Mitigating NO_X emissions does not help alleviate wintertime particulate pollution in Beijing-Tianjin-Hebei (BTH), China

Xia Li[1,5], Naifang Bei[2], Bo Hu[3], Yuan Wang[4], Suixin Liu[1], Jiarui Wu[1], Yuepeng Pan[3], Tianxue Wen[3], Zirui Liu[3], Lang Liu[1], Ruonan Wang[1], Min Zuo[1], Zhenxing Shen[2], Junji Cao[1,6], Xuexi Tie[1], Luisa T. Molina[7], and Guohui Li[1,6*]

[1]Key Lab of Aerosol Chemistry and Physics, SKLLQG, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an, Shaanxi, 710061, China
[2]School of Human Settlements and Civil Engineering, Xi'an Jiaotong University, Xi'an, Shaanxi, 710049, China
[3]State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, 100029, China
[4]Division of Geological and Planetary Sciences, California Institute of technology, Pasadena, CA 91125, USA
[5]University of the Chinese Academy of Sciences, Beijing, 100049, China
[6]CAS Center for Excellence in Quaternary Science and Global Change, Xi'an, Shaanxi, 710061, China
[7]Molina Center for Energy and the Environment, La Jolla, California, CA 92037, USA

[*]**Correspondence to:** Guohui Li (ligh@ieecas.cn)

Abstract: Stringent mitigation measures have reduced wintertime $PM_{2.5}$ concentrations by 42.2% from 2013 to 2018 in the BTH. The observed nitrate aerosols have not exhibited a significant decreasing trend and constituted a major fraction (about 20%) of the total $PM_{2.5}$, although the surface-measured NO_2 level has decreased by over 20%. It still remains elusive about contributions of nitrogen oxides (NO_X) emissions mitigation to the nitrate and $PM_{2.5}$ level. The WRF-Chem model simulations of a persistent haze episode in January 2019 in the BTH reveal that NO_X emissions mitigation does not help lower wintertime nitrate and $PM_{2.5}$ concentrations under current conditions in the BTH, because the substantial O_3 increase induced by NO_X mitigation offsets the HNO_3 loss and enhances sulfate and secondary organic aerosols formation. Our results are further consolidated by occurrence of the severe PM pollution in the BTH during the COVID-19 outbreak with a significant reduction of NO_2.

Plain Language Summary: Rapid industrialization and urbanization have caused severe particulate matter (PM) pollution in winter in Beijing-Tianjin-Hebei (BTH) region, China. Strict mitigation measures have been conducted to improve the air quality, but heavy PM pollution still frequently engulfs the region. The observed nitrate aerosols have not exhibited a significant decreasing trend and constituted a major fraction (about 20%) of the $PM_{2.5}$, although the surface-measured NO_2 level has decreased by over 20%. We quantify the contributions of nitrogen oxides (NO_X) emissions mitigation to the nitrate and $PM_{2.5}$ level in the BTH using a fully coupled WRF-Chem model and further explore how to efficiently alleviate nitrate aerosols under current situations. Our simulations of a persistent heavy haze episode in January 2019 in the BTH reveal that NO_X emissions mitigation does not help lower wintertime nitrate and $PM_{2.5}$ concentrations under current conditions in the BTH and mitigation of NH_3 emissions constitutes the priority measure to effectively decrease the nitrate and $PM_{2.5}$ level.

1. Introduction

The severe and persistent particulate matter (PM) pollution in China is attributed to a synergy of massive anthropogenic emissions and unfavorable synoptic situations, as well as the topography (An et al., 2019; Bei et al., 2016a, b; Long et al., 2016). Great efforts have been made by the Chinese central and local governments to mitigate anthropogenic emissions since 2013 with release of "Air Pollution Prevention and Control Action Plan" (APPCAP) (Li et al., 2019; Zhang et al., 2019). Although anthropogenic emissions of major air pollutants, including sulfur dioxide (SO_2), nitrogen oxides (NO_X), black carbon (BC) and organic carbon (OC) have decreased considerably since 2013 (Zhang et al., 2019; Zheng et al., 2019), persistent and heavy PM pollution still frequently engulfs the Beijing-Tianjin-Hebei (BTH) during wintertime, and observations have revealed that nitrate aerosols concentration has progressively increased in recent several years and constituted a major fraction of $PM_{2.5}$ in the BTH (Sun et al., 2015; Tao et al., 2017; Zhang et al., 2015). It still remains elusive about the contribution of NO_X emissions mitigation to the nitrate and $PM_{2.5}$ level.

Nitrate aerosols are formed via nitrous acid (HNO_3) to balance inorganic cations in the particle phase, and the reaction of NO_2 with OH to form HNO_3 and with NO_3 to form N_2O_5 constitute the major HNO_3 formation pathway in the atmosphere (Liu et al., 2019). Hence, the nitrate formation is not only dependent on its precursor (NO_X) and inorganic cations (such as NH_4^+), also significantly influenced by the atmospheric oxidizing capability (AOC) which is mainly determined by O_3 and its photochemical derivative OH, as well as existence of sulfate aerosols (Brasseur et al., 1999; Seinfeld and Pandis, 2006). Therefore, effective mitigation of the nitrate aerosols is still challenging considering the complexity of its formation process.

In the present study, we report analyses of nitrate measurements in the BTH during wintertime, and perform simulations of a persistent and heavy PM pollution episode in

January 2019 using a fully coupled WRF-Chem model to quantitatively estimate contributions of NO_X emissions mitigation to the nitrate and $PM_{2.5}$ level and seek an efficient measure to further alleviate PM pollution in the BTH under current situation.

2. WRF-Chem model and configurations

The WRF-Chem (Weather Research and Forecasting model coupled with Chemistry) model (Fast et al., 2006; Grell et al., 2005) modified by Li et al. (2010; 2011a, b; 2012) is used in the present study to simulate the particulate pollution episode. The wet and dry deposition of aerosols follows the method used in the CMAQ (Community Multiscale Air Quality Model) module (Binkowski and Roselle, 2003) and Wesely (1989), respectively. The photolysis rates are calculated using the FTUV (Fast Radiation Transfer Model), considering both the aerosol and cloud effects on photolysis (Li et al., 2005, 2011b; Tie et al., 2003). The inorganic aerosols are calculated using ISORROPIA (Version 1.7) (Nenes et al., 1998). Besides the SO_2 gas-phase oxidations by OH and sCI, a SO_2 heterogeneous reaction parameterization is adopted in the model, in which the SO_2 oxidation in aerosol water by O_2 catalyzed by Fe^{3+} is limited by mass transfer resistances in the gas-phase and gas-particle interface (Li et al., 2017). The secondary organic aerosol (SOA) is predicted using the volatility basis-set (VBS) modeling method, with contributions from glyoxal and methylglyoxal (Volkamer et al., 2007; Zhao et al., 2006).

