (f) NO_2 for 2015-2019 in four megacity clusters (BTH: Beijing-Tianjin-Hebei, YRD: Yangtze River Delta, SCB: Sichuan Basin, PRD: Pearl River Delta). The

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

Atmospheric Chemistry and Physics Discussions

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. 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.,

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

2019; 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.

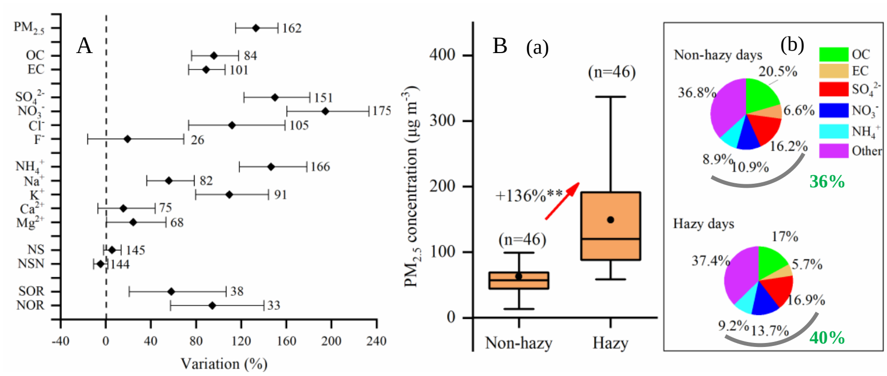

Fig. 4. (A) Variations in $PM_{2.5}$ concentration, aerosol component concentration, NS, NSN, SOR, and NOR from non-hazy to hazy days in China during 2000–2019. (B) (a) Summary of differences in $PM_{2.5}$ concentration between non-hazy and hazy days in China; (b) the average proportions of components 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 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

changes in concentrations, SO_4^{2-} showed a downward trend from Period I to Period III on the non-hazy days, decreasing by 19.9% and 49.6%, 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). The NO_x emissions in China stayed at a high level because the Chinese government did not start promulgating measures to reduce NO_x emission until 2011 (Fig. S2) (Zheng et al., 2018). The lack of downward trends in NH_4^+ concentrations is due to increasing emissions of NH_3 from agriculture and the absence in the past of NH_3 control policies (Kang et al., 2016). Zhang et al. (2020) 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^-. 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. S5).

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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

and 5a, d). 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., 2019). 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.

