Cover Letter

Dear editor,

On behalf of my co-authors, we thank you very much for giving us an opportunity to revise our manuscript. We gratefully appreciate the editors and reviewers for their time spent making positive and constructive comments. These comments are all valuable and helpful for revising and improving our manuscript entitled **"Exploring Atmospheric Nitrate Formation Mechanisms during the Winters of 2013 and 2018 in the North China Region via Modeling and Isotopic Analysis" (Manuscript Number: egusphere-2024-3044)**, and for providing important guidance for our research.

Based on the two reviewers' comments, we have made substantial revisions to our manuscript, including reducing the number of figures and tables by merging or moving them to the supplementary materials, supplementing additional details about the experimental designs, reanalyzing the results, calculating the impact of transport, enhancing our discussion, and improving the conclusion. Therefore, we believe that this paper has been greatly enhanced by making changes. The revised portions are marked in red in the revised version. The summary of the corrections and the detailed item-by-item responses to the comments are as follows.

Thank you and best regards.

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

Reviewer #1:

Comments on Liu et al., 2024

General summary:

Overall, I think there is clear evidence that a lot of work has been done and much data produced. The writing is clear. The technical analysis seems logical and results reported well, although I cannot speak much to the actual modelling technical components as that is outside my expertise.

My primary critique revolves around the structure and narrative of the paper. Namely, there is so much information presented that it is sometimes difficult to keep track of what the overall main point is that the authors are trying to get across. I think this is exemplified in two ways: first, the title itself about "Exploring…mechanisms", while accurate to the content, highlights that there is less focus on a definitive point/conclusion than just summarizing and overviewing a lot of results from modelling. Second, there is a massive Results section, but no Discussion. There is some discussion happening within the Results, but the paper would likely improve by having less space dedicated to describing every result from the modelling and more space on what those results mean for things like policy implications, the need to treat interior cities differently from coastal ones in regulations, etc. Overall, I would suggest that the authors take a fresh look at the content of the paper as a whole narrative and re-evaluate if everything in the results needs to be included and described at the detail it currently is at.

That said, I do think that there is a good information here, and a valuable contribution. And I have largely minor critiques on the technical side and scientific content. But for the authors' sake, I think the paper's eventual impact could be greatly improved by focusing the narrative, simplifying/summarizing some of the base results further, and speaking more to the broader implications of this work.

Reply: Thank you for your valuable suggestions for improvement. We agree that the current results section had been overly detailed, which may have detracted from the overall focus of the paper. In response to your feedback, we have implemented the following adjustments:

1. Revised the Title

In line with your suggestions, we had revised the title into: "Enhanced Atmospheric Oxidation and Particle Reductions Driving Changes to Nitrate Formation Mechanisms Across Coastal and Inland Regions of North China."

2. Streamlined the Results Section

In Section 3.2, we removed some comparisons with previous literature to highlight the unique findings of this study. We streamlined the content by summarizing key trends in a more concise format, with a particular focus on the differences between inland and coastal regions. Additionally, we merged relevant figures, as shown in Figure 11.

3. Enhanced the Discussion

To enhance the discussion, we enriched the results section with additional commentary to emphasize the broader implications and scientific significance of our findings. In Section 3.4 (lines 413–489), we enhanced the discussion of model-isotope comparisons and their implications.

Specifically, we proposed concrete policy recommendations, such as intensifying control measures targeting photochemical reactions in inland cities (lines 584–588). We proposed that coastal cities should focus more on regulations related to aerosol surface area (lines 630–636).
Additionally, in Section 3.6, we conducted a comparative analysis of emission reduction experiments between Beijing and Qingdao, providing targeted strategies for improving air quality based on the unique characteristics of each city.

Major points:

I cannot see a supplemental section on the Preprint review page? This made it impossible to examine things referenced in the methods. (Apologies if this was a mistake on my part).

Results: There is a huge amount of information and data both presented and discussed. While I commend the authors for being upfront with their data, it can be a bit overwhelming at times and causes some of the focus to be lost. I would recommend looking back over this section to determine what exactly are the main points and stories you are aiming to get across, and pare down any information and number discussion that distracts away from those points. Perhaps greater summarization of regional trends (e.g., inland vs. coastal) rather than relaying data from multiple cities would help focus the section, too. You do this already some by focusing on Beijing vs. Qingdao, but even further summarization/simplification could help in some spots.

There are a lot of figures, and many of them are similar in theme (e.g., comparing an atmospheric chemical in 2013 and in 2018 and their difference). Perhaps combining many of these into a single, larger figure would be more effective as the reader could cross compare more easily and not hit figure fatigue.

Data availability: This is an unacceptable statement for data availability, as per ACP standards. Data are to be hosted in a publicly accessible location. See further guidance from https://www.atmospheric-chemistry-and-physics.net/policies/data_policy.html:

If the data are not publicly accessible at the time of final publication, the data statement should describe where and when they will appear, and provide information on how readers can obtain the data until then. Nevertheless, authors should make such embargoed data available to reviewers during the review process in order to foster reproducibility. The Copernicus review system allows to define such assets as 'access limited to reviewers' and reviewers must then sign that they will use such data only for the purpose of reviewing without making copies, sharing, or reusing.