In the present study, the WRF-Chem model adopts one grid with horizontal resolution of 6 km (301 × 301 grid points) centered at 38.0°N, 116.0°E (See Figure S1), and 35 sigma vertical levels with a stretched vertical grid with spacing ranging from 30 m near the surface, to 500 m at 2.5 km and 1 km above 14 km. The meteorological initial and boundary conditions are from the NCEP (National Centers for Environmental Prediction) 1° × 1° reanalysis data, and the chemical initial and boundary conditions are interpolated from the 6 h

output of WACCM (Whole Atmosphere Community Climate Model) (Marsh et al., 2013; Neale et al., 2013). The spin-up time of the WRF-Chem model is 100 hours. The SAPRC-99 (Statewide Air Pollution Research Center, version 1999) chemical mechanism is used in simulations. The anthropogenic emission inventory used in this study is developed by Zhang et al. (2009) and Li et al. (2017). The biogenic emissions are calculated online using the MEGAN (Model of Emissions of Gases and Aerosol from Nature) developed by Guenther et al. (2006). More detailed model configurations (Table S1) and monitoring data are provided in *SI Appendix*.

3. Results and discussion

3.1 Variations of air pollutants and aerosol species from 2013 to 2018 in the BTH

Aggressive emission mitigation measures have been carried out in the BTH to decrease air pollutants since implementation of the "Action Plan" in 2013 (Zhang et al., 2019; Zheng et al., 2019). Table 1 shows comparisons of the average mass concentrations of air pollutants during wintertime (referred as to the period from 1 December of the year to 28 February of the next year) in the BTH from 2013 to 2018. The wintertime SO_2 level has been remarkably decreased by around 78.3% from 2013 to 2018, and the average $PM_{2.5}$ concentration has decreased from 153.0 to 88.5 μg m^{-3}, or by 42.2%. However, the O_3 concentration displays an increasing trend, with the enhancement of around 30.3%. Besides, NO_2 concentration exhibits a slow decreasing trend compared to SO_2, reduced by about 22.0%.

Although the wintertime $PM_{2.5}$ concentrations in 2018 have decreased substantially compared to that in 2013, the occurrence frequency with daily $PM_{2.5}$ concentrations exceeding 75 μg m^{-3} in the winter of 2018 is about 53.3%, showing persistent particulate pollution in the BTH. Figure 1 shows the variations of the filter measured average concentrations and percentage of the $PM_{2.5}$ constituents at an urban site in Beijing from 2013 to 2018 during wintertime

pollution days with $PM_{2.5}$ concentrations exceeding 75 μg m^{-3}. The average wintertime $PM_{2.5}$ concentration at the site in Beijing decreases from 170.4 μg m^{-3} in 2013 to 108.3 μg m^{-3} in 2018, reduced by about 36.4% (See Figure S2), which is primarily contributed by decreases in sulfate (51.6%), unspecified constituents (mainly mineral dust, 47.1%), organic aerosols (41.0%), ammonium (37.5%), and nitrate (12.5%). However, the black carbon concentration increases from 2.9 to 4.3 μg m^{-3}, with an enhancement of 48.3%, which is likely caused by the rapid growth of vehicles in Beijing.

Figure 2 presents variations of wintertime sulfate, nitrate, and ammonium concentrations from 2014 to 2018 in Tianjin, Tangshan, Baoding, and Shijiazhuang in the BTH when the $PM_{2.5}$ level exceeds 75 μg m^{-3}. Generally, the wintertime sulfate concentrations exhibit a decreasing trend in the four cities, particularly in Shijiazhuang with the sulfate reduction of about 27.4%. However, the nitrate and ammonium concentrations do not display a decreasing trend, and their contributions to $PM_{2.5}$ have increased from 11.1% to 18.9% and 5.9% to 10.1% on average in the four cities, respectively (See Figure S3). Due to lack of effective mitigation measures for NH_3, the NH_3 emissions in China still remain stable since 2010 (Zheng et al., 2019). Therefore, when the metal cation (mainly contained in mineral dust) decreases, NH_3 becomes the dominant contributor of cation to balance anion in the particle phase. Although sulfate aerosols have decreased in the four cities from 2014 to 2018, the ammonium concentration does not decrease or even increase due to decreased competence of metal cation and/or increased nitrate concentrations.

3.2 Contributions of NO_X emissions mitigation to nitrate and $PM_{2.5}$ level in the BTH

The NO_X emissions have been effectively mitigated since 2013 in China (Zheng et al. 2019) and the observed wintertime NO_2 concentrations have decreased by more than 20% in the BTH from 2013 to 2018 (Table 1). However, nitrate concentrations do not exhibit an evident

decreasing trend in the BTH and have become a major fraction of $PM_{2.5}$ in the BTH with contributions of around 20% in 2018 (Figure 1b and S3). Therefore, simulations of a persistent and heavy particulate pollution episode from 29 December 2018 to 29 January 2019 in the BTH have been performed using the WRF-Chem model to quantitatively evaluate contributions of NO_X emissions mitigation to nitrate and $PM_{2.5}$ concentrations and investigate how to effectively alleviate nitrate aerosols. In the base simulation with the emission inventory of the base year of 2018 (F_BASE), the model performs reasonably well in simulating air pollutants ($PM_{2.5}$, O_3, NO_2, and SO_2), sulfate, nitrate, ammonium and organic aerosols and NH_3. See *SI Appendix* for detailed model validation and quantitative statements of model biases (Figure S4-S7).

Pan et al. (2016b) have redefined the importance of nitrate aerosols during PM pollution and indicated that controlling NO_X emissions should be a priority in mitigating the serious air pollution. Previous studies have also shown that decreasing NO_X might represent a positive feedback mechanism to reduce the conversion of primary gas pollutants into secondary aerosols (He et al., 2014; Ma et al., 2010; Xu et al., 2015; Wang et al., 2014). Therefore, a sensitivity simulation is firstly conducted in the present study, in which the NO_X emission in the base year of 2013 is used (F_EM13). Compared to F_EM13, on average in the BTH, the NO_2 concentration in F_BASE decreases by around 17.1% but the O_3 concentration increases by 44.2%, which is generally consistent with the observed NO_2 and O_3 trend from 2013 to 2018 (Table 1). However, the average $PM_{2.5}$ concentration in F_BASE is 91.8 μg m^{-3}, 2.9% higher than that in F_EM13 (Figure 3a). The $PM_{2.5}$ enhancement in F_BASE against F_EM13 is contributed by the increase in secondary aerosols, i.e., sulfate (0.5 μg m^{-3}), nitrate (0.9 μg m^{-3}), ammonium (0.3 μg m^{-3}), and SOA (0.9 μg m^{-3}).

