

# Response to Reviewer1

## **General comments:**

*Li et al. present a model analysis of secondary inorganic aerosol (SIA) in major cities of Eastern China. They show data of PM<sub>2.5</sub> from a network across China from 2012 to 2016 and speciated PM<sub>2.5</sub> from major supersites in Eastern China. They analyze the response of sulfate and nitrate to the reductions in NO<sub>x</sub> that have occurred in the 4 year period, and to a theoretical series of reductions spanning 10 to 80%. Due to the response of oxidants to NO<sub>x</sub>, the changes in SIA are approximately linear in summer but highly non-linear in winter, indicating NO<sub>x</sub> saturation of oxidant production in winter.*

*The results are relevant to the understanding of air pollution and its recent trends in China and is of interest to the readership of ACP. **Publication is recommended following attention to the specific comments below.***

**Response:** The paper has been revised according to the reviewer's comments. For details, see the line-by-line responses below.

## **Specific Comments:**

*Line 71: Neither of the stated assumptions, stagnant atmosphere or a fixed NO<sub>2</sub>/NO<sub>y</sub> ratio, is a condition for a box model. Suggest eliminating this statement.*

**Response: Accepted.** This sentence is rephrased as "...the basic hypotheses in box models to predict nitrate production are also unreasonable in the real atmosphere...". For details, see *Line 73-74*.

*Line 77-78: Is the NO<sub>x</sub> sensitivity of Chinese ozone a well accepted result? Increasing O<sub>3</sub> trends have been attributed, for example, to effects associated with decreasing PM<sub>2.5</sub>, e.g., Li, K., D.J. Jacob, H. Liao, L. Shen, Q. Zhang, and K.H. Bates, Anthropogenic drivers of 2013–2017 trends in summer surface ozone in China. *Proceedings of the National Academy of Sciences*, 2019. **116**(2): p. 422.*

**Response: Accepted.** More references are supplemented to support the claim that the production of O<sub>3</sub> is usually limited by VOC<sub>s</sub> in Chinese cities (Xie et al., 2014; Dong et al., 2014; Liu et al., 2010). Li et al. (2021) and Liu and Wang (2020) examined the influencing factors on surface O<sub>3</sub> trends in China from 2013 to 2017 using regional models. They highlighted that the control of NO<sub>x</sub> emissions explained 11–35% of increased O<sub>3</sub> due to the nonlinear NO<sub>x</sub>-VOC<sub>s</sub>-O<sub>3</sub> chemistry, and that for most regions the magnitudes could be comparable to those resulting

from the meteorological influences and aerosol effects. For details, see *Line 77-86*.

*Line 248: It appears that the oxidation ratio of sulfur decreases, but nitrogen increases, between the warm and cold seasons. Is that correct? In this case, there is more going on than just enhanced secondary oxidant formation. There is also a change in chemical mechanism between S and N.*

**Response: Accepted.** The seasonal distinctions for SOR and NOR, i.e., higher SOR in summer-autumn than winter and opposite for NOR, have been reported by Shu et al. (2019). They attributed the weakened conversion from NO<sub>2</sub> to nitrate in summer to the volatility and evaporative loss of nitrate (Sun et al., 2012). The sharp increase of particles and moderate ambient humidity in winter also benefit the heterogeneous formation of SIA, leading to high NOR and SOR (Wang et al., 2012). For details, see *Line 267-274*.

*Line 249: Here and above, specify more clearly what is meant by the two pathways – presumably this is the difference between OH + NO<sub>2</sub> (gas phase) and N<sub>2</sub>O<sub>5</sub> hydrolysis (heterogeneous), but it is not clear from this text or figure 6 what this specifically means.*

**Response: Accepted.** The two pathways represent the NO<sub>2</sub>+OH gas-phase oxidation and heterogeneous reactions for nitrate production calculated from B0 and E0 simulations. It is specified clearly in the figure captions and main text. For details, see *Line 148-153* and *Line 275-283*.

