Responses to reviewers (original comments by reviewers are in blue).

Reviewer #2:

Summary:

The authors present an interesting study on wintertime atmospheric nitrate formation in the North China Region for 2013 and 2018, using model simulations aimed at validating the model against isotope observations. This research is highly valuable given the increasing contribution of nitrate to particulate matter, especially during the winter months. The authors have conducted detailed work on the topic; however, the presentation of their findings appears somewhat unfocused. Much of the model simulations and interpretations regarding nitrate changes reiterate findings from previous studies. The novel aspect of this research lies in the validation of model chemistry through comparison with isotope observations. However, most of the isotope data and modeling results are included in the supplementary material, which was not accessible for review. This component is critical for the interpretation of the work and requires thorough examination. The comparisons between model simulations and isotope observations were presented in broad terms, raising concerns about the reliability of using d^{18}O and d^{15}N values to determine oxidation pathways, given that the d^{18}O values of atmospheric oxidants remain poorly constrained and recent documentation of potential d^{18}O source effects from nighttime NO emissions. Moreover, the study lacked discussion on uncertainties in the isotope data and their potential impact on the interpretation within the modeling framework. Additionally, the model constrained nitrate production to a single grid cell, while the nitrate observations were derived from field samples that likely included contributions from long-range transport of nitrate produced upwind of the grid cell. Addressing this discrepancy is crucial for robust interpretation. Overall, while I appreciate the detailed efforts of the authors, the study appears unfocused due to the lack of integration and discussion of the model outputs, particularly the concentration and isotope comparisons. I recommend revisiting and refocusing the work to strengthen its coherence and clarity before it can be considered suitable for publication in ACP.

Reply: Thank you for your detailed feedback and valuable suggestions on our research. We understand the reviewer's concerns regarding the presentation of the study and some issues. We have made significant revisions to the manuscript, and addressed the following points in the revision:

1. Comparison between model simulations and isotope observations

To improve the comparison between model simulations and isotope data, we have significantly expanded the comparative analysis of model simulations and isotope data in Section 3.4, providing a more detailed analysis. Additionally, we have addressed the concerns regarding the reliability of using d^{18}O and d^{15}N values to determine oxidation pathways. Furthermore, in Section 2.4, we have incorporated a comprehensive discussion on the uncertainties in isotope data and their potential impact on the interpretation within the modeling framework.

2. Use of isotope data

The isotope data are presented in the supplementary materials, which the reviewer was unable to access for uncertain reasons. In the revised version, the supplementary materials are accessible, and we have added additional details on the isotope data and model results in the main text to better explain the study's findings.

3. Regarding the constraint of using a single grid cell in the model

We agree with the reviewer's point that the model's restriction of nitrate formation to a single grid cell may introduce discrepancies compared with to field observations, which likely include contributions from long-range transport of nitrate produced upwind. To address this issue, we supplemented a detailed discussion in the manuscript (Section 3.4, lines 447–488) highlighting the potential discrepancies between the model results and actual observational data due to the exclusion of long-range transport effects. Additionally, we employed a backward trajectory analysis method to trace the source regions of nitrate and quantify the contributions of long-range transport to nitrate formation pathways. Furthermore, we conducted an error analysis between the observational and simulated results to assess the impact of long-range transport on model errors. Finally, we explored methods to quantitatively evaluate the influence of transport processes and refine the model's representation of regional transport dynamics.

4. Overall structure and focus of the paper

We agree that the overall structure and focus of the paper require further optimization to enhance coherence and clarity. In the revised version, we made several improvements: we revised the introduction to include a discussion on the applications and limitations of global models (lines 82–92), removed redundant results (e.g., findings already established in Section 3.2), consolidated figures and tables (e.g., Figure 11), highlighted the land–sea differences in the results, and refined the content and language throughout the manuscript to improve readability and precision.

Comments:

Lines 60 – 64: How was this determined?

Reply: The differences in nitrate formation pathways between inland and coastal cities during winter, as mentioned in lines 59–70, were derived from an analysis of the literature. Scholars have revealed significant variations in nitrate formation mechanisms between inland cities (e.g., Beijing) and coastal cities (e.g., Shanghai) during winter by isotope observations. In Beijing, the OH pathway contributes to 66–92% of nitrate formation, whereas the heterogeneous reaction of N_2O_5 (hetN_2O_5) accounts for 8–34% (Chen et al., 2020). In contrast, in Shanghai, the OH pathway contributes to 48-74% of nitrate formation, which is significantly lower than that in Beijing (He et al., 2020). This discrepancy highlights the distinct nitrate formation mechanisms between inland and coastal cities. We have revised the phrasing in the manuscript accordingly.

Line 64 – 66: This sentence doesn't make sense to me.

Reply: Thank you for your careful and constructive feedback on our work. We have revised the text to clarify the role of coastal conditions in nitrate formation. The updated text now reads: "In coastal areas, which are influenced by high humidities, high sea salt levels and the combined effects of marine emissions and air masses (Zhong et al., 2023; Athanasopoulou et al., 2008; Zhao et al., 2024), the contribution of the OH pathway is smaller than that in inland cities, whereas the hetN_2O_5 pathway plays a more significant role." (lines 64–67).

Lines 55 – 98: This appears to be a block of text and clear paragraph breaks are not apparent. This makes it hard for the reader to follow the main points in the introduction section.

Reply: Thank you for your valuable feedback. We have restructured the paragraph to improve readability by splitting it into two separate sections, which can now be found in lines 59–80 and lines 105–124.

Lines 78 – 79: The motivation for the work should be stronger than pointed out in this line. It is unclear to the readers how the nitrate formation cited in the works of this paragraph are from model studies or from some other mechanistic constraint. Further, there have been global model studies of nitrate formation that would enable some insight into the land-ocean influence on nitrate formation.

Reply: Thank you for the valuable suggestions. While there are global model studies of nitrate formation, global models typically have coarse resolutions (generally 0.5°×0.625° or higher), making it difficult for them to capture the complex chemical processes occurring in localized areas. As a result, these models tend to reflect global average conditions and may not accurately represent local nitrate formation mechanisms (Alexander et al., 2020). Moreover, the treatment of aerosol chemistry in global models is relatively simplified, particularly concerning heterogeneous reactions on aerosol surfaces. Although these models have updated the probabilities for aerosol absorption reactions, significant uncertainties still exist regarding key parameters such as the N_2O_5 uptake coefficient and HNO_3 deposition rate (Heald et al., 2012). These uncertainties can lead to either an overestimation or underestimation of nitrate formation at local scales, especially in terms of ammonia emissions and nitrate production rates.

In contrast, regional multiscale models offer greater accuracy, which is why we focused on nitrate formation mechanisms in localized areas, particularly in heavily polluted urban centers or specific regions. By employing higher-resolution simulations and more detailed chemical reaction mechanisms, local nitrate formation processes can be captured more accurately.

Following your suggestion, we have revised the motivation section of the manuscript to highlight the advantages of regional-scale models (lines 92–94). Additionally, we have incorporated a discussion of the progress of both global and regional models in the study of nitrate formation, adjusting the sequence and emphasizing the contrast between the two approaches (lines 81–104). Furthermore, we have placed greater emphasis on the focus of this study in the final paragraph of the introduction (lines 125–132).

Alexander, B., Sherwen, T., Holmes, C. D., Fisher, J. A., Chen, Q., 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.

Heald, C. L., Collett Jr, J. L., Lee, T., Benedict, K. B., Schwandner, F. M., Li, Y., Clarisse, L., Hurtmans, D. R., Van Damme, M., Clerbaux, C., Coheur, P. F., Philip, S., Martin, R. V., and Pye, H. O. T.: Atmospheric ammonia and particulate inorganic nitrogen over the United States, Atmos. Chem. Phys., 12, 10295-10312, 10.5194/acp-12-10295-2012, 2012.

Lines 82 – 98: The jump from a discussion of nitrate formation (prior to lines 82) to the role of nitrate during haze events (Lines 82-98), back to nitrate formation mechanisms (Lines 99-108), is hard for the reader to follow.