In order to further assess the impact of NO_X emissions mitigation on the nitrate and $PM_{2.5}$ level in the BTH, the first sensitivity scenario is designed, in which the NO_X emission in

F_BASE is reduced from 10% to 50% with a 10% interval. As shown in Figure 3a, the variations in $PM_{2.5}$ concentration are not as expected, with an average enhancement of about 3.2% (3.0 μg m^{-3}) in the BTH when NO_X emissions are reduced by 50%. Although the NO_2 level is decreased monotonically from 6.4% to 40.0% in the BTH with NO_X emissions decreased from 10% to 50% (Figure 3b), the nitrate concentration increases by 1.1% and then decreases by 10.3%. Additionally, the SOA, sulfate, and ammonium concentrations are increased from 3.3% to 10.9%, 4.4% to 26.7%, and 1.9% to 6.3% in the BTH, respectively (Figure 3a).

Therefore, mitigation of NO_X emissions is not beneficial to the air quality at present during wintertime in the BTH (Figure 3c-3d). Decreasing NO_X emissions does not proportionally reduce the nitrate concentrations, and particularly enhances formation of sulfate, ammonium, and SOA, which is primarily caused by the increase in O_3 concentrations (Figure 3b). In winter in the BTH, the weak insolation significantly decrease photolysis and slow the O_3 formation. During PM pollution period, the lower atmosphere is stable or stagnant, which is quite favorable for accumulation of air pollutants. The titration of NO_X (mainly NO) emissions remarkably influence the O_3 level in the PBL. Figure S8 shows the variations of observed O_3 and NO_2 concentrations as a function of the $PM_{2.5}$ level over all the monitoring sites in the BTH during the wintertime from 2013 to 2018. With deterioration of PM pollution, the O_3 concentration decreases but it is opposite for the NO_2 concentration. Therefore, when the NO_X emissions are decreased from 10% to 50%, the O_3 concentration is increased from 11.8% to 83.8% in the BTH (Figure 3b). Increased O_3 concentrations enhance the AOC, not only promoting the SOA and sulfate formation, but also accelerating conversion of NO_2 to HNO_3 to counterbalance HNO_3 decrease due to mitigation of NO_X emissions.

Our results on contributions of NO_X emission mitigation to $PM_{2.5}$ concentrations are also supported by occurrence of the severe PM pollution in the BTH during outbreak of the

Coronavirus Disease 2019 (COVID-19) pandemic with a significant reduction of NO_2. Due to the outbreak of COVID-19, the nationwide preventive lockdown has been carried out since late January 2020 in China, by shutdown of commercial activities and restrictions of population movement. The nationwide lockdown has lasted for more than three weeks and caused remarkable reductions in emissions of air pollutants (Huang et al., 2020; Le et al., 2020; Shi and Brasseur, 2020). Observations from the Tropospheric Monitoring Instrument (TROPOMI) have shown a more than 70% decrease of the column-integrated NO_2 amount during the lockdown period in 2020 over eastern China, compared to that in the same time period in 2019 (Le et al., 2020). Surface measurements have also revealed that the NO_2 concentrations have decreased by about 60% between the period 1-22 January 2020 and the period 23 January-29 February 2020 in northern China (Shi and Brasseur, 2020). However, several severe PM pollution events have still occurred in the BTH, with the maximum daily $PM_{2.5}$ concentration exceeding 250 μg m^{-3} in Beijing, although the observed NO_2 level has decreased substantially. Therefore, additional two sensitivity experiments have been devised based on F_BASE, in which the NO_X emissions are further decreased by 60% and 80% to represent variations of the NO_X emission mitigation during the lockdown period. When the NO_X emissions are decreased from 60% to 80%, the NO_2 concentrations in the BTH are reduced from 51.0% to 75.7% compared to those in F_BASE (Figure 3a), which is within the range of the observed NO_2 variation due to the nationwide lockdown. However, the $PM_{2.5}$ level is increased by 2.2% with a 60% reduction of NO_X emissions and decreased by 3.2% with an 80% reduction of NO_X emissions (Figure 3a), showing the significant NO_X emissions reduction does not help lower the $PM_{2.5}$ level during the lockdown period in the BTH. The main reason is that the substantial increase in O_3 concentrations (more than 100%) causes enhancement of SOA and sulfate to offset the nitrate loss.

3.3 Priority measure to alleviate wintertime PM pollution in the BTH under current situation

Apparently, mitigation of NO_X emissions alleviates O_3 titration during wintertime in the BTH, increasing O_3 concentrations and further the AOC to enhance formation of secondary aerosols. Therefore, decreasing the AOC might effectively lower the nitrate and $PM_{2.5}$ level in the BTH. The second sensitivity scenario is therefore designed, in which the VOCs emission in F_BASE is reduced from 10% to 50% with a 10% interval to lower the O_3 concentration. With a 50% reduction of VOCs emissions, the O_3 concentration is decreased by 19.6% in the BTH (See Figure S9b), showing considerable weakening of the AOC. However, the decreases in sulfate, nitrate, and ammonium concentrations are not substantial, only about 13.0%, 18.6%, and 6.1%, respectively (See Figure S9a). The SOA concentration is decreased by about 37.6%, caused to a large degree by the reduction of SOA precursors. Overall, the decrease in $PM_{2.5}$ concentration is not significant (See Figure S9c-9d), around 6.9% (6.3 μg m^{-3}) in the BTH, when VOCs emissions are reduced by 50%.

As a large agricultural country, China produces a huge amount of NH_3 emissions, with agricultural activities accounting for more than 80% (Huang et al., 2012; Paulot et al., 2014; Zhang et al., 2018). Recent studies have pointed out that NH_3 plays an important role in the $PM_{2.5}$ formation and NH_3 control has been advocated as a potential measure by policy makers, given that atmospheric NH_3 facilitates secondary inorganic aerosol formation, i.e., ammonium sulfate/bisulfate and ammonium nitrate (Fu et al., 2017; Guo et al., 2018; Weber, et al., 2016). Figure S9 presents the pattern comparisons of simulated and measured near-surface NH_3 mass concentrations averaged during January 2019. Compared with measurements, the WRF-Chem model reasonably well simulates the spatial distributions of the NH_3 mass concentrations in the BTH. The NH_3 level is quite high in the plain region of the BTH, with mass concentrations exceeding 5 μg m^{-3}. It is well known that the major

source of NH_3 is agricultural activities, mainly including livestock and fertilizer use (Huang et al., 2012; Streets et al., 2003). Additionally, nonagricultural sources (e.g., vehicles, coal combustion, etc.) are also responsible for the high NH_3 emissions in China, especially in urban areas (Chang et al., 2016; Pan et al., 2016a).