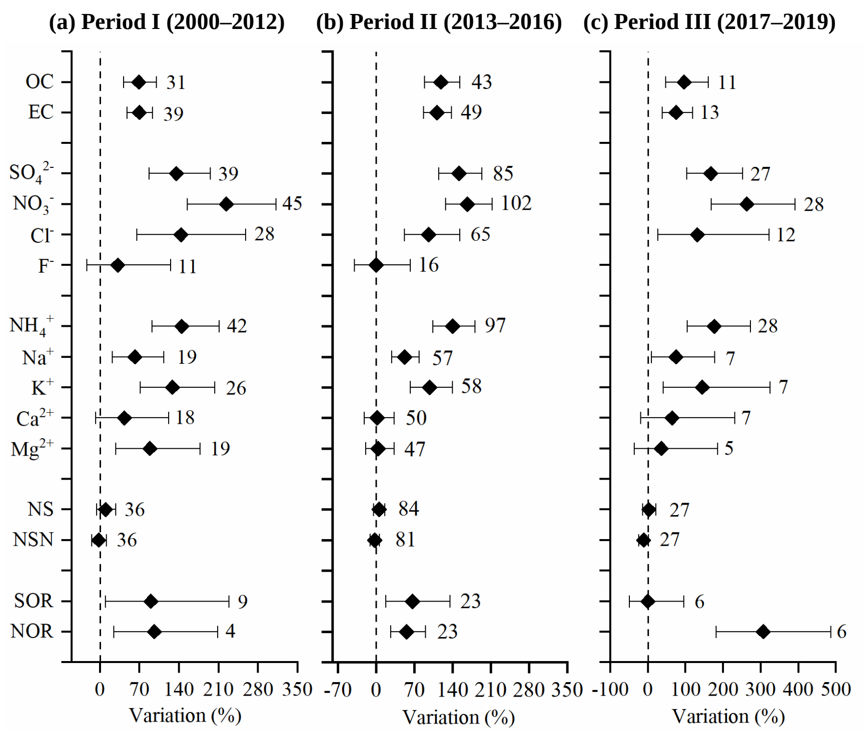

Fig. 5. Variations in $PM_{2.5}$ composition, NS, NSN, SOR, and NOR from non-hazy to hazy days in (a) Period I (2000–2012), (b) Period II (2013–2016), (c) Period III (2017–2019). NS is the slope of the regression equation between $[NH_4^+]$ and $[SO_4^{2-}]$, NSN is the slope of the regression equation 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.

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 S6 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 BTH, YRD, SCB and PRD megacity clusters decreased by 25.9 ± 0.3%, 24.4 ± 0.3%, and 22.9 ± 0.3%, respectively (Fig. 6 and Fig. S7). The reductions of $PM_{2.5}$ exhibited a similar trend (Figs. S6 and S8). 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., 2019), 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.

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

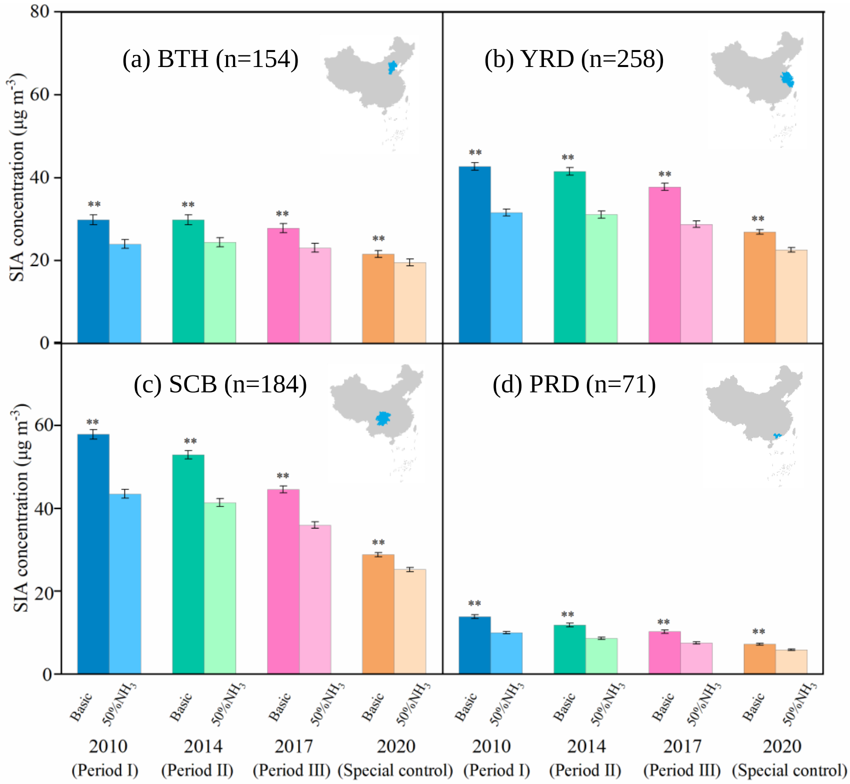

Fig. 6. Simulated SIA concentrations (in μg m^{-3}) without (basic) and with 50% ammonia (NH_3) emissions reductions in January for the years 2010, 2014, 2017 and 2020 in four megacity clusters (BTH: Beijing-Tianjin-Hebei, YRD: Yangtze River Delta, SCB: Sichuan Basin, PRD: Pearl River Delta). Inset maps 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 PM2.5), 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), 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.