Reply: Thank you for raising this issue. Following your suggestion, we have revised the text to improve clarity and logical flow, particularly in the discussion of nitrate formation mechanisms and their role in winter haze events. Specifically, we rephrased the introduction of the North China Plain (NCP) region (lines 105–107), restructured the discussion to highlight the shift from sulfate-dominated to nitrate-dominated haze following the Clean Air Action Plan (CAAP) implementation (lines 107–112), and expanded on nitrate formation mechanisms in coastal regions, emphasizing the influences of marine air masses and sea–land and breezes (lines 120–124).

Lines 99 – 101: Do coastal cities have a nitrate concentration change that is different compared to the inland cities? I am still unclear the motivation to explore mechanism differences between inland and coastal cities as it relates to nitrate concentration changes. Do we expect potential differences in chemistry to influence the rate of nitrate concentration change from these types of locations?

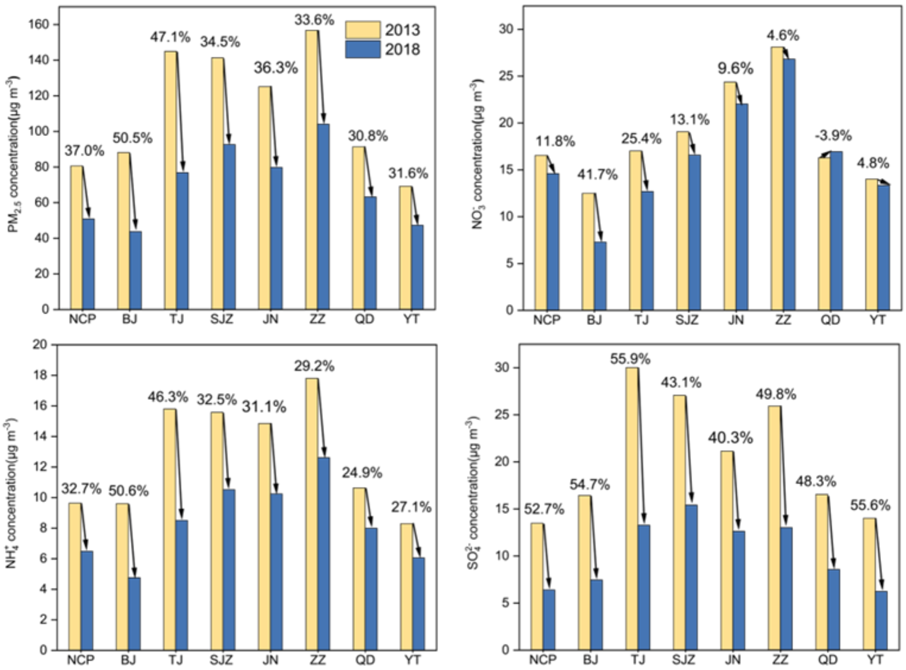

Figure R1 Concentrations of PM$_{2.5}$ and its components in seven major cities in the NCP region during the winters of 2013 and 2018

Reply: Thank you for your thoughtful and constructive feedback on our work. We observed that from 2013 to 2018, nitrate concentrations in inland cities decreased by 4.6%–41.7% during the emission reduction period, whereas the decline in coastal cities was smaller. For example, nitrate concentrations in Qingdao increased by 3.9%, and those in Yantai decreased by only 4.8%. Overall, the reduction in nitrate concentrations in coastal cities was significantly lower than in inland cities and did not align with the expected emission reduction results.

A key distinction between coastal and inland cities lies in their climatic conditions, which has motivated us to investigate whether differences in nitrate formation mechanisms exist between these regions. Specifically, we aimed to address the following questions. (1) Are there differences in nitrate formation mechanisms between coastal and inland cities? (2) If there are differences, how do they influence the variations in nitrate concentrations? (3) How can tailored emission control strategies be developed for coastal and inland cities on the basis of their distinct formation mechanisms to achieve effective pollution control?

Our findings indicated that changes in chemical composition significantly influenced the reaction rates of different formation pathways, thereby affecting nitrate concentration variations. This result underscored the need for developing targeted emission reduction strategies tailored to the unique chemical environments of inland and coastal cities.

Lines 104: I think finishing off the introduction with a statement of goals or objectives of the study would be important so readers know what to anticipate from this study, since the introduction was very broad.

Reply: We thank you for your comments and suggestions very much. We have added a concise statement of the research objectives at the end of the introduction, which can be found in lines 125–132.

Lines 126: What is MEIC?

Reply: The Multiresolution Emission Inventory for China (MEIC) is an emission inventory developed and maintained by Tsinghua University. This inventory includes a wide range of anthropogenic emission sources, including transportation, industry, and energy. The inventory provides emission data for various greenhouse gases and air pollutants across China. Further information can be accessed on the official website (http://meicmodel.org/). The full name and description of MEIC have been added to the revised manuscript (lines 153–155).

Lines 129: I think MEGAN needs a citation (rather than a link).

Reply: Thank you for your valuable suggestions. We have added the following reference to the revised version:

Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P. I., and Geron, C.: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). Atmospheric Chemistry and Physics, 6(11), 3181-3210. doi: 10.5194/acp-6-3181-2006, 2006.

Lines 144-150: What layer height is the IRR calculations used for interpreting nitrate formation? The layer closest to the surface? An integrated column from the surface to some layer height? Further, the IRR will calculate the nitrate production within a grid cell while not including the influence of transported nitrate. This could bias the interpretation if compared to isotope data. The readers should check out previous CMAQ work that have used IRR for simulation of nitrate formationd (Walters et al., Modeling the Oxygen Isotope Anomaly ($\Delta^{17}O$) of Reactive Nitrogen in the Community Multiscale Air Quality Model: Insights into Nitrogen Oxide Chemistry in the Northeastern United States, ES&T-Air, 1(6), 451-463, 2024).

Reply: Thank you for your insightful question. Our IRR calculations were applied to the layer closest to the surface, which was approximately 31 meters in height. This layer was considered the most representative of the predominant nitrate formation processes.

The IRR module confines nitrate formation to individual grid cells and does not account for the influence of nitrate transported from upwind regions. This limitation can introduce bias when comparing model results with isotope data, which may integrate contributions over a broader spatial domain, including long-range transport effects. To address this issue, we have employed a backward trajectory analysis method that incorporates both temporal and spatial constraints to identify the source regions of nitrate and quantify their formation pathway contributions. This approach allows us to better account for the influence of regional transport on nitrate formation, particularly in areas such as Qingdao and Beijing, where spatial heterogeneity in formation pathways is significant.

Our results demonstrate that backward trajectory correction significantly improves the estimation of the hetN_2O_5 pathway, especially in regions influenced by regional transport. However, the overadjustment of the OH+NO_2 pathway highlights the need for further optimization of the correction method. Key areas for improvement include refining OH radical concentration estimates, accounting for aerosol aging processes, and optimizing the quantification of regional transport. Currently, the overly broad consideration of transport regions may obscure local formation signals, suggesting a need for more precise spatial delineation in transport modeling. We appreciate the reviewer's suggestion to refer to previous CMAQ work by Walters et al. (2024). These scholars achieved relatively accurate results without considering transport effects, indicating that if the trends in nitrate formation pathways are similar across regions and vertical layers, the impact of transport on overall simulation accuracy may be limited. However, in regions with significant spatial heterogeneity, such as Qingdao and Beijing, incorporating transport effects through backward trajectory analysis remains crucial for improving model performance. This detailed discussion has been added to Section 3.5 (lines 447–488) of the revised manuscript.

Walters, W. W., Pye, H. O. T., Kim, H., and Hastings, M. G.: Modeling the Oxygen Isotope Anomaly ($\Delta^{17}O$) of Reactive Nitrogen in the Community Multiscale Air Quality Model: Insights into Nitrogen Oxide Chemistry in the Northeastern United States, ACS ES&T Air, 1, 451-463, 10.1021/acsestair.3c00056, 2024.

Lines 162-163: Are these observations compared to near surface simulations or with a different layer height?

Reply: These observational results were compared with the simulated results for the near-surface layer.

Lines 173: Where is the supplement?