In rare cases where the data cannot be deposited publicly (e.g., because of commercial constraints), a detailed explanation of why this is the case is required. The data needed to replicate figures in a paper should in any case be publicly available, either in a public database (strongly recommended), or in a supplement to the paper.

Reply: Thank you for your valuable feedback. In response, we have made the following revisions:

1. Supplementary Materials

We have submitted the supplementary materials as required and ensured that all relevant content is clearly labeled. It appears that, perhaps 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 references clearly indicated. We will verify the completeness of these materials in our submission of revised version. We kindly invite you to review them and welcome any further comments

2. Results Section Length

Thank you for highlighting the issue of excessive detail in the results section. We have carefully revised this section to eliminate repetitive descriptions of secondary information and city-specific data. Specifically, in Section 3.2, we have streamlined the content by summarizing key trends in a more concise format, particularly focusing on the differences between inland and coastal regions. In Section 3.4, we have added detailed comparisons and summaries of model simulations and isotope data for Beijing and Qingdao. Additionally, in Section 3.6, we have placed greater emphasis on the comparative analysis of emission reductions between Beijing and Qingdao, ensuring a clearer and more focused narrative.

3. Number of Charts

Your suggestion regarding the number of charts is greatly appreciated. To streamline the presentation and enhance data comparability, we have merged charts with similar themes. The chemical differences in air composition between 2013 and 2018, including the GR, HONO, N_2O_5, and NO_x concentrations over the North China Plain during winter, have been merged into a single figure (Figure 11).

4. Data Availability Statement

Thank you for your valuable feedback. We recognize that the initial statement may have lacked sufficient detail. 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).

Specific points:

71: Is this coastal or inland Greenland?

Reply: Thank you for your question. The Greenland research station mentioned in the paper is located at (72.6°N, 38.5°W) within Greenland's polar environment, and it is geographically closer to the coastal regions.

73: What is it about the air mass origin that affects the nitrate formation? Or why is this being set apart and discussed here after the review of the coastal vs. inland cities? Isn't air mass origin also the primary reason for those differences? The structure of the paragraph is just confusing me a little bit here.

Reply: Thank you for the question. Regarding the influence of air mass origin on nitrate formation, we have addressed this issue separately in the paper because the source of the air mass is a crucial factor driving the differences between coastal and inland cities, that impacts the underlying mechanisms, specifically the effects of pollutant composition and humidity on nitrate formation pathways.

Specifically, marine air masses are typically associated with higher humidity, lower NOx mixing ratios, and longer NO_3 radical lifetimes, which significantly promote reactions via the hetN_2O_5 pathway. In contrast, continental air masses usually exhibit higher NOx mixing ratios and NH_3 concentrations, which are more favorable for nitrate formation through the OH + NO_2 pathway. To better understand these regional differences, we have compared the nitrate formation mechanisms

between coastal and inland cities and further investigated the influence of air mass origin in Section 3.5.3 (lines 608–611). This analysis provides a more comprehensive understanding of the underlying driving mechanisms behind these regional disparities.

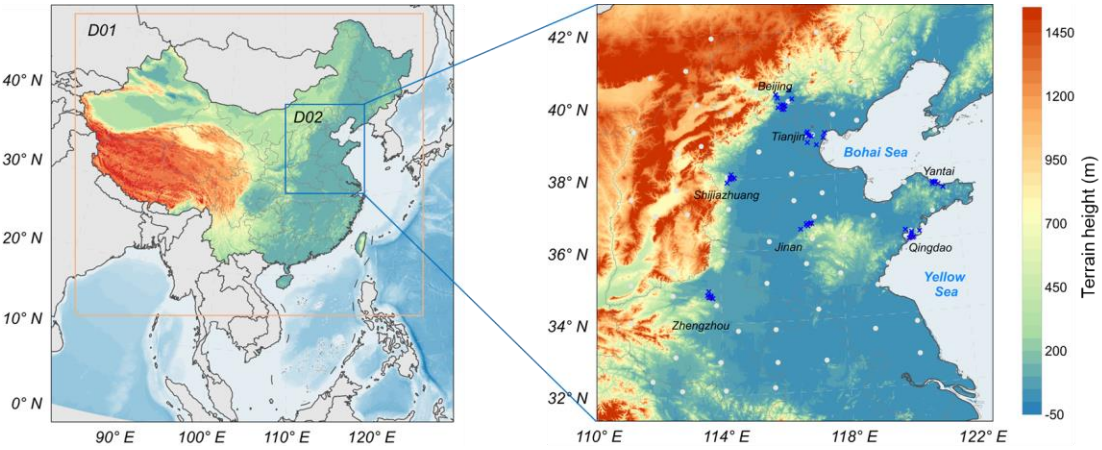
Fig. 2: Data source for terrain heights should be cited

Reply: Thank you for your suggestion. We have supplemented a citation for the terrain elevation data in the manuscript (lines 144–145). The data are sourced from the GEBCO Compilation Group (2024) GEBCO 2024 Grid (doi:10.5285/1c44ce99-0a0d-5f4f-e063-7086abc0ea0f).

165: Was there a specific data network that you were sourcing within that website? For example, that website is just a portal to access many different data networks, such as WMO and GHCN, and if you know the exact data source network, that could be cited here and be more clear.