Thus, we have further performed the third sensitivity scenario, in which the NH_3 emission in F_BASE is reduced from 10% to 50% with a 10% interval. With a 50% reduction of NH_3 emissions, the nitrate and ammonium concentrations are decreased by 34.5% and 36.5% in the BTH (Figure 4a), respectively. The sulfate concentrations are also reduced by 6.5%, which is mainly caused by the loss of aerosol liquid water due to decrease in nitrate and ammonium aerosols (Wu et al., 2019). The SOA concentration in the BTH is slightly decreased by 0.1% when the NH_3 emissions are reduced by 10% and then increased from 0.1% to 0.6% when the NH_3 emissions are reduced from 20% to 50%. The $PM_{2.5}$ decrease is about 12.3% (11.3 μg m^{-3}) in the BTH (Figure 4c-4d), when NH_3 emissions are reduced by 50%, showing mitigating NH_3 emissions is much more effective to reduce PM pollution in the BTH than NO_X and VOCs emissions.

4. Conclusions

The Chines government has made great efforts to mitigate emissions of primary PM, SO_2 and NO_X to alleviate PM pollution since 2013. The observed near-surface wintertime concentrations of $PM_{2.5}$, SO_2, and NO_2 have decreased by 42.2%, 78.3% and 22.0% from 2013 to 2018 in the BTH, respectively, but persistent PM pollution still frequently occurs. Observations show that nitrate aerosols have not exhibited a significant decreasing trend and play an increasing role in PM pollution during wintertime in the BTH, with a $PM_{2.5}$ contribution of about 20%. Our sensitivity simulations of a persistent heavy PM pollution episode in January 2019 in the BTH reveal that NO_X emissions mitigation does not help

lower nitrate and $PM_{2.5}$ concentrations during wintertime. A 50% reduction of NO_X emissions only decreases nitrate mass by 10.3% but increases $PM_{2.5}$ concentrations by around 3.2% because the O_3 increase induced by NO_X mitigation offsets the loss of HNO_3 and enhances sulfate and SOA formation. Our results are also consolidated by occurrence of server PM pollutions in the BTH during the COVID-19 outbreak when the NO_X emissions have been remarkably reduced and the observed NO_2 level has decreased by more than 60%.

Although the emissions reduction of VOCs has been proposed to be particularly important to mitigate PM pollution, our results reveal that a 50% reduction in VOCs emissions decreases $PM_{2.5}$ concentrations by around 7% in the BTH. However, when NH_3 emissions are reduced by 50%, the $PM_{2.5}$ level is decreased by about 12%, mainly caused by substantial decreases in nitrate and ammonium aerosols. Therefore, we suggest that, in addition to primary PM emissions, mitigating NH_3 emissions is the priority measure to effectively alleviate PM pollution during wintertime in the BTH under the current situation.

Acknowledgments. This work is financially supported by the Strategic Priority Research Program of Chinese Academy of Sciences (XDB40030203), the National Key R&D Plan (2017YFC0210000), and National Research Program for Key Issues in Air Pollution Control (DQGG0105).

References

An, Z. S., Huang, R. J., Zhang, R. Y., Tie, X. X., Li, G. H., Cao, J. J., et al. (2019) Severe haze in northern China: A synergy of anthropogenic emissions and atmospheric processes. *Proceedings of the National Academy of Sciences of the United States of America*, *116*(18), 8657-8666. https://doi.org/10.1073/pnas.1900125116

Bei, N. F., Li, G. H., Huang, R. J., Cao, J. J., Meng, N., Feng, T., et al. (2016a) Typical synoptic situations and their impacts on the wintertime air pollution in the Guanzhong basin, China. *Atmospheric Chemistry and Physics*, *16*(11), 7373-7387. https://doi.org/10.5194/acp-16-7373-2016

Bei, N. F., Xiao, B., Meng, N., & Feng, T. (2016b) Critical role of meteorological conditions in a persistent haze episode in the Guanzhong basin, China. *Science of the Total Environment*, *550*, 273-284. https://doi.org/10.1016/j.scitotenv.2015.12.159

Binkowski, F. S., & Roselle, S. J. (2003) Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component 1. Model description. *Journal of Geophysical Research*, *108*(D6), 4183. https://doi.org/10.1029/2001JD001409

Brasseur, G. P., Orlando, J. J., & Tyndall, G. S. (1999) *Atmospheric Chemistry and Global Change*. Cambridge, MA: Oxford University Press. https://doi.org/10.1029/EO080i040p00468-02

Chang, Y. H., Zou, Z., Deng, C. R., Huang, K., Collett, J. L., Lin, J., & Zhuang, G. S. (2016) The importance of vehicle emissions as a source of atmospheric ammonia in the megacity of Shanghai. *Atmospheric Chemistry and Physics*, *16*(5), 3577-3594. https://doi.org/10.5194/acp-16-3577-2016

Elser, M., Huang, R., Wolf, R., Slowik, J. G., Wang, Q., Canonaco, F., et al. (2016) New insights into $PM_{2.5}$ chemical composition and sources in two major cities in China during extreme haze events using aerosol mass spectrometry. *Atmospheric Chemistry and Physics*, *16*(5), 3207-3225. https://doi.org/10.5194/acp-16-3207-2016

Fast, J. D., Jr, W. I. G., Easter, R. C., Zaveri, R. A., Barnard, J. C., Chapman, E. G., et al. (2006) Evolution of ozone, particulates, and aerosol direct radiative forcing in the vicinity of Houston using a fully coupled meteorology-chemistry-aerosol model. *Journal of Geophysical Research-Atmospheres*, *111*(D21), D21305. https://doi.org/10.1029/2005JD006721

Fu, X., Wang, S. X., Xing, J., Zhang, X. Y., Wang, T., & Hao, J. M. (2017) Increasing Ammonia Concentrations Reduce the Effectiveness of Particle Pollution Control Achieved via SO_2 and NOx Emissions Reduction in East China. *Environmental Science & Technology Letters*, *4*(6), 221-227. https://doi.org/10.1021/acs.estlett.7b00143

Gao, M., Carmichael, G. R., Wang, Y., Saide, P. E., Yu, M., Xin, J., et al. (2016) Modeling study of the 2010 regional haze event in the North China Plain. *Atmospheric Chemistry and Physics*, *16*(3), 1673-1691. https://doi.org/10.5194/acp-16-1673-2016

Grell, G. A., Peckham, S. E., Schmitz, R., McKeen, S. A., Frost, G., Skamarock, W. C., & Eder, B. (2005) Fully coupled "online" chemistry within the WRF model. *Atmospheric Environment*, *39*(37), 6957-6975. https://doi.org/10.1016/j.atmosenv.2005.04.027

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., & Geron, C. (2006) Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemistry and Physics*, *6*, 3181-3210. https://doi.org/10.5194/acp-6-3181-2006

Guo, H., Otjes, R., Schlag, P., Kiendler-Scharr, A., Nenes, A., & Weber, R. J. (2018) Effectiveness of ammonia reduction on control of fine particle nitrate. *Atmospheric Chemistry and Physics*, *18*(16), 12241-12256. https://doi.org/10.5194/acp-18-12241-2018