Reply: We apologize for the inconvenience. We have submitted the supplementary materials as requested and ensured that all relevant content is clearly labeled. It appears that, possibly due to a system error, the reviewer may not have been able to access these materials. To resolve this issue, we have added the supplementary materials at the end of the document with all the references clearly indicated. We will verify the completeness of these materials in our submission of the revised version. We kindly invite you to review them and welcome any further comments.

Lines 178 – 180: This sentence reads a bit odd to me. The way it is worded, it seems like the Thermo Scientific IC system extracted the samples in ultrapure water; however, I think the authors mean the IC system was used to measure ion concentrations.

Reply: We apologize for the confusion. Your understanding is entirely accurate. The samples were first extracted using ultrapure water (> 18.2 MΩ·cm), after which the concentrations of water-soluble inorganic ions (including NO_3^-, SO_4^{2-}, and NH_4^+) were measured using a Thermo Scientific Dionex ICS-1100 ion chromatograph system. We have revised the sentence to enhance clarity and precision.

Revised sentence: Water-soluble inorganic ions, such as NO_3^-, SO_4^{2-}, and NH_4^+, were extracted from the samples using ultrapure water (> 18.2 MΩ·cm), and their concentrations were measured with a Thermo Scientific Dionex ICS-1100 IC system, as described in a previous study (Qi et al., 2020). This revision can be found in lines 206–209 of the revised manuscript.

Qi, J., Yu, Y., Yao, X., Gang, Y., and Gao, H.: Dry deposition fluxes of inorganic nitrogen and phosphorus in atmospheric aerosols over the Marginal Seas and Northwest Pacific, Atmos. Res., 245, 105076, 10.1016/j.atmosres.2020.105076, 2020.

Lines 180 – 181: What were the blank values? Also, it is mentioned that the ionic concentrations were blank corrected, but blanks would also impact the isotope data. Are blanks corrected for in the isotope data? If so, how?

Reply: We apologize for the omission of information regarding the blank samples.

First, the average concentrations of NO_3^-, SO_4^{2-}, and NH_4^+ in the blank sample membranes were 0.067 mg L^{-1}, 0.051 mg L^{-1}, and 0.055 mg L^{-1}, respectively. Under the same sampling and extraction conditions, the blank values were converted to atmospheric concentrations of approximately 0.071 μg m^{-3}, 0.054 μg m^{-3}, and 0.058 μg m^{-3}, respectively. The blank membranes were placed in the high-volume sampler for 2 hours without sampling during the sampling period.

On the basis of the absolute nitrogen content in the blank samples, the influence of the blank on the isotopic values of the observed samples was less than 5%; therefore, it was not considered. A detailed explanation is provided below. Our isotope blank measurements followed the same procedure as the sample isotope analysis. Specifically, in the sample measurements, after purging with high-purity nitrogen, 20 nmol of nitrogen was added to the headspace vial containing the *Pseudomonas aureofaciens* (ATCC13985) strain. For the blank measurements, no sample was added, and after 24 hours, 10 M NaOH was directly injected to quench the reaction before analysis. The peak area in the chromatogram represents the absolute amount of N_2O reduced by the strain, and the $\delta^{15}N$ and $\delta^{18}O$ values correspond to the $\delta^{15}N$ and $\delta^{18}O$ values of the sample. The peak area for the samples was approximately 10, whereas the peak areas for the two blank measurements were only 0.371 and 0.336, indicating an influence on the isotope values of less than 5%, which was negligible and thus not considered.

Lines 191-202: Where is this information at? This is critical to be reviewed since the calculation will have a major influence on the interpretation of the results.

Reply: This information is provided in the supplementary materials. As explained above, the reviewer was unable to access the supplementary materials for some reason. We have attached the supplementary materials at the end of the manuscript and ensured that all the referenced content is clearly indicated. We will double-check the materials during the next submission to ensure that everything is complete and accurate.

Lines 208- 2010: What are these benchmarks?

Table 1: I don't know what the benchmark section of the table means.

Reply: Thank you for your question. In this study, the benchmark values (Lines 244-248 in the revised manuscript) used are based on benchmarks set in previous studies (Emery et al.,2001, Emery et al., 2017, Huang et al., 2021) to evaluate the accuracy and validity of the meteorological model results. For example, the benchmark for T2 (2-meter temperature) is "≤±0.5°C," indicating that the model's predicted temperature should not deviate from observations by more than ±0.5°C. These benchmark values help assess whether the model's prediction errors are within an acceptable range, ensuring the model's accuracy.

For the explanation of the "Benchmark" section in Table 1, we listed the standard benchmark values for each meteorological parameter to assess the statistical performance of the model results. Specifically, the error for T2 (2-meter temperature) should not exceed ±0.5°C, the error for wind speed (WS10) should be within ±0.5 m/s, and the IOA value should be greater than 0.6. The error for the wind direction (WD10) should be within ±10°. We have clarified the definitions and sources of the benchmark values, with specific standards provided in Table 1 and calculation formulas detailed in Table S3 (supporting information), ensuring that readers an better understand their significance.

Emery, C., Tai, E., and Yarwood, G.: Enhanced meteorological modeling and performance evaluation for two Texas ozone episodes, Prepared for the Texas natural resource conservation commission, by ENVIRON International Corporation, 2001.
Emery, C., Liu, Z., Russell, A. G., Odman, M. T., Yarwood, G., and Kumar, N.: Recommendations on statistics and benchmarks to assess photochemical model performance, Journal of the Air & Waste Management Association, 67, 582-598, 10.1080/10962247.2016.1265027, 2017.
Huang, L., Zhu, Y., Zhai, H., Xue, S., Zhu, T., Shao, Y., Liu, Z., Emery, C., Yarwood, G., Wang, Y., Fu, J., Zhang, K., and Li, L.: Recommendations on benchmarks for numerical air quality model applications in China – Part 1: $PM_{2.5}$ and chemical species, Atmos. Chem. Phys., 21, 2725-2743, 10.5194/acp-21-2725-2021, 2021

Lines 257-265: Are there regional differences in the model efficacy of nitrate concentrations?

Reply: We sincerely appreciate your constructive comments. Indeed, the performance of nitrate concentration models varies across different regions, which is a common phenomenon in model simulations (Sun et al., 2022; Liu et al., 2020; Chuang et al., 2022; Xie et al., 2022). These regional differences in model performance are closely related to local pollution sources, meteorological conditions, and parameters of atmospheric chemical reaction mechanisms (Xie et al., 2022). Therefore, although model performance may vary across regions, the overall evaluation results remain acceptable (Fu et al., 2020). In this study, we conducted a comprehensive evaluation of nitrate concentrations in the North China Plain, and the results demonstrated that the model's accuracy is acceptable for this region.

Sun, J., Qin, M., Xie, X., Fu, W., Qin, Y., Sheng, L., Li, L., Li, J., Sulaymon, I. D., Jiang, L., Huang, L., Yu, X., and Hu, J.: Seasonal modeling analysis of nitrate formation pathways in the Yangtze River Delta region, China, Atmospheric Chemistry and Physics, 22, 12629-12646, https://doi.org/10.5194/acp-22-12629-2022, 2022.
Liu, L., Bei, N., Hu, B., Wu, J., Liu, S., Li, X., Wang, R., Liu, Z., Shen, Z., and Li, G.: Wintertime nitrate formation pathways in the North China Plain: Importance of N_2O_5 heterogeneous hydrolysis, Environmental Pollution, 266, 115287, https://doi.org/10.1016/j.envpol.2020.115287, 2020.
Chuang, M.-T., Wu, C.-F., Lin, C.-Y., Lin, W.-C., Chou, C. C. K., Lee, C.-T., Lin, T.-H., Fu, J. S., and Kong, S. S.-K.: Simulating nitrate formation mechanisms during $PM_{2.5}$ events in Taiwan and their implications for the controlling direction, Atmospheric Environment, 269, https://doi.org/10.1016/j.atmosenv.2021.118856, 2022.
Fu, X., Wang, T., Gao, J., Wang, P., Liu, Y., Wang, S., Zhao, B., and Xue, L.: Persistent heavy winter nitrate pollution driven by increased photochemical oxidants in northern China, Environmental Science & Technology, 54, 3881-3889, https://doi.org/10.1021/acs.est.9b07248, 2020.
Xie, X., Hu, J., Qin, M., Guo, S., Hu, M., Wang, H., Lou, S., Li, J., Sun, J., Li, X., Sheng, L., Zhu, J., Chen, G., Yin, J., Fu, W., Huang, C., and Zhang, Y.: Modeling particulate nitrate in China: Current

findings and future directions, Environment International, 166, 107369, https://doi.org/10.1016/j.envint.2022.107369, 2022.