Reply: We have clarified in the manuscript (line 146) that the terrain elevation data were obtained from the GEBCO website (https://www.gebco.net/data_and_products/gridded_bathymetry_data/) which provides access to the GEBCO 2024 grid dataset.

168: A little more information about these 68 stations would be beneficial, such as are they all within a specific region/geographic bounds? Were there any selection criteria applied to choose the stations?



Reply: These 68 observation stations were all located within the simulated D02 domain, which corresponded to the North China region. The selection of these stations was based on the availability of observational data. Specifically, all stations within this area that had observational data were included.

185: Just to confirm, are all the instrumentation specifics the same that you used here as in this cited paper? You might add a brief line or addition to the end of the sentence currently ending in "denitrifier method" to add the instrumentation used, so that the reader doesn't have to go look that basic information up in another paper.

Reply: Thank you for your valuable feedback. We now specify that the instrument used was the Gasbench-IRMS (Delta V, Thermo Scientific), which is the same as the one employed in our previous research. This clarification was added at the end of the sentence (lines 210–212) in the revised manuscript.

Revised sentence: The $\delta^{18}O$ and $\delta^{15}N$ values of NO_3^- in the TSP samples were determined via the bacterial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) with the Gasbench-IRMS

system (Delta V model, Thermo Scientific).

204: I think that some more information needs to be given here on how you used these indicators to evaluate the simulation effect. You have cited some proposed benchmarks, but it isn't clear to me readily how you will be using this information in your paper. In a very soon following section (3.1) about model evaluation where you present simulated values and some of the benchmarks, I was able to eventually infer how you were doing the evaluation, but it should really be more explicitly clear in the methodology.

Reply: Thank you for your comment. We have included several evaluation metrics and benchmarks in the methodology section (Table 1 and Table 2); however, due to the extensive number of evaluation formulas, we have provided a comprehensive description of the calculation methods and formulas in the supporting information. You can find these details in Table S3 of the supporting information.

220: I'm unclear exactly how the numbers being discussed here from the 68 sites were gathered and compared. Are these pairwise calculations, or overall means, or involving some sort of spatial dimension, etc? Are the comparisons all at hourly resolution, or aggregated to daily or something else? There needs to be more clarity on this, likely in the methodology of the 2.5 section. Also, how did you evaluate parameters that lacked cited benchmarks (perhaps something else that could be included in the methodology?)? For example, some of the Pearson correlation coefficients are somewhat low, for wind especially.

Reply: Thank you for your questions. For the data collected from the 68 observation stations, comparisons were conducted at on an hourly basis. At each station, the observed value was compared with the simulated value from the corresponding model grid cell on a point-by-point, and hour-by-hour basis. These paired comparisons were then aggregated across all 68 stations, and statistical evaluation metrics (e.g., MB, RMSE, and IOA) were generated from the entire dataset to provide an overall assessment of the model's performance.

To make these comparisons, we used the grid cell corresponding to the geographic coordinates of each observation point. This process ensured precise spatial and temporal alignment between the model simulation data and the observational data. Both data processing and comparisons were conducted on an hourly basis, without any daily averaging or other forms of temporal aggregation. Further details on this methodology can be found in Section 2.5 (lines 249–254) of the revised manuscript.

Model evaluation is both a critical and challenging part of model research. The current evaluation framework is based on findings from numerous studies. The relevant literature indicates that the current evaluation metrics are sufficient for analyzing model performance. We aim to further supplement and refine our model evaluation process through these calculations. Regarding the missing cited benchmarks, commonly used methods in the literature, such as those for wind speed and wind direction, were adopted, and we acknowledged that the observed underestimation is a common phenomenon in the model. For instance, the calculation of the Pearson correlation coefficient is intended to assist in assessing model performance. Although some parameters, particularly the correlation coefficient for wind speed, yield lower values, this phenomenon is consistent with the well-documented tendency of the WRF model to overestimate wind speed, which is an issue that is frequently reported in the literature (Tan et al., 2017; Jacobson and Kaufman,

2006). Moreover, evaluating wind direction data is complicated by its cyclic nature (since 360° and 0° represent the same direction), which may lead to some deviations in the correlation and error metrics.

Tan, J., Zhang, Y., Ma, W., Yu, Q., Wang, Q., Fu, Q., Zhou, B., Chen, J., and Chen, L.: Evaluation and potential improvements of WRF/CMAQ in simulating multi-levels air pollution in megacity Shanghai, China, Stochastic Environmental Research and Risk Assessment, 31, 2513-2526, doi:10.1007/s00477-016-1342-3, 2017.
Jacobson, M. Z. and Kaufman, Y. J.: Wind reduction by aerosol particles, Geophysical Research Letters, 33, doi:10.1029/2006GL027838, 2006.

Section 3.4: The model has output for "Others" but your isotopic method doesn't. However, I don't see any discussion of this in this section, but I feel it needs addressed in some form. If 5-8% of reactions are "others" in the model, but you don't distinguish those in the isotopic method, does that mean that you assume you are attributing those "others" reactions to either OH+NO2 or hetN2O5? Is that baked into the uncertainties in any way, or handled specifically?

Reply:

Thank you for your valuable comments. We apologize for the lack of detailed information on our methods, which may have caused confusion.