Guo, S., Hu, M., Zamora, M. L., Peng, J., Shang, D., Zheng, J., et al. (2014) Elucidating severe urban haze formation in China. *Proceedings of the National Academy of Sciences of the United States of America*,

337 *111*(49), 17373-17378. https://doi.org/10.1073/pnas.1419604111

338 He, H., Wang, Y., Ma, Q., Ma, J., Chu, B., Ji, D., et al. (2014) Mineral dust and NOx promote the
339 conversion of SO_2 to sulfate in heavy pollution days. *Scientific Reports, 4*, 4172.
340 https://doi.org/10.1038/srep04172

341 Huang, R. J., Zhang, Y., Bozzetti, C., Ho, K. F., Cao, J. J., Han, Y. M., et al. (2014) High secondary aerosol
342 contribution to particulate pollution during haze events in China. *Nature, 514*(7521), 218-222.
343 https://doi.org/10.1038/nature13774

344 Huang, X., Ding, A. J., Gao, J., Zheng, B., Zhou, D. R., Qi, X. M., et al. (2020) Enhanced secondary
345 pollution offset reduction of primary emissions during COVID-19 lockdown in China. *National*
346 *Science Review*, nwaa137. https://doi.org/10.31223/osf.io/hvuzy

347 Huang, X., Song, Y., Li, M. M., Li, J. F., Huo, Q., Cai, X. H., et al. (2012) A high-resolution ammonia
348 emission inventory in China. *Global Biogeochemical Cycles, 26*, GB1030.
349 https://doi.org/10.1029/2011GB004161

350 Le, T. H., Wang, Y., Liu, L., Yang, J. N., Yung, Y. L., Li, G. H., & Seinfeld, J. H. (2020) Unexpected air
351 pollution with marked emission reductions during the COVID-19 outbreak in China. *Science*,
352 *369*(6504), 702-706. https://doi.org/10.1126/science.abb7431

353 Li, G. H., Bei, N. F., Cao, J. J., Huang, R. J., Wu, J. R., Feng, T., et al. (2017) A possible pathway for rapid
354 growth of sulfate during haze days in China. *Atmospheric Chemistry and Physics*, *17*(5), 3301-3316.
355 https://doi.org/10.5194/acp-17-3301-2017

356 Li, G. H., Bei, N. F., Tie, X. X., & Molina, L. T. (2011a) Aerosol effects on the photochemistry in Mexico
357 City during MCMA-2006/MILAGRO campaign. *Atmospheric Chemistry and Physics*, *11*(11),
358 5169-5182. https://doi.org/10.5194/acp-11-5169-2011

359 Li, G. H., Lei, W. F., Bei, N. F., & Molina, L. T. (2012) Contribution of garbage burning to chloride and
360 $PM_{2.5}$ in Mexico City. *Atmospheric Chemistry and Physics*, *12*(18), 8751-8761.
361 https://doi.org/10.5194/acp-12-8751-2012

362 Li, G. H., Lei, W. F., Zavala, M., Volkamer, R., Dusanter, S., Stevens, P., & Molina, L. T. (2010) Impacts
363 of HONO sources on the photochemistry in Mexico City during the MCMA-2006/MILAGO
364 Campaign. *Atmospheric Chemistry and Physics*, *10*(14), 6551-6567.
365 https://doi.org/10.5194/acp-10-6551-2010

366 Li, G. H., Zavala, M., Lei, W. F., Tsimpidi, A. P., Karydis, V. A., Pandis, S. N., et al. (2011b) Simulations
367 of organic aerosol concentrations in Mexico City using the WRF- CHEM model during the
368 MCMA-2006/MILAGRO campaign. *Atmospheric Chemistry and Physics*, *11*(8), 3789-3809.
369 https://doi.org/10.5194/acp-11-3789-2011

370 Li, G. H., Zhang, R. Y., Fan, J., & Tie, X. X. (2005) Impacts of black carbon aerosol on photolysis and
371 ozone. *Journal of Geophysical Research-Atmospheres*, *110*(D23), D23206.
372 https://doi.org/10.1029/2005JD005898

373 Li, K., Jacob, D. J., Liao, H., Zhu, J., & Zhai, S. (2019) A two-pollutant strategy for improving ozone and
374 particulate air quality in China. *Nature Geoscience*, *12*(11).
375 https://doi.org/10.1038/s41561-019-0464-x
376 Li, M., Zhang, Q., Kurokawa, J. I., Woo, J. H., He, K., Lu, Z., et al. (2017) MIX: a mosaic Asian
377 anthropogenic emission inventory under the international collaboration framework of the MICS-Asia
378 and HTAP. *Atmospheric Chemistry and Physics*, *17*(2), 935-963.
379 https://doi.org/10.5194/acp-17-935-2017

380 Liu, L., Wu, J. R., Liu, S. X., Li, X., Zhou, J. M., Feng, T., et al. (2019) Effects of organic coating on the
381 nitrate formation by suppressing the N_2O_5 heterogeneous hydrolysis: a case study during wintertime
382 in Beijing-Tianjin-Hebei (BTH). *Atmospheric Chemistry and Physics*, *19*(12), 8189-8207.

https://doi.org/10.5194/acp-19-8189-2019

Liu, W. J., Shen, G. F., Chen, Y. C., Shen, H. Z., Huang, Y., Li, T. C., et al. (2018) Air pollution and inhalation exposure to particulate matter of different sizes in rural households using improved stoves in central China. *Journal of Environmental Science*, *63*, 87-95. https://doi.org/10.1016/j.jes.2017.06.019

Long, X., Tie, X., Cao, J., Huang, R., Feng, T., Li, N., et al. (2016) Impact of crop field burning and mountains on heavy haze in the North China Plain: a case study. *Atmospheric Chemistry and Physics*, *16*(15), 9675-9691. https://doi.org/10.5194/acp-16-9675-2016

Ma, Q., He, H., & Liu, Y. (2010) In situ DRIFTS study of hygroscopic behavior of mineral aerosol. *Journal of Environmental Science*, *22*(4), 555-560. https://doi.org/10.1016/S1001-0742(09)60145-5

Marsh, D. R., Mills, M., Kinnison, D., Lamarque, J. F., Calvo, N., & Polvani, L. (2013) Climate change from 1850 to 2005 simulated in CESM1(WACCM). *Journal of Climate*, *26*(19), 7372-7391. https://doi.org/10.1175/JCLI-D-12-00558.1

Neale, R. B., Richter, J., Park, S., Lauritzen, P. H., Vavrus, S. J., Rasch, P. J., & Zhang, M. (2013) The Mean Climate of the Community Atmosphere Model (CAM4) in Forced SST and Fully Coupled Experiments. *Journal of Climate*, *26*(14), 5150-5168. https://doi.org/10.1175/JCLI-D-12-00236.1

Nenes, A., Pandis, S. N., & Pilinis, C. (1998) ISORROPIA: A new thermodynamic equilibrium model for multiphase multi-component inorganic aerosols. *Aquatic Geochemistry*, *4*, 123-152.