Lines 266- 298: This is interesting but it appears to me that a lot of these results and implications have already been published in previous works. Can the authors focus on this section to have more of a focus on what information is new compared to what has already been published?

Reply: Thank you for the valuable suggestion. Some results and discussions of the increased proportion of nitrate overlap with those of existing studies. However, we focused on nitrate concentrations, which demonstrated significantly different reductions between coastal and inland regions. Specifically, we have clarified the significant differences in nitrate concentration trends between coastal and inland cities, with inland cities experiencing a more pronounced reduction (4.6% to 41.7%) than coastal cities, where nitrate reductions were smaller (e.g., Yantai decreased by 4.8%, whereas Qingdao increased by 3.9%). This regional differentiation in nitrate concentration trends has not been extensively explored in previous studies, and our research provides new insights into the complex interplay between emission controls and atmospheric chemistry. We have streamlined this section and expanded the comparative analysis of nitrate formation mechanisms. These revisions aim to clearly demonstrate the new insights and value of our work, particularly in understanding the regional differences in nitrate pollution dynamics. These changes can be found in lines 316–325 of the revised manuscript.

Lines 312-313: I am unsure what is meant by “reduced by -2.1% to 7.8%”. Did some site reduce and some increased?

Reply: We apologize for the confusion. Some sites decreased and some increased. This phenomenon reflects the varying changes in the contribution of the hetN_2O_5 pathway to nitrate formation in different cities. According to Table 3, the contribution increased in Zhengzhou from 2013 to 2018, whereas it decreased in six cities: Beijing (-4.4%), Tianjin (-4.6%), Shijiazhuang (-5.9%), Jinan (-7.8%), Qingdao (-4.5%), Yantai (-2.2%), and Zhengzhou (+2.1%). We have revised the text (lines 334–336 of the revised manuscript) to clarify this point and avoid any potential misunderstanding. Thank you for bringing this to our attention.

Lines 382- 385: Are there major takeaways or implication for this finding? Does this imply that NOx oxidation is more efficient at the coastal site compared to urban or vice versa? Will this impact the change in nitrate concentrations due to emission regulations?

Reply: Thank you for the insightful question. Our study revealed significant differences in nitrate formation pathways between coastal and inland regions. Table 3 shows that the TNO_3 production rate is higher in coastal cities than in inland cities, indicating that the NO_x oxidation efficiency is greater in coastal regions. Given the differences in nitrate formation mechanisms across regions, targeted emission reduction strategies can be implemented on the basis of the dominant formation pathways to effectively control nitrate concentrations.

Lines 394-396: the d^{18}O value of atmospheric oxidants can vary widely. What values were chosen and are there temperature dependence factors that need to be accounted for? Further, recent work has shown that nighttime emissions of NO can carry over the emission d^{18}O value, lowering d^{18}O and Δ^{17}O compared to the assumption of complete photochemical cycle (Albertin et al., Measurement report: Nitrogen isotopes (d^{15}N) and first quantification of oxygen isotope anomalies (Δ^{17}O, d^{18}O) in atmospheric nitrogen dioxide, Atmos, Chem. Phys, 21, 10477-10497, 2021). This would be very important for urban areas with large nighttime NO emissions. Was this accounted for?

Reply: Your consideration is entirely correct. We apologize for not providing a sufficiently detailed description of our methods, which may have caused confusion. In our supplementary materials, we have included more comprehensive information on the methodology.

First, there are temperature dependence factors for the d^{18}O value. The δ^{18}O values for atmospheric oxidants such as ·OH and O_3 are shown in Table R1. We calculated the endmember δ^{18}O and δ^{15}N values for each formation pathway, and incorporated temperature dependence factors into the thermodynamic fractionation calculations based on Luo et al. (2022).

Additionally, as you noted, numerous scholars have reported significant diurnal variations in atmospheric δ^{18}O-NO_2, including the studies you reference (Albertin et al., 2021; Albertin et al., 2024) and those conducted in Hefei (31.82 °N, 117.28 °E; Fig. 2(a); Zhang et al., 2025) and Nanchang (28.68 °N, 115.93 °E; Fig. 2(b); Cao, 2022), China. During the day, δ^{18}O–NO_2 is significantly greater than that at night, because of the prominent δ^{18}O–O_3 signal in the photochemical cycling of NO and NO_2 during the day; conversely, at night, more δ^{18}O–NO_2 signals from emissions are present (Walters et al., 2016). However, numerous observational studies of δ^{18}O–NO_3^- do not reveal significant diurnal variations, especially in winter. Examples include Tianjin (39.11°N, 117.16°E; Fig. 2(c); Feng et al., 2020) in the North China Plain (NCP) and Nanjing (32.22°N, 118.75°E; Fig. 2(d); Zhang et al., 2022). This phenomenon may occur due to its longer atmospheric lifetime and diffusion. Therefore, in our seasonal study, the diurnal variation was not considered in the calculations. We have referenced the widely used δ^{18}O-NOx value of 117 ± 5‰ (Michalski et al., 2014) for calculating the endmember values of the ·OH+NO_2 and hetN_2O_5 pathways to distinguish the contributions of the two pathways. In future studies, we will attempt to account for the diurnal variations in δ^{18}O-NO_2 and their impact on the generated δ^{18}O–NO_3^-.

Table R1 Values of δ^{18}O from atmospheric components

Components	Values (‰)	References
O_3	From 80 to 130	Michalski et al., 2011
O_2	23.5	Kroopnick and Craing; 1972
H_2O (g) in Beijing winter	−27.9	Wen et al., 2010
H_2O (g) in Qingdao winter	−18.6	Wang et al., 2022
·OH in Beijing winter	From −72.4 to −64.9	$\delta^{18}O\text{-}OH = \delta^{18}O\text{-}H_2O_{(g)} + 1000(^{18}\alpha_{X/Y} - 1)$ (Walters and Michalski, 2016)
·OH in Qingdao winter	From −61.2 to −57.8	

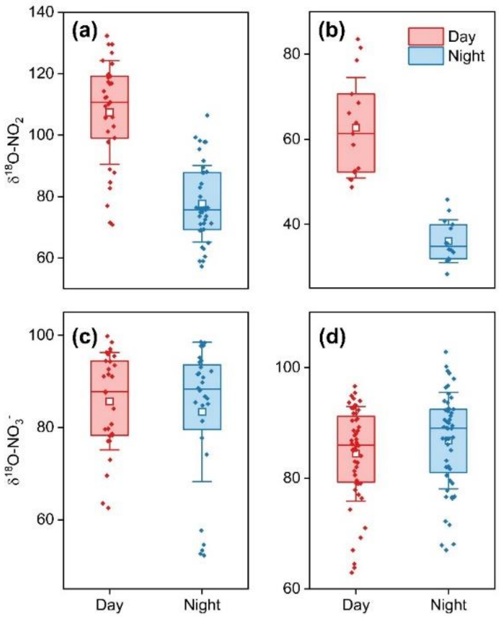

Figure R2 The diurnal values of atmospheric $\delta^{18}O-NO_2$ in Hefei winter (Zhang et al., 2025) (a) and in Nanchang summer (Cao, 2022) (b), and $\delta^{18}O-NO_3^-$ in Tianjin winter (Feng et al., 2020) (c) and in Nanjing winter (Zhang et al., 2022) (d).

Albertin, S., Savarino, J., Bekki, S., Barbero, A., and Caillon, N.: Measurement report: Nitrogen isotopes ($\delta^{15}N$) and first quantification of oxygen isotope anomalies ($\Delta^{17}O$, $\delta^{18}O$) in atmospheric nitrogen dioxide, Atmos. Chem. Phys., 21, 10477-10497, 10.5194/acp-21-10477-2021, 2021.