The CMAQ model took a comprehensive approach by including the contributions of 5-8% of "other" pathways, which was its main advantage. Conversely in our isotopic calculations, we focused only on the $\cdot OH+NO_2$ and $hetN_2O_5$ pathways because the $\delta^{18}O$ end-member values for multiple reaction pathways were quite similar. Hence, those 5–8% of "other" pathways were attributed to the $\cdot OH+NO_2$ and $hetN_2O_5$ pathways in our isotope calculations, potentially resulting in an overestimation of these two pathways compared to the CMAQ model. Notably, that the uncertainty in the pathway contribution calculations based on stable isotopes was approximately 10–30%. Nevertheless, as a receptor model, the isotopic method, based on observational data, provided robust evidence that supported the general patterns revealed by CMAQ (Figure R1). Additionally, we supplemented isotope calculation uncertainties in the manuscript and added a detailed comparison and discussion of both isotopic and CMAQ model results in the relevant section**.** A detailed explanation follows.

In our previous research, we compiled theoretical calculations of the thermodynamic fractionation of $\delta^{18}O$ for the commonly considered atmospheric NO_3^- formation pathways (Table R1), and P7, P8, and P9 were considered as the "other" reactions (Luo et al., 2020). However, due to the end-member values of $\delta^{18}O$ being too close to those of $hetN_2O_5$, such as 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 ‰. Conversely, the end-member values for P7, P8, and P9 were 105.8 ± 4.8 ‰, 126.4 ± 4.8 ‰, and 135.0 ± 4.8 ‰, respectively. This consideration was immature in actual pathway calculations; in more extensive research (Table R2), researchers primarily consider $\cdot OH+NO_2$ and $hetN_2O_5$ the two main formation pathways when calculating atmospheric NO_3^- formation.

In our isotope analysis, we employed the Stable Isotope Mixing Model in R (SIAR) to determine the relative contributions of different formation pathways to atmospheric NO_3^-. The main sources of uncertainty stem from the standard deviations (SD) in each pathway's end-member calculations and the posterior probability distributions generated by the model. As mentioned before, focusing

on the most dominant pathways, rather than multiple pathways (Zhang et al., 2021; Luo et al., 2022), enhances the model's reliability and reduces overall uncertainty. The posterior probability for each pathway's contribution is obtained using the Hilborn sampling-importance-resampling method. For detailed information about the model framework and computational methods, please refer to Moore and Semmens (2008). We have added an explanation of model uncertainties in the Methods section (lines 237–239) and in Section 3.4 (lines (413–430) of the manuscript.

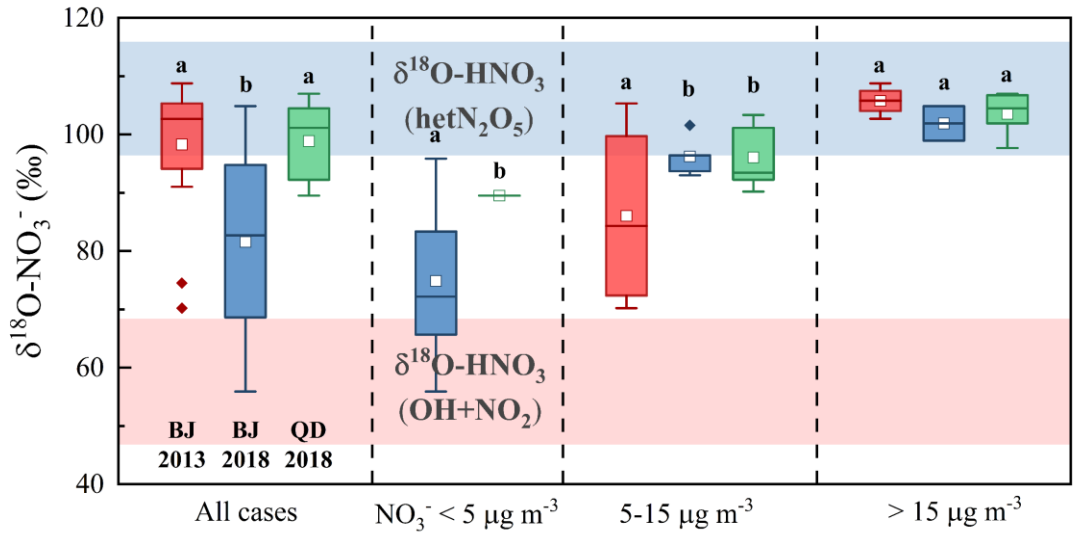


Figure R1. Boxplot of $\delta^{18}O$ of atmospheric NO_3^- collected in Beijing in the winters of 2013 and 2018 and in Qingdao in the winter of 2018 under different nitrate conditions. The shadows of red and blue indicate the ranges of $\delta^{18}O$–NO_3^- generated via the daytime and nocturnal pathways, respectively. Categories that share common letters do not differ in significance, which is set to 0.05.