Pan, Y. P., Tian, S. L., Liu, D. W., Fang, Y. T., Zhu, X. Y., Zhang, Q., et al. (2016a) Fossil Fuel Combustion-Related Emissions Dominate Atmospheric Ammonia Sources during Severe Haze Episodes: Evidence from N-15-Stable Isotope in Size-Resolved Aerosol Ammonium. *Environmental Science & Technology*, *50*(15), 8049-8056. https://doi.org/10.1021/acs.est.6b00634

Pan, Y. P., Wang, Y. S., Zhang, J. K., Liu, Z. R., Wang, L. L., Tian, S. L., et al. (2016b) Redefining the importance of nitrate during haze pollution to help optimize an emission control strategy. *Atmospheric Environment*, *141*, 197-202. https://doi.org/10.1016/j.atmosenv.2016.06.035

Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., & Henze, D. K. (2014) Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH_3). *Journal of Geophysical Research-Atmospheres*, *119*(7), 4343-4364. https://doi.org/10.1002/2013JD021130

Seinfeld, J. H., & Pandis, S. N. (2006) Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edition. New York: John Wiley and Sons Inc. https://doi.org/10.1063/1.882420

Shi, X. Q., & Brasseur, G. P. (2020) The Response in Air Quality to the Reduction of Chinese Economic Activities During the COVID-19 Outbreak. *Geophysical Research Letters*, *47*(11). https://doi.org/10.1029/2020GL088070

State Council of the People's Republic of China, Notice of the general office of the state council on issuing the air pollution prevention and control action plan. http://www.gov.cn/zwgk/2013-09/12/content_2486773.htm. Accessed 4 August 2020.

Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., Fu, Q., He, D., et al. (2003) An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Research*, *108*(D21), 8809. https://doi.org/10.1029/2002JD003093

Sun, Y. L., Wang, Z. F., Du, W., Zhang, Q., Wang, Q. Q., Fu, P. Q, et al. (2015) Long-term real-time measurements of aerosol particle composition in Beijing, China: seasonal variations, meteorological effects, and source analysis. *Atmospheric Chemistry and Physics*, *15*(17), 10149-10165. https://doi.org/10.5194/acp-15-10149-2015

Tao, J., Zhang, L., Cao, J. J., & Zhang, R. Y. (2017) A review of current knowledge concerning $PM_{2.5}$ chemical composition, aerosol optical properties and their relationships across China. *Atmospheric Chemistry and Physics*, *17*(15), 9485-9518. https://doi.org/10.5194/acp-17-9485-2017

Tie, X. X., Madronich, S., Walters, S., Zhang, R. Y., Rasch, P., & Collins, W. (2003) Effect of clouds on photolysis and oxidants in the troposphere. *Journal of Geophysical Research*, *108*(D20), 4642. https://doi.org/10.1029/2003JD003659

Volkamer, R., San Martini, F., Molina, L. T., Salcedo, D., Jimenez, J. L., & Molina, M. J. (2007) A missing sink for gas-phase glyoxal in Mexico City: formation of secondary organic aerosol. *Geophysical Research Letters*, *34*(19), L19807. https://doi.org/10.1029/2007GL030752

Wang, G. H., Zhang, R. Y., Gomez, M. E., Yang, L. X., Zamora, M. L., Hu, M., et al. (2016) Persistent sulfate formation from London Fog to Chinese haze. *Proceedings of the National Academy of Sciences of the United States of America*, *113*(48), 13630-13635. https://doi.org/10.1073/pnas.1616540113

Wang, Y., Yao, L., Wang, L., Liu, Z., Ji, D., Tang, G., et al. (2014) Mechanism for the formation of the January 2013 heavy haze pollution episode over central and eastern China. *Science China-Earth Science*, *57*(1), 14-25. https://doi.org/10.1007/s11430-013-4773-4

Weber, R. J., Guo, H. Y., Russell, A. G., & Nenes, A. (2016) High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years. *Nature Geoscience*, *9*(4), 282-285. https://doi.org/10.1038/NGEO2665

Wei, S. Y., Shen, G. F., Zhang, Y. Y., Xue, M., Xie, H., Lin, P. C., et al. (2014) Field measurement on the emissions of PM, OC, EC and PAHs from indoor crop straw burning in rural China. *Environmental Pollution*, *184*(SI), 18-24. https://doi.org/10.1016/j.envpol.2013.07.036

Wesely, M. L. (1989) Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. *Atmospheric Environment*, *23*(6), 1293-1304. https://doi.org/10.1016/0004-6981(89)90153-4

Wu, J. R., Bei, N. F., Hu, B., Liu, S. X., Zhou, M., Wang, Q. Y., et al. (2019) Is water vapor a key player of the wintertime haze in North China Plain? *Atmospheric Chemistry and Physics*, *19*(13), 8721-8739. https://doi.org/10.5194/acp-2018-1289

Xu, W, Luo, X. S., Pan, Y. P., Zhang, L., Tang, A. H., Shen, J. L., et al. (2015) Quantifying atmospheric nitrogen deposition through a nationwide monitoring network across China. *Atmospheric Chemistry and Physics*, *15*(21), 12345-12360. https://doi.org/10.5194/acp-15-12345-2015

Zhang L, Chen, Y. F., Zhao, Y. H., Henze, D. K., Zhu, L. Y., Song, Y., et al. (2018) Agricultural ammonia emissions in China: Reconciling bottom-up and top-down estimates. *Atmospheric Chemistry and Physics*, *18*(1), 339-355. https://doi.org/10.5194/acp-18-339-2018

Zhang, Q., He, K. B., & Huo, H. (2012) Policy: Cleaning China's air. *Nature*, *484*(7393), 161-162. https://doi.org/10.1038/484161a

Zhang, Q., Streets, D. G., & Carmichael, G. R. (2009) Asian emissions in 2006 for the NASA INTEX-B mission. *Atmospheric Chemistry and Physics*, *9*(14), 5131-5153. https://doi.org/10.5194/acp-9-5131-2009

Zhang, Q., Zheng, Y. X., Tong, D., Shao, M., Wang, S. X., Zhang, Y. H., et al. (2019) Drivers of improved $PM_{2.5}$ air quality in China from 2013 to 2017. *Proceedings of the National Academy of Sciences of the United States of America*, *116*(49), 24463-24469. https://doi.org/10.1073/pnas.1907956116

Zhang, R. Y., Li, G. H., Fan, J. W., Wu, D. L., & Molina, M. J. (2007) Intensification of Pacific storm track linked to Asian pollution. *Proceedings of the National Academy of Sciences of the United States of America*, *104*(13), 5295-5299. https://doi.org/10.1073/pnas.0700618104