Albertin, S., Savarino, J., Bekki, S., Barbero, A., Grilli, R., Fournier, Q., Ventrillard, I., Caillon, N., and Law, K.: Diurnal variations in oxygen and nitrogen isotopes of atmospheric nitrogen dioxide and nitrate: implications for tracing NOx oxidation pathways and emission sources, Atmos. Chem. Phys., 24, 1361-1388, 10.5194/acp-24-1361-2024, 2024.

Cao, L. Nitrogen and oxygen isotope tracing of urban atmospheric nitrate sources and atmospheric processes—taking Beijing and Nanchang as examples. Dissertation for master's degree of East China University of Technology.

Feng, X., Li, Q., Tao, Y., Ding, S., Chen, Y., and Li, X.: Impact of Coal Replacing Project on atmospheric fine aerosol nitrate loading and formation pathways in urban Tianjin: Insights from chemical composition and ^{15}N and ^{18}O isotope ratios, Sci. Total Environ., 708, 134797, 10.1016/j.scitotenv.2019.134797, 2020.

Kroopnick, P., and Craig, H.: Atmospheric Oxygen: Isotopic Composition and Solubility Fractionation, Science, 175, 54-55, 10.1126/science.175.4017.54, 1972.

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Wen, X. F., Zhang, S. C., Sun, X. M., Yu, G. R., and Lee, X.: Water vapor and precipitation isotope ratios in Beijing, China, Journal of Geophysical Research: Atmospheres, 115, 10.1029/2009JD012408, 2010.

Zhang, Y., Zhang, W., Fan, M., Li, J., Fang, H., Cao, F., Lin, Y., Wilkins, B. P., Liu, X., Bao, M., Hong, Y., and Michalski, G.: A diurnal story of $\Delta^{17}O(NO_3^-)$ in urban Nanjing and its implication for nitrate aerosol formation, npj Climate and Atmospheric Science, 5, 10.1038/s41612-022-00273-3, 2022.

Zhang, Z., Zhou, T., Jiang, Z., Ma, T., Su, G., Ruan, X., Wu, Y., Cao, Y., Wang, X., Liu, Z., Li, W., Zhang, H., Lin, M., Liu, P., and Geng, L.: High-Resolution Measurements of Multi-Isotopic Signatures ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) of Winter NO_2 in a Megacity in Central China, Environ. Sci. Technol., 59, 3634-3644, 10.1021/acs.est.4c07724, 2025.

Lines 405-406: What were the "Other" pathways? Do you have an idea if their $d^{18}O$ values of the formed nitrate are close to the het pathway? If not then the model compared to the observations would appear biased towards accurately getting the het reaction pathway correct.

Reply: We apologize for not providing a sufficient explanation regarding the pathway calculations for stable isotopes. P7–P10 were roughly defined as "other" pathways (line 425–427 in the revised manuscript) in Table R2 in our previous study (Luo et al., 2020), and we compiled theoretical calculations of the thermodynamic fractionation of $\delta^{18}O$ endmember. As you noted, the endmember values of $\delta^{18}O$ were too close to those of hetN_2O_5; for example, in the calculations for the winter of 2018 in Qingdao, the end-member $\delta^{18}O$ value for the hetN_2O_5 pathway was 102.6 ± 4.2‰, whereas those for P7, P8, and P9 were 105.8 ± 4.8‰, 126.4 ± 4.8‰, and 135.0 ± 4.8‰, respectively. This consideration remains immature in actual pathway calculations; extensive numbers of researchers have primarily used $\cdot OH+NO_2$ and hetN_2O_5 as the two main formation pathways to calculate atmospheric NO_3^- formation (Li et al., 2023; Xiao et al., 2025). We followed the two-pathway approach.

In contrast, the CMAQ model considers a comprehensive set of reaction rates and computes the refined pathway contribution, which is its principal strength. Consequently, stable isotopes, which serve as direct observational evidence, provide qualitative but robust confirmation of the validity of the CMAQ model. The two methods indicated that in Beijing during the winter of 2018, the contribution of the hetN_2O_5 pathway decreased with that in 2013, whereas the contribution of hetN_2O_5 in the coastal city of Qingdao was greater than that in the inland city of Beijing (Figure R3).

Table R2 Calculated δ^{18}O values of NOy for each nitrate production pathway (Luo et al., 2020).

Pathway		Expression
R1	$NO + O_3 \rightarrow NO_2 + O_2$	$\delta^{18}O\text{-}NO_2 = \phi\ \delta^{18}O\text{-}O_3 + (1\text{-}\phi)\ \delta^{18}O\text{-}R/HO_2$
R2	$NO + RO_2/HO_2 \rightarrow NO_2 + O_2$	
R3	$NO_2 + O_3 \rightarrow NO_3$	$\delta^{18}O\text{-}NO_3 = 2/3\ \delta^{18}O\text{-}NO_2 + 1/3\ \delta^{18}O\text{-}O_3$
R4	$NO_2 + NO_3 \rightarrow N_2O_5$	$\delta^{18}O\text{-}N_2O_5 = 2/5\ \delta^{18}O\text{-}NO_2 + 3/5\ \delta^{18}O\text{-}NO_3$
R5	$NO_2 + OH \rightarrow HNO_3$	$\delta_{18}O\text{-}HNO3 = 2/3\ \delta^{18}O\text{-}NO_2 + 1/3\ \delta^{18}O\text{-}OH$
R6	$N_2O_5 + H_2O \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = 5/6\ \delta^{18}O\text{-}N_2O_5 + 1/6\ \delta^{18}O\text{-}H_2O$
R7	$NO_3 + HC/DMS \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = \delta^{18}O\text{-}NO_3$
R8	$N_2O_5 + Cl^- \rightarrow pNO_3^-$	$\delta^{18}O\text{-}HNO_3 = \delta^{18}O\text{-}N_2O_5$
R9	$ClNO_3 + H_2O \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = 2/3\ \delta^{18}O\text{-}NO_2 + 1/3\ \delta^{18}O\text{-}O_3$
R10	$NO_2 + H_2O \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = \delta^{18}O\text{-}NO_2$

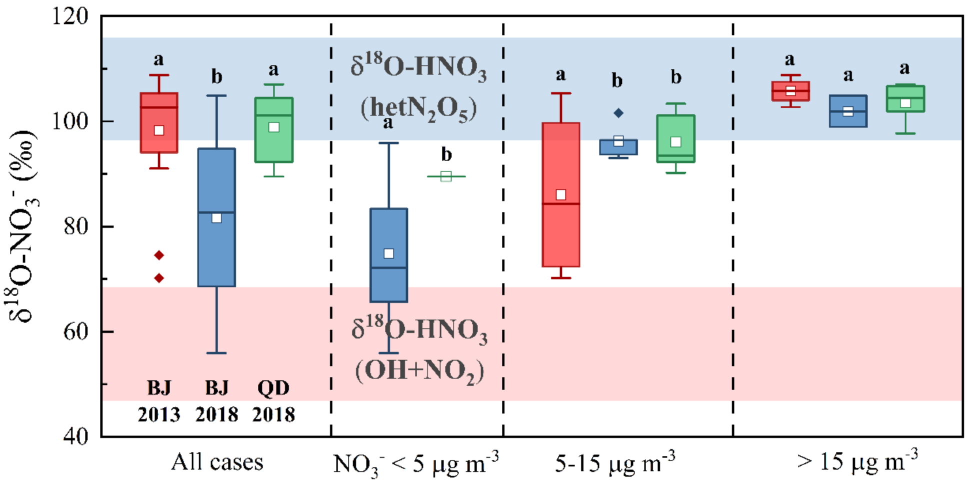

Figure R3. Boxplots of δ^{18}O of atmospheric NO_3^- collected in Beijing in the winters of 2013 and 2018 and in Qingdao in the winter of 2018 under different nitrate conditions. The shadows of red and blue indicate the ranges of $\delta^{18}O\text{–}NO_3^-$ generated via the daytime and nocturnal pathways, respectively. Categories that share common letters do not differ in significance, which is set to 0.05

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Lines 415-416: It would be important for the partitioning of HNO_3 to pNO_3, but it wouldn't have a major impact on the formation of nitrate. Though it could influence the aerosol properties that could influence N_2O_5 reactions on aerosol surface for HNO3 production.