Table R1. Calculated $\delta^{18}O$ 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	$NO_2 + H_2O \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = \delta^{18}O\text{-}NO_2$

Table R2. Comparison of the contributions of major atmospheric NO_3^- formation pathways in China

Region	City	Lon (°E)	Lat (°N)	Method	Year	Season	·OH+NO_2 (%)	hetN_2O_5 (%)	NO_3·+HC (%)	Reference
NCP	Zibo	118.0547	36.8258	$\Delta^{17}O$	2022-2023	Winter	17.7	32.6	49.7	Feng et al., 2023
	Zhoukou	114.6464	33.6033				53.4	31.1	15.5	
	Beijing	117.1231	39.0601	$\Delta^{17}O$	2021	Winter	18.0	29.1	52.9	Yan et al., 2023
						Spring	26.9	35.2	37.9	
	Beijing	116.3660	39.9746	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	17.4	61.9	20.7	Luo et al., 2023
	Tianjin	117.4177	39.5557	$\Delta^{17}O$	2022	Winter	29.7	34.8	35.5	Zhang et al., 2024
						Spring	51.0	31.9	17.0	
						Summer	41.8	33.6	24.6	
						Autumn	13.2	34.7	52.1	
	Shijiazhuang	114.4942	38.0980	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	6.3	66.0	27.7	Luo et al., 2023
	Tianjin	117.3350	38.9944	$\delta^{18}O$	2019-2020	Winter	31.4	68.6		Zhang et al., 2022
						Spring	57.4	42.6		
						Summer	84.1	15.9		
						Autumn	62.0	38.0		
	Jiaozuo	113.2606	35.1865	$\delta^{18}O$	2020	Winter	30.0	70.0		Li et al., 2022a
						Summer	61.0	39.0		
	Beijing	116.3711	39.9744	$\Delta^{17}O$	2016	Winter	42.6	25.4	31.7	Fan et al., 2022
					2017	Summer	46.2	23.0	31.4	
	Beijing	116.4167	40.0333	$\delta^{18}O$	2017-2018	Winter	67.4	32.6		Zhang et al., 2021a
	Tianjin	117.1500	39.0833				58.1	41.9		
	Shijiazhuang	114.6377	38.0128				50.5	49.5		

	Jinan	117.0500	36.6667				50.6	49.4		
	Jiaozuo	113.2667	35.1833				50.7	49.3		
	Beijing	117.7000	40.0667	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	45.3	46.5	8.2	Zhang et al., 2021b
	Shijiazhuang	114.6377	38.0128	$\delta^{18}O$	2017-2018	Autumn	51.8	48.2		Luo et al., 2021
						Winter	22.5	77.5		
						Spring	51.5	48.5		
						Summer	71.1	28.9		
	Beijing	116.3400	39.9300	$\delta^{18}O$	2013-2014	Spring	18.8	81.2		Zong et al., 2020
						Summer	41.2	58.8		
						Autumn	17.9	82.1		
						Winter	17.3	82.7		
	Beijing	116.3667	39.9667	$\delta^{18}O$	2018	Winter	52.0	48.0		Fan et al., 2020
	Beijing	116.4167	40.0333	$\delta^{18}O$	2017-2018	Winter	48.0	52.0		Zhang et al., 2020a
	Beijing	116.3800	39.9800	$\delta^{18}O$	2013	Spring	56.5	27.2	16.3	Luo et al., 2020a
	Jinan	117.0500	36.6667	$\delta^{18}O$	2018	Summer	39.1	60.9		Zhang et al., 2020b
	Beijing	116.7000	40.0667	$\Delta^{17}O$	2015	Winter	29.5	35.1	35.6	Song et al., 2020
	Beijing	116.4167	40.0333	$\delta^{18}O$	2017-2018	Winter	47.0	53.0		Zhang et al., 2020c
	Beijing	116.7000	40.0667	$\Delta^{17}O$	2014	Spring	27.0	35.0	38.0	Wang et al., 2019
						Summer	40.9	36.1	32.9	
						Autumn	25.0	35.0	40.0	
						Winter	31.0	34.0	34.0	
	Beijing	116.6800	40.4100	$\Delta^{17}O$	2014-2015	Winter	23.5		76.5	He et al., 2018
	Dongying	118.9833	37.7500	$\delta^{18}O$	2013	Summer	47.4	52.6		Zong et al., 2018
Central	Wuhan	114.3000	30.5300	$\delta^{18}O$	2018-2019	Spring	35.0	65.0		Deng et al., 2024
						Summer	69.7	30.3		
						Autumn	34.5	65.5		

						Winter	7.8	92.2		
	Shiyan	111.4000	33.2000	$\delta^{18}O$	2021	Spring	64.0	19.0	17.0	Xiao et al., 2024
						Summer	84.0	8.0	8.0	
						Autumn	64.0	19.0	18.0	
						Winter	25.0	38.0	37.0	
	Wuhan	104.3600	30.5200	$\delta^{18}O$	2013-2014	Spring	17.9	82.1		Zong et al., 2020
						Summer	60.4	39.6		
						Autumn	28.5	71.5		
						Winter	11.2	88.8		
	Lanzhou	103.8551	36.0305	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	22.2	57.6	20.4	Luo et al., 2023
YRD	Shanghai	121.4279	31.2595	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	18.3	47.9	33.8	Luo et al., 2023
	Shanghai	121.5000	31.3000	$\delta^{18}O$	2019	Summer	70.5	29.5		Huang et al., 2024
						Winter	20.7	79.3		
	Shanghai	121.5100	31.3400	$\delta^{15}N$ and $\delta^{18}O$	2018	Winter	16.7	28.3	55.0	Zhu et al., 2021
					2019	Summer	56.1	24.8	19.1	
	Shanghai	121.5700	31.2600	$\Delta^{17}O$	2016	Winter	63.8		36.2	He et al., 2020
						Spring	62.7		37.3	
	Shanghai	121.5000	31.2900	$\delta^{18}O$	2013-2014	Spring	32.6	67.4		Zong et al., 2020
						Summer	60.0	40.0		
						Autumn	27.7	72.3		
						Winter	6.2	93.8		
	Nanjing	118.7000	32.2000	$\Delta^{17}O$	2018	Winter	20.9	27.4	34.0	Yu et al., 2023
	Hangzhou	120.1700	30.2300	$\Delta^{17}O$	2015-2016	Autumn	18.9	34.0	47.1	Fan et al., 2023
						Winter	24.1	34.8	41.1	
						Spring	18.3	35.0	46.7	
						Summer	40.5	35.2	24.3	