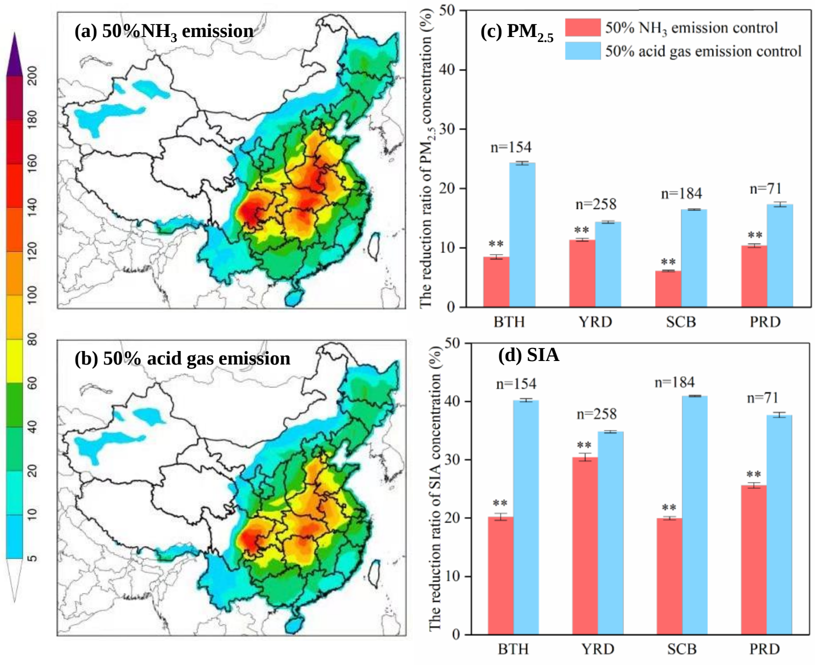

Fig. 7. Left: the spatial distributions of simulated $PM_{2.5}$ concentrations (in μg m^{-3}) in January 2017 with (a) 50% reductions in ammonia (NH_3) emissions and (b) 50% reductions in acid gas (NO_x and SO_2) emissions. Right: the % decreases in $PM_{2.5}$ (c) and SIA (d) concentrations for the simulations 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. Uncertainties and limitations

Some limitations should be noted in interpreting the results of the present study: this study examined annual trends 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 the study sites regarding the continuity of temporal variations. For instance, meteorological factors may vary across the underlying periods. In addition, there is heterogeneous geographic coverage across China in that most of the study sites were in the northeast coastal areas and megacities (Fig. S2). However, these more heavily populated regions are where information on effectiveness of mitigating $PM_{2.5}$ is most needed. In addition, WRF-CMAQ model performance has some uncertainty. In this study, the monthly predicted $PM_{2.5}$ concentrations were compared with the observations retrieved by the Space-Time Extra-Tree (STET) model (Wei et al., 2020, 2021). The WRF-CMAQ model captured similar spatial distributions to the STET model, but with some bias in identifying $PM_{2.5}$ hotspots (Fig. S3). The main reason for these disparities is that satellite retrievals have some spatial missing values in the rainy southern or high-latitude northern regions in China due to cloud contaminations or snow/ice cover in winter, respectively. Satellite $PM_{2.5}$ is derived from the Moderate Resolution Imaging Spectroradiometer Aerosol Optical Depth (MODIS AOD) products together with abundant natural and human factors using machine learning. The satellite historical $PM_{2.5}$ predictions are reliable (average R^2 = 0.80 and RMSE = 11.26 μg/m^3) by validating against the in-situ surface observations on a monthly basis (Wei et al., 2021). A more comprehensive evaluation of model performance was limited by the lack of field measurements of $PM_{2.5}$ and associated SIA concentrations in 2010.

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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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.

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

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., 2018). 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

Atmospheric Chemistry and Physics Discussions

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., 2021). The assessment of the impact of ultra-low emissions is provided in Table S5. 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

https://doi.org/10.5194/acp-2021-716
Preprint. Discussion started: 27 October 2021

Atmospheric Chemistry and Physics Discussions

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., 2020).

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. 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.

Competing interests

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.

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Preprint. Discussion started: 27 October 2021

Atmospheric Chemistry and Physics Discussions

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