Zhang, R. Y., Wang, G. H., Guo, S., Zamora, M. L., Ying, Q., Lin, Y., et al. (2015) Formation of urban fine particulate matter. *Chemical Reviews*, 115(10), 3803-3855. https://doi.org/10.1021/acs.chemrev.5b00067

Zhao, B., Wu, W. J., Wang, S. X., Xing, J., Chang, X., Liou, K. N., et al. (2017) A modeling study of the nonlinear response of fine particles to air pollutant emissions in the Beijing-Tianjin-Hebei region. *Atmospheric Chemistry and Physics*, *17*(19), 12031-12050. https://doi.org/10.5194/acp-17-12031-2017

Zhao, J., Levitt, N. P., Zhang, R., & Chen, J. (2006) Heterogeneous reactions of methylglyoxal in acidic media: implications for secondary organic aerosol formation. *Environmental Science & Technology*, *40*(24), 7682-7687. https://doi.org/10.1021/es060610k

Zheng, H., Kong, S. F., Wu, F. Q., Cheng, Y., Niu, Z. Z., Zheng, S. R., et al. (2019) Intra-regional transport of black carbon between the south edge of the North China Plain and central China during winter haze episodes. *Atmospheric Chemistry and Physics*, *19*(7), 4499-4516. https://doi.org/10.5194/acp-19-4499-2019

Table 1. Comparisons of the average mass concentrations of air pollutants during wintertime in the BTH from 2013 and 2018.

Air pollutants	$PM_{2.5}$ (μg m^{-3})	O_3 (μg m^{-3})	NO_2 (μg m^{-3})	SO_2 (μg m^{-3})	CO (mg m^{-3})
2013	153.0	37.9	69.2	108.7	2.6
2014	112.0	42.4	60.3	82.2	2.4
2015	106.8	43.4	63.3	58.3	2.4
2016	136.9	48.2	71.8	52.0	2.6
2017	78.7	47.6	50.6	28.8	1.5
2018	88.5	49.4	54.0	23.6	1.5
Change (%) between 2013 and 2018	-42.2	30.3	-22.0	-78.3	-42.3

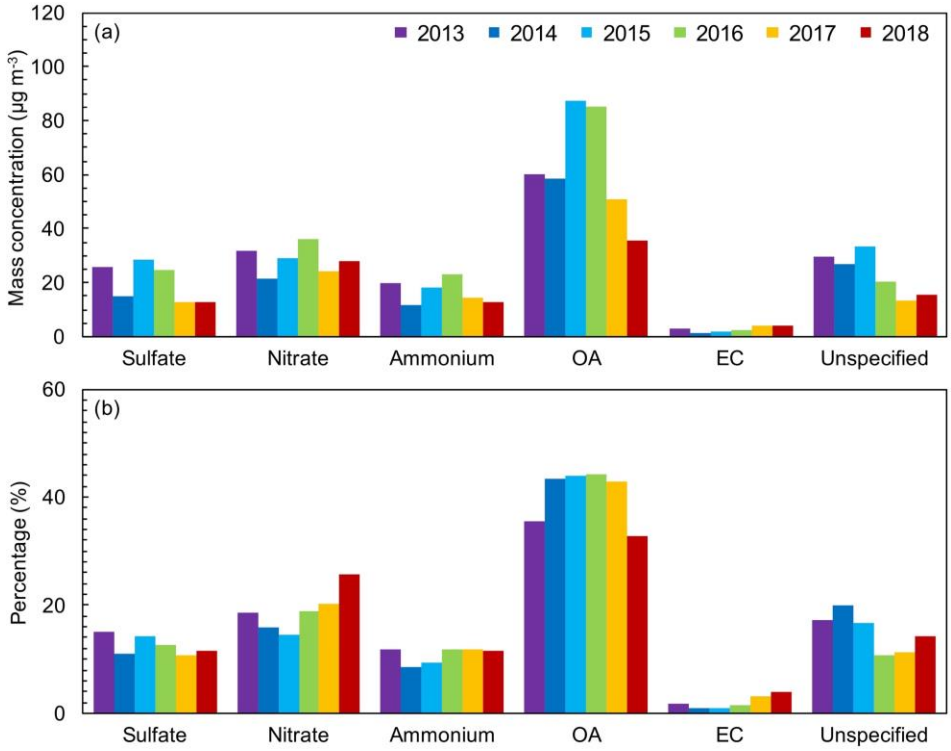

Figure 1. Variations of the filter measured average (a) mass concentrations of the $PM_{2.5}$ constituents and (b) their contributions to the $PM_{2.5}$ mass at an urban site in Beijing from 2013 to 2018 during wintertime PM pollution days with $PM_{2.5}$ concentrations exceeding 75 μg m^{-3}.

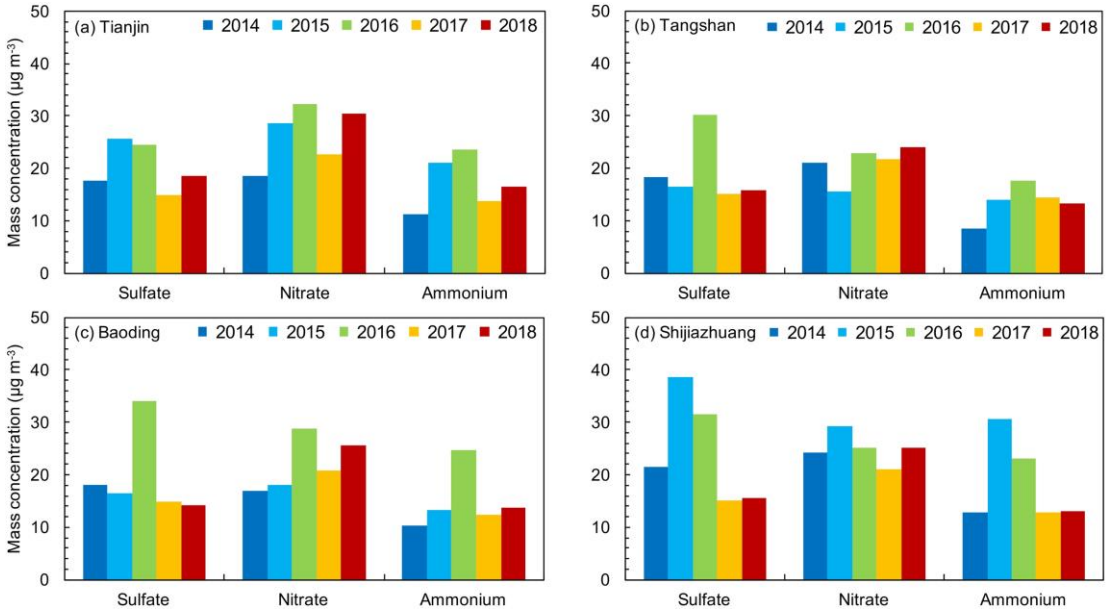

Figure 2. Variations of the filter measured wintertime sulfate, nitrate, and ammonium concentrations from 2014 to 2018 when the $PM_{2.5}$ level exceeds 75 μg m^{-3} in (a) Tianjin, (b) Tangshan, (c) Baoding and (d) Shijiazhuang in the BTH.