Southeast	Xiamen	118.0900	24.4360	$\delta^{18}O$	2019-2021	Cold	20.2	38.2	21.6	Li et al., 2022b
						Warm	30.3	31.5	18.3	
	Nanchang	115.8085	28.6832	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	17.2	43.6	39.2	Luo et al., 2023
	Nanchang	115.9333	28.6833	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	30.4	36.8	32.8	Zhang et al., 2021c
	Nanchang	115.8085	28.6832	$\delta^{18}O$	2017-2018	Autumn	18.0	38.6	43.4	Luo et al., 2020b
						Winter	7.5	33.8	58.7	
						Spring	33.2	34.5	32.3	
						Summer	58.7	28.1	13.2	
	Nanchang	115.9000	28.7000	$\delta^{15}N$ and $\delta^{18}O$	2017	Autumn	37.1	60.3	2.6	Xiao et al., 2020
	Ganzhou	114.7600	25.6600	$\delta^{18}O$	2019	Winter	41.6	29.5	28.9	Cheng et al., 2022
						Summer	73.5	14.1	12.4	
Southwest	Chengdu	104.0527	30.5598	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	23.5	40.8	35.7	Luo et al., 2023
	Chengdu	104.3800	30.6400	$\delta^{18}O$	2013-2014	Spring	46.5	53.5		Zong et al., 2020
						Summer	61.8	38.2		
						Autumn	29.1	70.9		
						Winter	11.3	88.7		
	Kunming	102.7000	25.0667	$\delta^{18}O$	2017-2018	Autumn	85.0	15.0		Guo et al., 2021
						Winter	74.4	25.6		
	Nanning	108.2833	22.8333			Autumn	87.9	12.1		
						Winter	68.4	31.6		
	Guiyang	106.7167	26.5667	$\delta^{18}O$	2013-2014	Winter	38.3	61.7		Li et al., 2021a
					2016	Summer	80.2	19.8		
	Nanning	108.3192	22.7990	$\delta^{15}N$ and $\delta^{18}O$	2017-2018	Winter	47.5	27.8	24.7	Luo et al., 2023
PRD	Guangzhou	113.3689	23.1938	$\delta^{18}O$	2015-2018	Spring	70.4	22.8	6.8	Xi et al., 2023
						Summer	85.6	10.9	3.5	
						Autumn	86.1	10.6	3.3	

						Winter	72.0	21.0	7.1	
	Guangzhou	113.3397	23.1075	$\Delta^{17}O$	2018	Autumn	61.0	12.0	27.0	Wang et al., 2023
	Guangzhou	113.3600	23.1500	$\delta^{18}O$	2013-2014	Spring	48.0	52.0		Zong et al., 2020
						Summer	66.9	33.1		
						Autumn	33.9	66.1		
						Winter	9.7	90.3		
	Harbin	126.6333	45.7469	$\Delta^{17}O$	2022-2023	Winter	55.3	28.2	16.5	Feng et al., 2023
	Shenyang	123.4300	41.7700	$\Delta^{17}O$	2015-2018	Spring	65.8	25.6	8.6	Li et al., 2022c
						Summer	95.3	3.0	1.7	
						Autumn	83.0	12.1	4.8	
						Winter	57.7	30.9	11.4	
	Fushun	124.9400	41.8500			Spring	40.0	34.5	25.5	
						Summer	85.7	9.6	4.7	
						Autumn	46.0	35.9	18.1	
						Winter	37.6	33.2	29.2	
Northeast	Harbin	126.7400	45.7300	$\delta^{18}O$	2017-2018	Winter	69.4	30.6		Zhao et al., 2021
	Changchun	125.4000	43.8500				50.2	49.8		
	Harbin	126.5300	45.8400				50.1	49.9		
	Yushu	126.5300	44.8600				37.3	62.7		
	Harbin	120.6817	45.7539	$\delta^{18}O$	2017-2018	Spring	46.4	53.6		Sun et al., 2020
						Summer	68.7	31.2		
						Autumn	56.1	43.9		
						Winter	44.8	55.2		
	Changchun	125.4000	44.0000	$\delta^{18}O$	2017-2018	Summer	79.7	20.3		Zhao et al., 2020
						Autumn	56.1	43.9		
						Winter	55.9	44.1		