Reply: We appreciate your careful review of our manuscript. While NH_3 has a limited direct influence on nitrate formation, it is pivotal in converting HNO_3 to particulate nitrate (pNO_3) at sufficient ammonia concentrations. In the revised manuscript, we updated this statement to: " The availability of NH_3 was considered a critical factor governing the partitioning of HNO_3 to particulate nitrate (pNO_3)." lines 497–498.

Lines 449-450: I think it might be better worded to say NH_3 plays a critical role in influence particulate nitrate concentrations. Using "formation" is slightly confusing for this work, because some much time and effort was devoted to talking about nitrate formation via oxidation chemistry, which isn't the same use of formation in this context.

Reply: We sincerely appreciate the reviewer's insightful comments. We have revised the sentence to more precisely describe the role of ammonia (NH_3) in influencing particulate nitrate concentrations. The modified sentence now reads: " In summary, NH_3 played a critical role in influencing particulate nitrate concentrations by affecting the gas–particle conversion of HNO_3 in the NCP region, although its availability was sufficient." (Lines 527-529)

Lines 458 – 459: The rate formation of HNO3 from the NO_2 + OH reaction: d[HNO3]/dt = k(NO_2+OH)[NO_2][OH] shows that it depends on both [NO_2] and [OH]

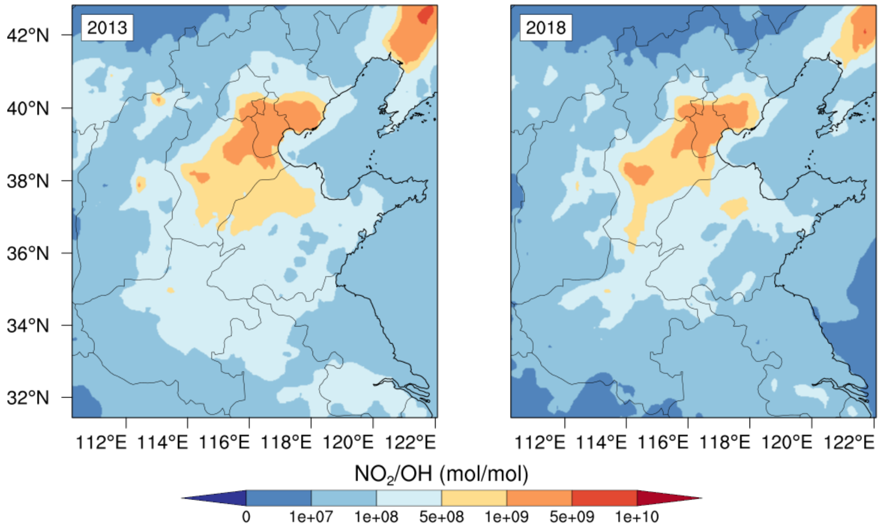

Figure 4 Spatial distributions of the NO_2/OH molar ratio in the NCP region during the winters of 2013 and 2018

Reply: We are truly grateful for your insightful comments and constructive suggestions. The reaction rate of HNO_3 formation via NO_2 + OH ($d[HNO_3]/dt = k(NO_2 + OH)[NO_2][OH]$) is evidently dependent on the concentrations of both NO_2 and OH. However, NO_2 concentrations remain much higher than OH radical concentrations, with the NO_2/OH molar ratio typically exceeding 10^8. This result indicates that NO_2 is in excess during this reaction. Therefore, we conclude that the reaction rate is influenced primarily by the concentration of OH radicals.

Lines 501-505: Why did [O_3] increase during this period?

Reply: Currently, the increase in ozone (O_3) concentrations is attributed primarily to both meteorological variations and anthropogenic influences, with the latter playing a more significant role. Studies indicate that meteorological changes and anthropogenic emissions jointly drive the rise in O_3, with anthropogenic contributions being more substantial. For example, Li et al. (2019) reported that O_3 concentrations in the North China Plain (NCP) increased by 3.3 ppb yr^{-1} ($p < 0.01$) from 2013 to 2019, with meteorological factors contributing 1.4 ppb yr^{-1} ($p = 0.02$) and anthropogenic influences accounting for 1.9 ppb yr^{-1} ($p < 0.01$). Similarly, Liu et al. (2020) demonstrated that, from 2013 to 2020, both meteorological variations (3.6 μg m^{-3}) and anthropogenic emissions (6.7 μg m^{-3}) contributed to the increase in the maximum daily 8-hour average ozone (MDA8 O_3) across China, with anthropogenic emissions playing a more dominant role.

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

Liu, Y., Geng, G., Cheng, J., Liu, Y., Xiao, Q., Liu, L., Shi, Q., Tong, D., He, K., and Zhang, Q.: Drivers of Increasing Ozone during the Two Phases of Clean Air Actions in China 2013–2020, Environmental Science & Technology, 57, 8954-8964, 10.1021/acs.est.3c00054, 2023.

Line 510-512: “uptake” coefficient?

Reply: Thank you for pointing this out. We have revised the term to “uptake” coefficient on line 591.

Lines 617-618: I think this is an inadequate Data availability statement.

Reply: Thank you for your valuable feedback regarding the data availability statement. We have updated the data availability statement to provide more comprehensive information on how to access the data. All datasets supporting the findings of this study are available through the following channels. Primary datasets and analysis results are available from the corresponding authors upon reasonable request. All plotting data and essential research data have been deposited in a publicly accessible repository on the Baidu Cloud (Data link: https://pan.baidu.com/s/153rcdB-vTidH-14PPaXu-A; Access code: egus).

Supporting Information

Enhanced Atmospheric Oxidation and Particle Reductions Driving Changes to Nitrate Formation Mechanisms across Coastal and Inland Regions of North China

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Text S1

Our isotope blank measurements followed the same procedure as the sample isotope analysis. Specifically, in the sample measurements, after purging with high-purity nitrogen, 20 nmol of nitrogen was added to the headspace vial containing the *Pseudomonas aureofaciens* (ATCC13985) strain. For the blank measurements, no sample was added, and after 24 hours, 10 M NaOH was directly injected to quench the reaction before the analysis. The peak area in the chromatogram represents the absolute amount of N_2O reduced by the strain, and the $\delta^{15}N$ and $\delta^{18}O$ values correspond to the $\delta^{15}N$ and $\delta^{18}O$ values of the sample. The peak area for the samples was around 10, while the peak areas for the two blank measurements were only 0.371 and 0.336, indicating an influence on the isotope values of less than 5%, which is negligible and thus not considered.