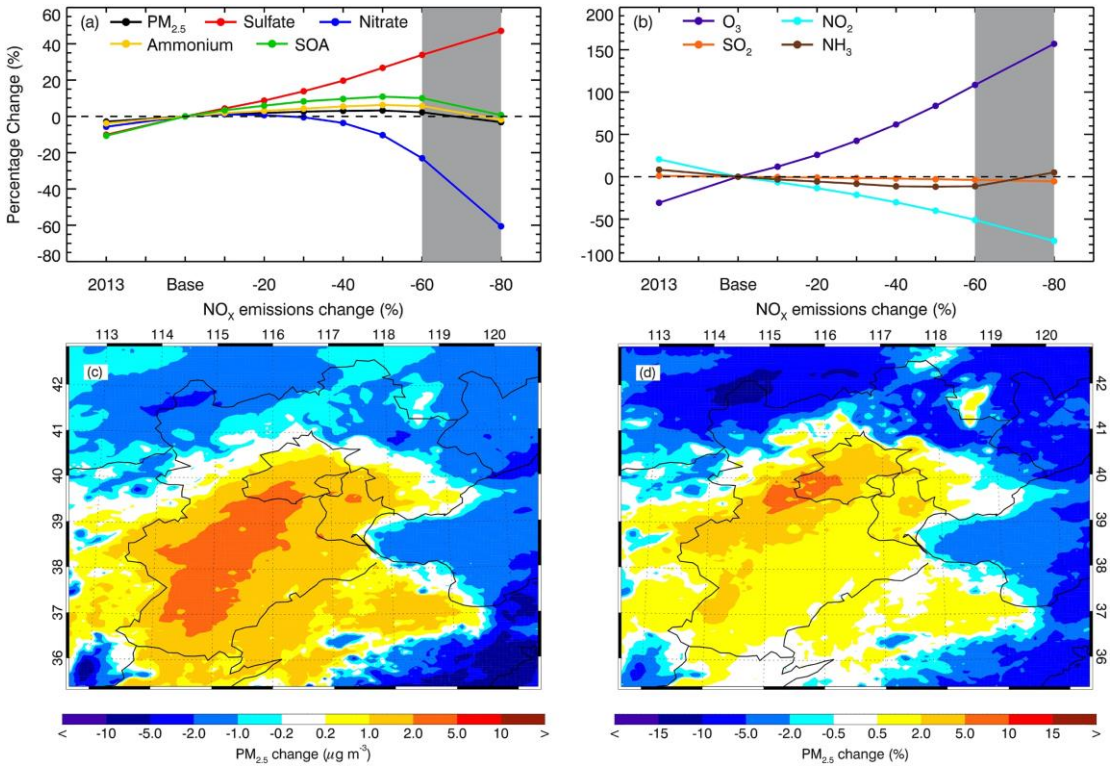

Figure 3. Variations of average concentrations of $PM_{2.5}$ and secondary aerosols (a) as well as the gas pollutants (b) in the BTH during the episode with the NO_X emissions changes, and mass (c) and percentage (d) distributions of the $PM_{2.5}$ variation during the simulation period when the NO_X emissions are reduced by 50%. The shading area in (a) and (b) shows the scenario of the NO_X emission reduction during the lockdown period due to the COVID-19 outbreak.

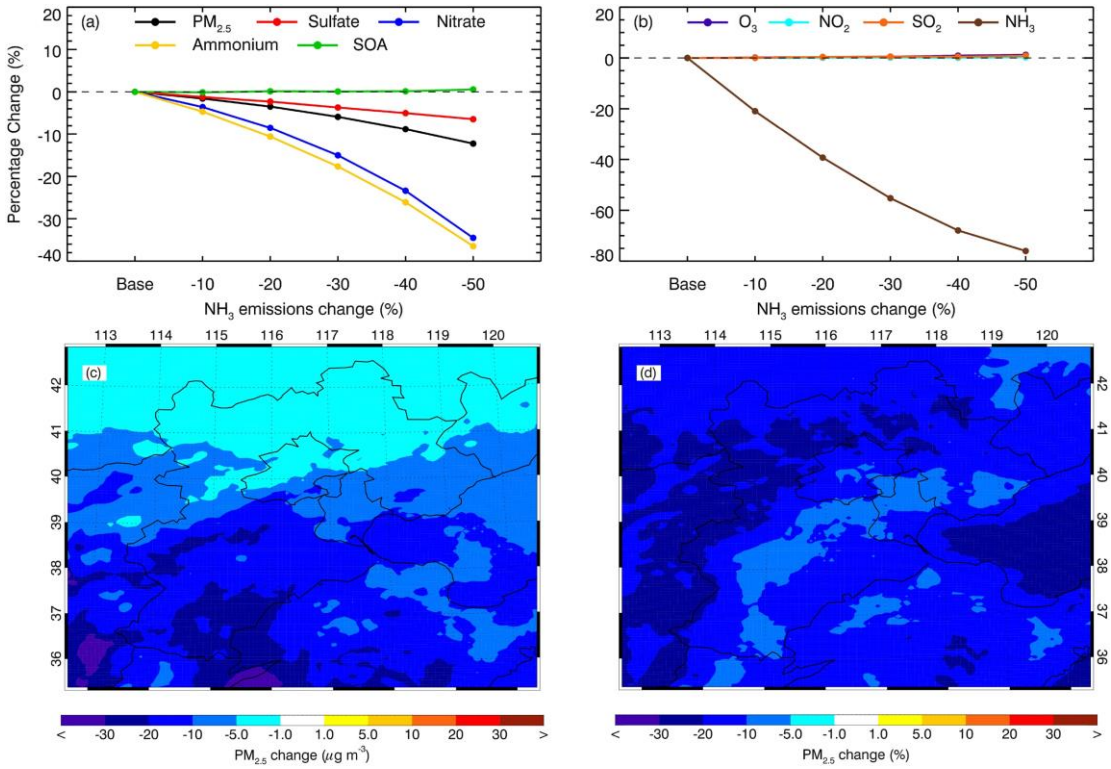

Figure 4. Variations of average concentrations of $PM_{2.5}$ and secondary aerosols (a) as well as the gas pollutants (b) in the BTH during the episode when the NH_3 emissions are reduced from 10% to 50%, respectively, and mass (c) and percentage (d) distributions of $PM_{2.5}$ reductions when the NH_3 emissions are reduced by 50%.