						Spring	58.0	42.0		
Island	Beihuangcheng Island	120.9167	36.4000	$\delta^{18}O$	2015	Autumn	35.0	65.0		Zong et al., 2017
						Winter	24.0	76.0		
						Spring	47.0	53.0		
						Summer	68.0	32.0		
	Dongsha Island	116.7167	20.7000	$\delta^{18}O$	2013	Spring	66.8	10.2	23.0	Yang et al., 2023
	Pengjiayu Island	122.1333	26.0500				62.1	23.4	14.5	
Marine	Bohai Sea and Yellow Sea		32 – 34	$\Delta^{17}O$	2018	Spring	60.0	24.0	16.0	Zhao et al., 2024
			34 – 36				49.0	31.0	19.0	
			36 – 38				26.0	35.0	39.0	
			38 – 40				14.0	34.0	52.0	
	Bohai Sea		38 – 40	$\delta^{18}O$	2014	Summer	65.9	34.1		Zong et al., 2022
						Winter	43.9	56.1		
					2016	Summer	49.3	50.7		
						Winter	41.1	58.9		
					2017	Summer	73.6	26.4		
						Winter	26.4	73.6		
					2018	Summer	61.0	39.0		
						Winter	32.0	68.0		
					2019	Summer	61.7	38.3		
						Winter	28.5	71.5		
NCP	Beijing	116.4125	40.2352	CMAQ	2013	Winter	77.8	14.3		Liu et al., under review
					2018		85.6	9.9		
	Tianjin	117.4812	39.0929		2013		67.8	19.7		
					2018		77.5	15.1		
	Shijiazhuang	114.5562	37.8247		2013		73.8	14.2		

					2018		83.6	8.3	
	Jinan	116.9187	36.8712		2013		63.7	27.7	
					2018		72.9	19.9	
	Zhengzhou	113.8719	34.7968		2013		77.6	10.6	
					2018		79.2	12.7	
	Qingdao	120.5000	36.1533		2013		51.5	41.5	
					2018		56.5	37.0	
	Yantai	121.4187	37.4197		2013		48.2	45.7	
					2018		50.4	43.5	
NCP		115.4817	36.6111	WRF-Chem	2021	Winter	51.0	45.0	Yang et al., 2024
NCP		114.8000	39.5000	WRF-Chem	2017	Winter	48.0	30.3	Zhao et al., 2023
YRD	Shanghai	120.8662	28.0818	CMAQ	2017	Winter	69.3	28.4	Sun et al., 2022
						Spring	81.8	15.3	
						Summer	82.9	12.2	
						Autumn	86.9	11.1	
	Nanjing	118.6491	28.7744			Winter	59.2	36.1	
						Spring	73.1	5.4	
						Summer	74.7	17.9	
						Autumn	69.7	25.4	
	Hefei	117.3881	28.5389			Winter	66.9	27.1	
						Spring	78.5	16.5	
						Summer	81.7	10.4	
						Autumn	72.5	21.8	
	Changzhou	119.6087	28.4776			Winter	68.9	26.8	
						Spring	74.9	20.9	
						Summer	78.7	14.3	

						Autumn	77.6	18.3	
	Hangzhou	119.7671	27.1448			Winter	59.7	35.5	
						Spring	70.5	23.3	
						Summer	76.4	10.7	
						Autumn	73.8	21.3	
YRD	Shanghai	120.9890	31.0970	F0AM	2019	Winter	42.9	55.5	Zang et al., 2022
		121.5330	31.2280				36.8	62.1	
NCP		114.8000	39.5000	WRF-Chem	2016	Summer	60.4	39.6	Li et al., 2021b
						Winter	91.9	8.1	
YRD		121.0000	31.1000			Summer	75.3	24.7	
						Winter	86.2	13.8	
NCP		114.8000	39.5000	WRF-Chem	2016	Winter	53.4	46.6	Liu et al., 2020
Taiwan		120.6753	21.1892	WRF-CMAQ PA	2017	Spring	> 45.0	30.0	Chuang et al., 2022
PRD		113.3600	23.1500	WRF-CMAQ PA	2015	Winter	47.0	34.0	Qu et al., 2021
Central	Xi'an	108.9552	34.2919	WRF-Chem	2017	Winter		24.0	Wu et al., 2021
NCP	Beijing	116.6800	40.4100	GEOS-Chem	2014-2015	Winter	34.4	44.9	Chan et al., 2021
NCP		114.8000	39.5000	WRF-CMAQ PA	2017	Winter	43.0	44.0	Fu et al., 2020
NCP	Beijing	116.6800	40.4100	Box model	2016-2017	Winter	68.8	31.2	Chen et al., 2020
YRD	Nanjing	118.6491	28.7744	Box model	2015	Winter		80	Sun et al., 2018
NCP	Beijing	116.6800	40.4100	CMAQ	2017	Winter		42	Qiu et al., 2019
NCP		114.8000	39.5000	WRF-Chem	2015	Winter		30.1	Liu et al., 2019
PRD		113.3600	23.1500	WRF-Chem	2013	Winter		57.4	Li et al., 2016

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based on $\delta^{18}O$-$\delta^{15}N$ space of particulate nitrate. Environ Pollut 276, 116708. https://doi.org/10.1016/j.envpol.2021.116708.

Zhang, Z., Jiang, Z., Guan, H., Liang, Y., Zheng, N., Guo, W., 2021a. Isotopic evidence for the high contribution of wintertime photochemistry to particulate nitrate formation in northern China. Journal of Geophysical Research: Atmospheres 126, e2021JD035324. https://doi.org/10.1029/2021JD035324.