*Line 258-259: Two comments. First, the global burden of nitrate production pathways may, or may not, be relevant at a regional level. Second, there are more updated papers indicating that the two pathways considered here are more equal at the global scale.*

*Alexander, B., T. Sherwen, C.D. Holmes, J.A. Fisher, Q. Chen, M.J. Evans, and P. Kasibhatla, Global inorganic nitrate production mechanisms: comparison of a global model with nitrate isotope observations. Atmos. Chem. Phys., 2020. 20(6): p. 3859-3877.*

**Response: Accepted.** We extend the discussions about the formation pathways for nitrate calculated in the WRF-Chem model and their comparisons with recent assessments in China and worldwide. The calculated contributions (60.19–91.71% for NO<sub>2</sub>+OH oxidation and 8.29–39.81% for heterogeneous pathways) are in line with previous assessments in China and globally (Alexander et al., 2009; Alexander et al., 2020; Wang et al., 2019; Wang et al., 2017; Luo et al., 2021; Liu et al., 2020; He et al., 2020). The nitrate formation from heterogeneous

reactions is moderately underestimated in this study, possibly due to the uncertainties of heterogeneous uptake coefficients and unclear reaction mechanisms applied in the model (Li et al., 2019; Xue et al., 2016; He et al., 2014). For details, see *Line 283-297*.

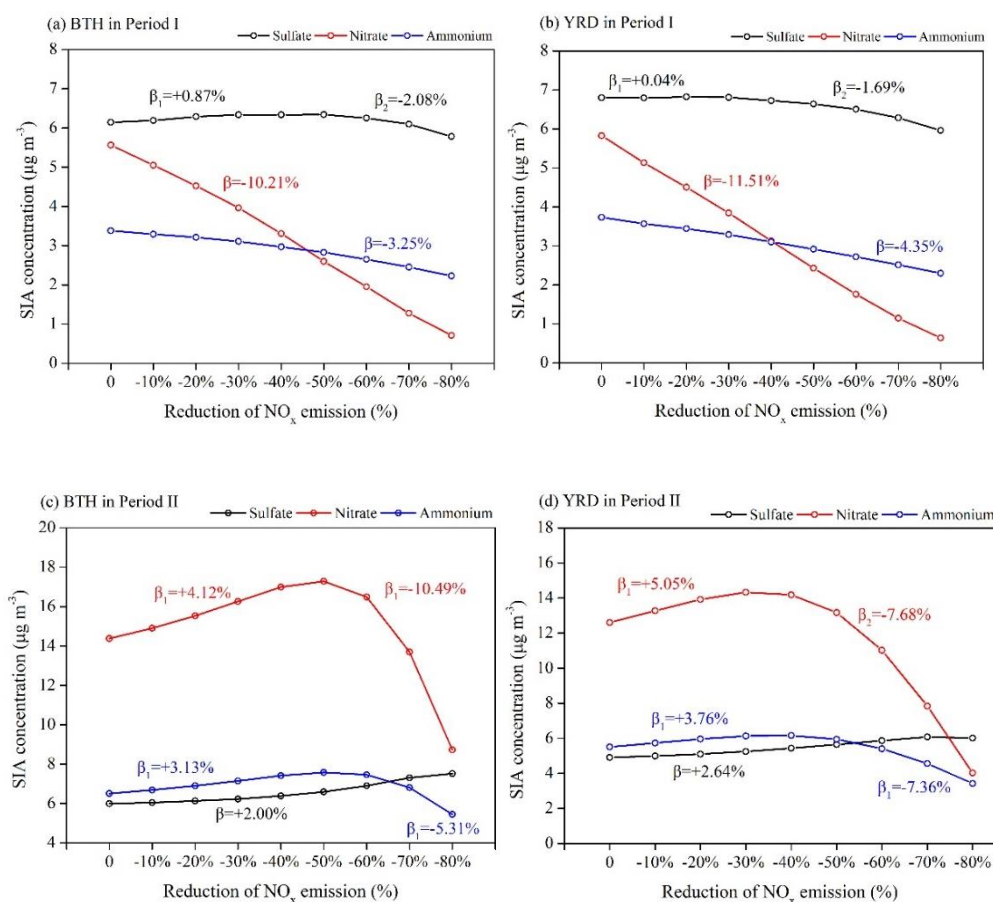
*Line 275: The responses do not appear “bell shaped”. Is there a better descriptor?*

**Response: Accepted.** The response is described as “quadratic parabola distribution”. For details, see *Line 314*.

*Line 301-319: The changes in sulfate in Figures 8 and 9 is quite difficult to discern, so it is not easy to match this text to the changes in the figure. Can sulfate be plotted on its own scale to illustrate these changes?*

*Line 329-330: Same comment for sulfate. Changes are very difficult to see.*

**Response: Accepted.** The responses of SIA components to the NO<sub>x</sub> emission controls are plotted in *Fig. 10* of the revised manuscript.