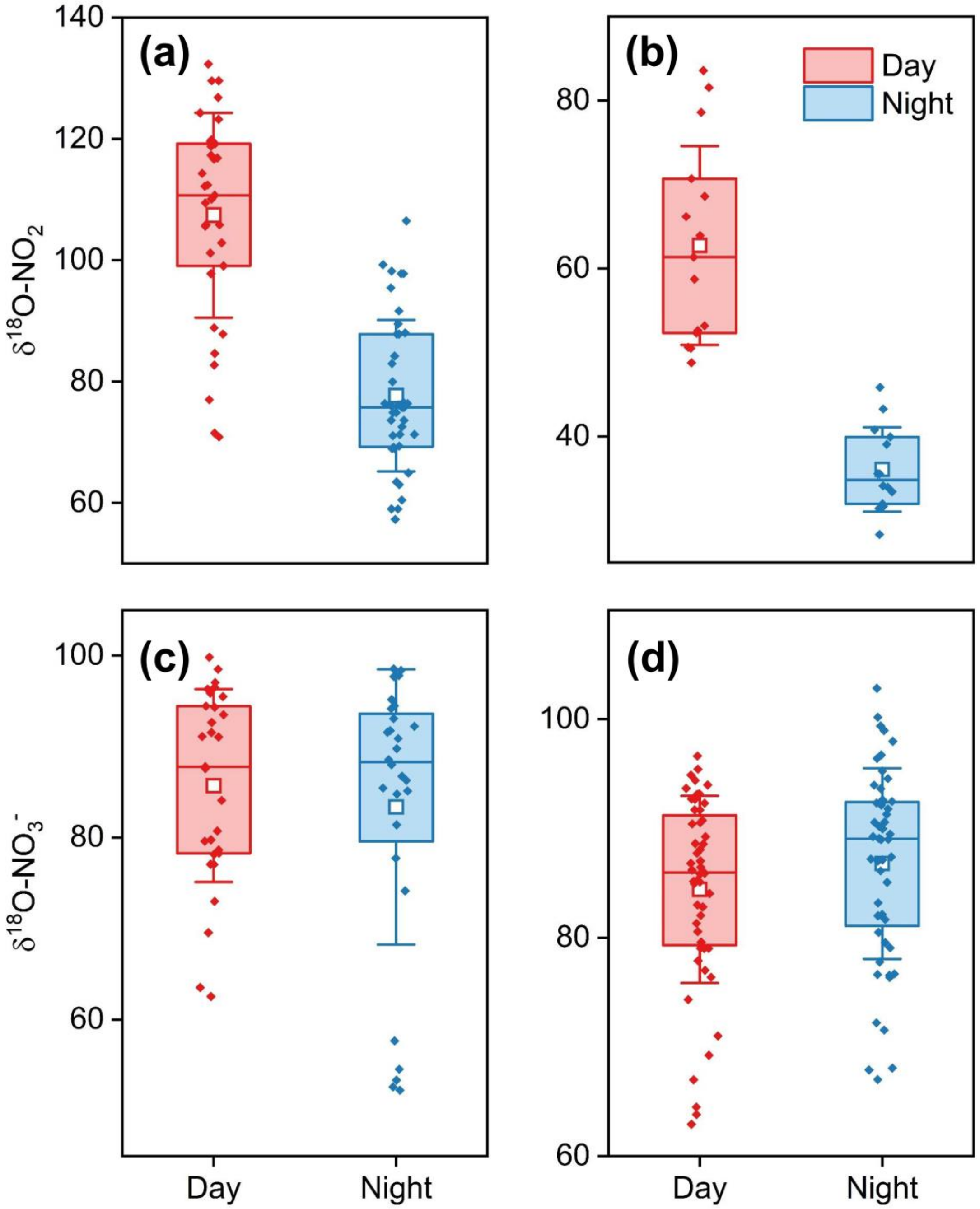

Figure S1 The diurnal values of atmospheric $\delta^{18}O\text{-}NO_2$ in Hefei winter (Zhang et al., 2025) (a) and in Nanchang summer (Cao, 2022) (b), and $\delta^{18}O\text{-}NO_3^-$ in Tianjin winter (Feng et al., 2020) (c) and in Nanjing winter (Zhang et al., 2022) (d).

Text S2

In most studies, the tropospheric δ^{15}N-NOx was often assumed as 0‰ following Walters and Michalski (2016), Luo et al. (2023) and Deng et al. (2024). In addition, the tropospheric δ^{18}O-$H_2O_{(g)}$ in Beijing in winter was determined as -27.9‰ in Wen et al. (2010), and in Qingdao, it was determined as -18.6‰ in Wang et al. (2022). The tropospheric δ^{18}O-NOx ranged from 112‰ to 122‰ (Michalski et al., 2014; Walters and Michalski, 2016). The f_{NO2} values in Beijing and Qingdao were 0.655 (Luo et al., 2023) and 0.786 (Lian et al., 2022) in winter, respectively.

$$\begin{aligned}\delta^{15}N - NO_3^- &= \gamma \times [\delta^{15}N - NO_3^-]_{OH} + (1-\gamma) \times [\delta^{15}N - NO_3^-]_{N_2O_5} \\ &= \gamma \times [\delta^{15}N - HNO_3]_{OH} + (1-\gamma) \times [\delta^{15}N - HNO_3]_{N_2O_5}\end{aligned} \tag{S1}$$

$$\begin{aligned}\delta^{18}O - NO_3^- &= \gamma \times [\delta^{18}O - NO_3^-]_{OH} + (1-\gamma) \times [\delta^{18}O - NO_3^-]_{N_2O_5} \\ &= \gamma \times [\delta^{18}O - HNO_3]_{OH} + (1-\gamma) \times [\delta^{18}O - HNO_3]_{N_2O_5}\end{aligned} \tag{S2}$$

$$\begin{aligned}[\delta^{15}N - HNO_3]_{OH} &= \delta^{15}N - NO_2 \\ &= 1000 \times \left[\frac{\left({}^{15}a_{\mathrm{NO_2/NO}} - 1\right)\left(1 - f_{NO_2}\right)}{\left(1 - f_{NO_2}\right) + \left({}^{15}a_{\mathrm{NO_2/NO}} \times f_{NO_2}\right)}\right] + \delta^{15}N - NOx\end{aligned} \tag{S3}$$

$$[\delta^{15}N - HNO_3]_{N_2O_5} = 1000 \times \left({}^{15}a_{N_2O_5/NO_2} - 1\right) + \delta^{15}N - NOx \tag{S4}$$

$$\begin{aligned}[\delta^{18}O - HNO_3]_{OH} &= \frac{2}{3} \times [\delta^{18}O - NO_2]_{OH} + \frac{1}{3} \times [\delta^{18}O - OH]_{OH} \\ &= \frac{2}{3} \times \left[\frac{1000 \times \left({}^{18}\alpha_{NO_2/NO} - 1\right) \times \left(1 - f_{NO_2}\right)}{\left(1 - f_{NO_2}\right) + \left({}^{18}\alpha_{NO_2/NO} \times f_{NO_2}\right)} + [\delta^{18}O - NOx]\right] \\ &\quad + \frac{1}{3} \times \left[\left(\delta^{18}O - H_2O_{(g)}\right) + 1000 \times \left({}^{18}\alpha_{OH/H_2O_{(g)}} - 1\right)\right]\end{aligned} \tag{S5}$$

$$[\delta^{18}O - HNO_3]_{N_2O_5} = \delta^{18}O - NO_2 + 1000 \times \left({}^{18}\alpha_{N_2O_5/NO_2} - 1\right) \tag{S6}$$

$$1000\left({}^{m}a_{x/y} - 1\right) = \frac{A}{T^4} \times 10^{10} + \frac{B}{T^3} \times 10^{8} + \frac{C}{T^2} \times 10^{6} + \frac{D}{T} \times 10^{4} \tag{S7}$$

Table S1 Values of $\delta^{18}O$ from atmospheric components

Components	Values (‰)	References
O_3	From 80 to 130	Michalski et al., 2011
O_2	23.5	Kroopnick and Craing; 1972
H_2O (g) in Beijing winter	−27.9	Wen et al., 2010
H_2O (g) in Qingdao winter	−18.6	Wang et al., 2022
·OH in Beijing winter	From −72.4 to −64.9	$\delta^{18}O\text{-}OH = \delta^{18}O\text{-}H_2O_{(g)} + 1000({}^{18}\alpha_{X/Y} - 1)$ (Walters and Michalski, 2016)
·OH in Qingdao winter	From −61.2 to −57.8	

Table S2 $^{15}\alpha_{A/B}$ and $^{18}\alpha_{A/B}$ regression coefficients as a function of the temperature (150 K ≤ T ≤ 450 K) (Walters and Michalski, 2015, 2016)

		A	B	C	D
$^{15}\alpha_{A/B}$	N_2O_5/NO_2	0.69398	-1.9859	2.3876	0.16308
	NO_2/NO	3.8834	-7.7299	6.0101	-0.17928
$^{18}\alpha_{A/B}$	NO/NO_2	-0.04129	1.1605	-1.8829	0.74723
	$\cdot OH/H_2O_{(g)}$	2.1137	-3.8026	2.5653	0.5941
	N_2O_5/NO_2	-0.54136	0.13073	1.2477	-0.1272