**Fig. 10.** Responses of the surface concentrations of SIA components to the NO<sub>x</sub> emission reduction scenarios and their emission control efficiencies in (a, b) Period I

and (c, d) Period II.

*Also, the small dependence of sulfate on NO<sub>x</sub> indicates that OH is also not a strong function of NO<sub>x</sub> in this model, but later the OH changes are quoted as being large compared to the changes in sulfate. If OH is the most important factor for sulfate changes, why are the modeled sulfate changes so much smaller than the changes in OH?*

**Response: Accepted.** From the response curves of OH and sulfate (*Fig. 8-10*), it is seen that the sulfate-NO<sub>x</sub> response pattern is similar to that of OH-NO<sub>x</sub> but with smaller changes. It is because that the concentration levels of sulfate are not only limited by the oxidants levels in the atmosphere but also many other factors, e.g., the abundance of its precursors (e.g., SO<sub>2</sub>, NH<sub>3</sub>), the chemical competition in sulfate and nitrate formation, and the heterogeneous uptake rates etc. (Dong et al., 2014; Meng et al., 1997). For details, see *Line 343-350* and *Line 376-377*.

#### References:

- Alexander, B., Hastings, M. G., Allman, D. J., Dachs, J., Thornton, J. A., and Kunasek, S. A.: Quantifying atmospheric nitrate formation pathways based on a global model of the oxygen isotopic composition ( $\delta$  O-17) of atmospheric nitrate, *Atmos Chem Phys*, 9, 5043-5056, 2009.
- Alexander, B., Sherwen, T., Holmes, C. D., Fisher, J. A., Chen, Q. J., Evans, M. J., and Kasibhatla, P.: Global inorganic nitrate production mechanisms: comparison of a global model with nitrate isotope observations, *Atmos Chem Phys*, 20, 3859-3877, 10.5194/acp-20-3859-2020, 2020.
- Dong, X. Y., Li, J., Fu, J. S., Gao, Y., Huang, K., and Zhuang, G. S.: Inorganic aerosols responses to emission changes in Yangtze River Delta, China, *Sci Total Environ*, 481, 522-532, 10.1016/j.scitotenv.2014.02.076, 2014.
- He, H., Wang, Y. S., Ma, Q. X., Ma, J. Z., Chu, B. W., Ji, D. S., Tang, G. Q., Liu, C., Zhang, H. X., and Hao, J. M.: Mineral dust and NO<sub>x</sub> promote the conversion of SO<sub>2</sub> to sulfate in heavy pollution days, *Scientific Reports*, 4, 4172, doi: 10.1038/Srep04172, 2014.
- He, P. Z., Xie, Z. Q., Yu, X. W., Wang, L. Q., Kang, H., and Yue, F. G.: The observation of isotopic compositions of atmospheric nitrate in Shanghai China and its implication for reactive nitrogen chemistry, *Sci Total Environ*, 714, 136727, doi: 10.1016/j.scitotenv.2020.136727, 2020.
- Li, M. M., Wang, T. J., Shu, L., Qu, Y. W., Xie, M., Liu, J. N., Wu, H., and Kalsoom, U.: Rising surface ozone in China from 2013 to 2017: A response to the recent atmospheric warming or pollutant controls?, *Atmos Environ*, 246, 118130, doi: 10.1016/j.atmosenv.2020.118130, 2021.