Table S3 Equations for calculating the statistical evaluation indices

Statistical index	Formula
1. Mean Bias	$\mathrm{MB} = \frac{1}{\mathrm{N}}\sum_{1}^{N}(\mathrm{Sim} - \mathrm{Obs})$
2. Root Mean Square Error	$\mathrm{RMSE} = \sqrt{\frac{1}{N}\sum_{1}^{N}(Sim - Obs)^2}$
3. Index of agreement, IOA	$\mathrm{IOA} = 1 - \frac{\sum_{i=1}^{N}(Sim-Obs)^2}{\sum_{i=1}^{N}(\lvert Sim-\overline{Obs}\rvert+\lvert Obs-\overline{Obs}\rvert)^2}$
4. Normalized Mean Bias	$\mathrm{NMB} = \frac{1}{N}\sum_{1}^{N}\left(\frac{Sim - Obs}{Obs}\right)$
5. Normalized Mean Error	$\mathrm{NME} = \frac{1}{N}\sum_{1}^{N}\left\lvert\frac{Sim - Obs}{Obs}\right\rvert$
6.Correlation coefficient (R)	$\mathrm{R} = \frac{1}{N}\sum_{i=1}^{N}[\frac{(Sim-\overline{Sim})(Obs-\overline{Obs})}{S_pS_o}]$ $S_P = [\frac{1}{N}\sum_{i=1}^{N}(Sim - \overline{Sim})^2]^{\frac{1}{2}}$ $S_o = [\frac{1}{N}\sum_{i=1}^{N}(Obs - \overline{Obs})^2]^{\frac{1}{2}}$

Table S4 Sources of nitrate observation data for the winter of 2013 and the winter of 2018 in the NCP

City	Winter, 2013	Winter, 2018
Beijing	Song et al. (2019)	Fan et al. (2020)
Tianjin	Yao et al. (2020)	Observation
Shijiahzuang	Wang et al. (2016)	Zhou et al. (2020)
Jinan	Cheng et al. (2021)	Observation
Zhengzhou	Wei et al. (2019)	Dong et al. (2020)
Qingdao	Observation	Observation
Yantai	/	/

The NO_3^- observation data collected during the winter of 2018 for Tianjin were sourced from direct observations by the group of Li Xiaodong at Tianjin University (sampling site: Building 19 rooftop, Tianjin University; coordinates: 39.11°N, 117.16°E). The NO_3^- observation data collected during the winter of 2018 in Jinan were sourced from observations by the group of Xue Likun at Shandong University (sampling site: Jinan City Environmental Monitoring Station; coordinates: 36.66°N, 117.05°E). For Qingdao, NO_3^- observation data for both the winter of 2018 and the winter of 2013 were derived from our own observations.

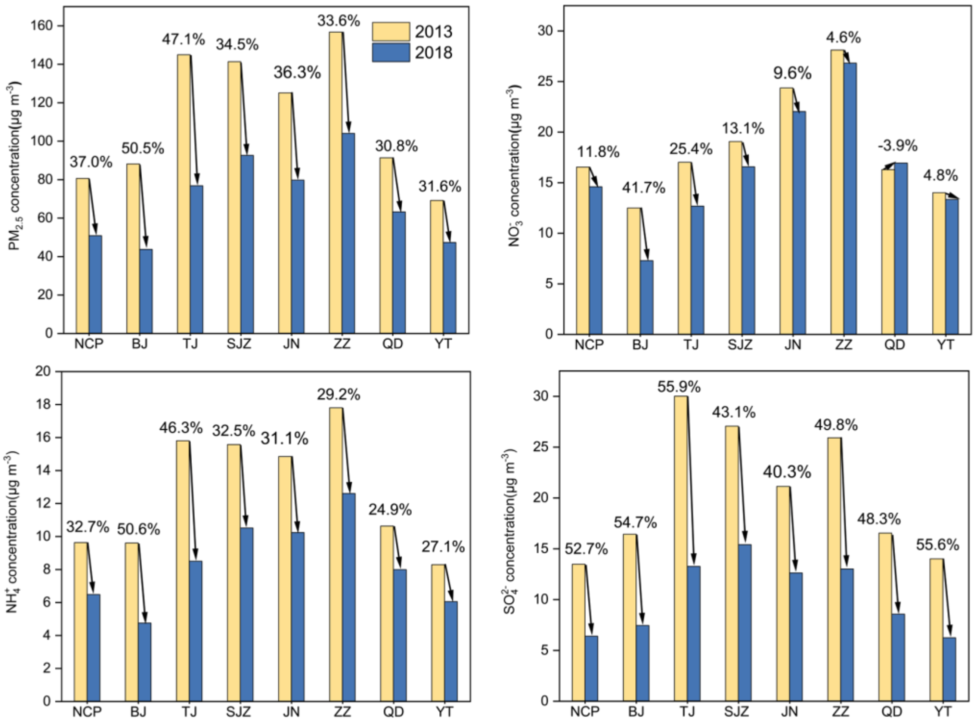

Figure S2 Concentrations of PM$_{2.5}$ and its components in seven major cities in the NCP region during the winters of 2013 and 2018

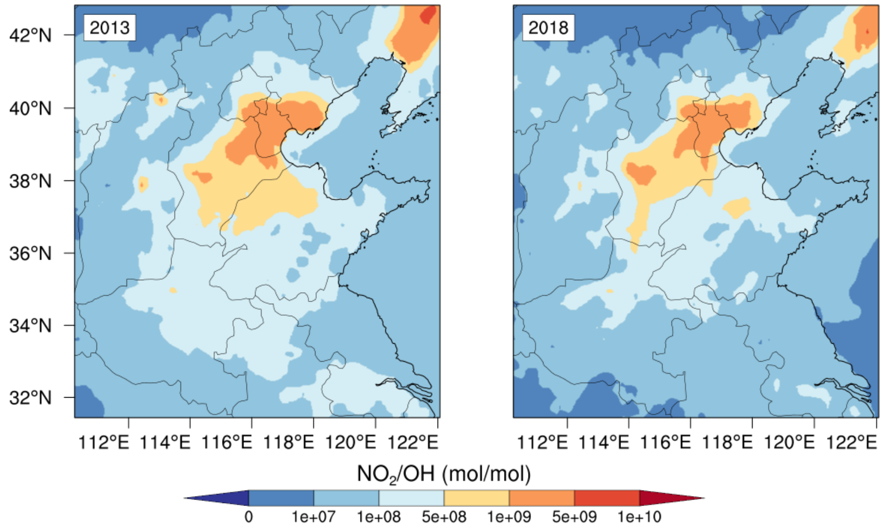

Figure S3 Spatial distribution of the NO$_2$/OH molar ratio in the NCP region during the winters of 2013 and 2018

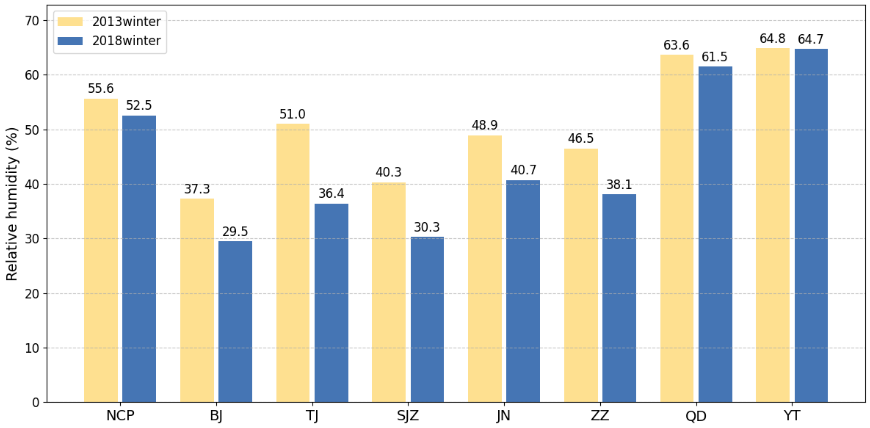

Figure S4 Relative humidity in the NCP and seven major cities (2013, 2018)

Reference

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Luo, L., Wu, S., Zhang, R., Wu, Y., Li, J., and Kao, S.-j.: What controls aerosol δ15N-NO3−? NOx emission sources vs. nitrogen isotope fractionation, Science of The Total Environment, 871, 162185, doi:10.1016/j.scitotenv.2023.162185, 2023.

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