- Li, M. M., Wang, T. J., Xie, M., Li, S., Zhuang, B. L., Huang, X., Chen, P. L., Zhao, M., and Liu, J. E.: Formation and Evolution Mechanisms for Two Extreme Haze Episodes in the Yangtze River Delta Region of China During Winter 2016, *J Geophys Res-Atmos*, 124, 3607-3623, 10.1029/2019jd030535, 2019.
- Liu, L., Bei, N. F., Hu, B., Wu, J. R., Liu, S. X., Li, X., Wang, R. N., Liu, Z. R., Shen, Z. X., and Li, G. H.: Wintertime nitrate formation pathways in the north China plain: Importance of N<sub>2</sub>O<sub>5</sub> heterogeneous hydrolysis, *Environ Pollut*, 266, 115287, doi: 10.1016/j.envpol.2020.115287, 2020.
- Liu, X. H., Zhang, Y., Xing, J., Zhang, Q. A., Wang, K., Streets, D. G., Jang, C., Wang, W. X., and Hao, J. M.: Understanding of regional air pollution over China using CMAQ, part II. Process analysis and sensitivity of ozone and particulate matter to precursor emissions, *Atmos Environ*, 44, 3719-3727, 10.1016/j.atmosenv.2010.03.036, 2010.
- Liu, Y. M. and Wang, T.: Worsening urban ozone pollution in China from 2013 to 2017-Part 2: The effects of emission changes and implications for multi-pollutant control, *Atmos Chem Phys*, 20, 6323-6337, 2020.
- Luo, L., Zhu, R. G., Song, C. B., Peng, J. F., Guo, W., Liu, Y. H., Zheng, N. J., Xiao, H. W., and Xiao, H. Y.: Changes in nitrate accumulation mechanisms as PM<sub>2.5</sub> levels increase on the North China Plain: A perspective from the dual isotopic compositions of nitrate, *Chemosphere*, 263, 127915, doi: 10.1016/j.chemosphere.2020.127915, 2021.
- Meng, Z., Dabdub, D., and Seinfeld, J. H.: Chemical coupling between atmospheric ozone and particulate matter, *Science*, 277, 116-119, DOI 10.1126/science.277.5322.116, 1997.
- Shu, L., Wang, T. J., Xie, M., Li, M. M., Zhao, M., Zhang, M., and Zhao, X. Y.: Episode study of fine particle and ozone during the CAPUM-YRD over Yangtze River Delta of China: Characteristics and source attribution, *Atmos Environ*, 203, 87-101, 10.1016/j.atmosenv.2019.01.044, 2019.
- Sun, Y. L., Wang, Z. F., Dong, H. B., Yang, T., Li, J., Pan, X. L., Chen, P., and Jayne, J. T.: Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor, *Atmos Environ*, 51, 250-259, 10.1016/j.atmosenv.2012.01.013, 2012.
- Wang, H. C., Lu, K. D., Chen, X. R., Zhu, Q. D., Chen, Q., Guo, S., Jiang, M. Q., Li, X., Shang, D. J., Tan, Z. F., Wu, Y. S., Wu, Z. J., Zou, Q., Zheng, Y., Zeng, L. M., Zhu, T., Hu, M., and Zhang, Y. H.: High N<sub>2</sub>O<sub>5</sub> Concentrations Observed in Urban Beijing: Implications of a Large Nitrate Formation Pathway, *Environ Sci Tech Lett*, 4, 416-420, 10.1021/acs.estlett.7b00341, 2017.
- Wang, X. F., Wang, W. X., Yang, L. X., Gao, X. M., Nie, W., Yu, Y. C., Xu, P. J., Zhou, Y., and Wang, Z.: The secondary formation of inorganic aerosols in the droplet mode through heterogeneous aqueous reactions under haze conditions, *Atmos*

Environ, 63, 68-76, 10.1016/j.atmosenv.2012.09.029, 2012.

Wang, Y. L., Song, W., Yang, W., Sun, X. C., Tong, Y. D., Wang, X. M., Liu, C. Q., Bai, Z. P., and Liu, X. Y.: Influences of Atmospheric Pollution on the Contributions of Major Oxidation Pathways to PM<sub>2.5</sub> Nitrate Formation in Beijing, *J Geophys Res-Atmos*, 124, 4174-4185, 10.1029/2019jd030284, 2019.

Xie, M., Zhu, K. G., Wang, T. J., Yang, H. M., Zhuang, B. L., Li, S., Li, M. G., Zhu, X. S., and Ouyang, Y.: Application of photochemical indicators to evaluate ozone nonlinear chemistry and pollution control countermeasure in China, *Atmos Environ*, 99, 466-473, 10.1016/j.atmosenv.2014.10.013, 2014.

Xue, J., Yuan, Z. B., Griffith, S. M., Yu, X., Lau, A. K. H., and Yu, J. Z.: Sulfate Formation Enhanced by a Cocktail of High NO<sub>x</sub>, SO<sub>2</sub>, Particulate Matter, and Droplet pH during Haze-Fog Events in Megacities in China: An Observation-Based Modeling Investigation, *Environ Sci Technol*, 50, 7325-7334, 10.1021/acs.est.6b00768, 2016.