Zhang, Z., Zheng, N., Liang, Y., Luo, L., Xiao, H., Xiao, H., 2020b. Dominance of heterogeneous chemistry in summertime nitrate accumulation: insights from oxygen isotope of nitrate ($\delta^{18}O$–NO_3^-). Acs Earth Space Chem 4 (6), 818-824. https://doi.org/10.1021/acsearthspacechem.0c00101.

Zhao, X., Zhao, X., Liu, P., Chen, D., Zhang, C., Xue, C., Liu, J., Xu, J., Mu, Y., 2023. Transport pathways of nitrate formed from nocturnal N_2O_5 hydrolysis aloft to the ground level in winter North China Plain. Environ Sci Technol 57 (7), 2715-2725. https://doi.org/10.1021/acs.est.3c00086.

Zhao, Z., Cao, F., Fan, M., Zhai, X., Yu, H., Hong, Y., Ma, Y., Zhang, Y., 2021. Nitrate aerosol formation and source assessment in winter at different regions in Northeast China. Atmos Environ 267, 118767. https://doi.org/10.1016/j.atmosenv.2021.118767.

Zhao, Z., Cao, F., Fan, M., Zhang, W., Zhai, X., Wang, Q., Zhang, Y., 2020. Coal and biomass burning as major emissions of NOx in Northeast China: implication from dual isotopes analysis of fine nitrate aerosols. Atmos Environ 242, 117762. https://doi.org/10.1016/j.atmosenv.2020.117762.

Zhao, Z.Y., Zhang, Y.L., Lin, Y.C., Song, W.H., Yu, H.R., Fan, M.Y., Hong, Y.H., Yang, X.Y., Li, H.Y., Cao, F., 2024. Continental emissions influence the sources and formation mechanisms of marine nitrate aerosols in spring over the Bohai Sea and Yellow Sea inferred from stable isotopes. Journal of Geophysical Research: Atmospheres 129, e2023JD040541. https://doi.org/10.1029/2023JD040541.

Zhu, Y., Zhou, S., Li, H., Luo, L., Wang, F., Bao, Y., Chen, Y., 2021. Formation pathways and sources of size-segregated nitrate aerosols in a megacity identified by dual isotopes. Atmos Environ 264, 118708. https://doi.org/10.1016/j.atmosenv.2021.118708.

Zong, Z., Tan, Y., Wang, X., Tian, C., Fang, Y., Chen, Y., Fang, Y., Han, G., Li, J., Zhang, G., 2018. Assessment and quantification of NOx sources at a regional background site in North China: comparative results from a Bayesian isotopic mixing model and a positive matrix factorization model. Environ Pollut 242, 1379-1386. https://doi.org/10.1016/j.envpol.2018.08.026.

Zong, Z., Tan, Y., Wang, X., Tian, C., Li, J., Fang, Y., Chen, Y., Cui, S., Zhang, G., 2020. Dual-modelling-based source apportionment of NOx in five Chinese megacities: providing the isotopic footprint from 2013 to 2014. Environ Int 137, 105592. https://doi.org/10.1016/j.envint.2020.105592.

Zong, Z., Tian, C., Sun, Z., Tan, Y., Shi, Y., Liu, X., Li, J., Fang, Y., Chen, Y., Ma, Y., Gao, H., Zhang, G., Wang, T., 2022. Long‐term evolution of particulate nitrate pollution in North China: isotopic evidence from 10 offshore cruises in the Bohai Sea from 2014 to 2019. Journal of Geophysical Research: Atmospheres 127, e2022JD036567. https://doi.org/10.1029/2022JD036567.

Zong, Z., Wang, X., Tian, C., Chen, Y., Fang, Y., Zhang, F., Li, C., Sun, J., Li, J., Zhang, G., 2017. First assessment of NOx sources at a regional background site in North China using isotopic analysis linked with modeling. Environ Sci Technol 51 (11), 5923-5931. https://doi.org/10.1021/acs.est.6b06316

Technical points:

45 : Do you mean “adsorbed” here rather than “absorbed”? The use of “onto” makes it seem like you might be referring to adsorption rather than absorption.

Reply: Thank you for the suggestion. We have replaced “absorbed” with "adsorbed" in line 47.

65: This paragraph is excessively long and should be broken up by paragraph breaks to aid readability.

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

133: I think the use of a colon (:) here is more appropriate than “i.e.”

Reply: Thank you for your suggestion. We have revised the text by replacing "i.e." with a colon (:) to improve clarity, as recommended. This change has been made in line 176.

182: Perhaps refer to it as the “bacterial denitrifier method” just to be explicitly clear.

Reply: You are correct. This method employs the Pseudomonas aureofaciens (ATCC13985) strain to completely reduce NO_3^- to N_2O gas for isotope analysis. We have revised the text accordingly, and the change can be found in lines 206–209.

Revised sentence: The $\delta^{18}O$ and $\delta^{15}N$ values of NO_3^- in the TSP samples were determined via the bacterial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001) with the Gasbench-IRMS system (Delta V model, Thermo Scientific).

Figure 3: The star symbol is used four times in total, but I’m guess you are only referring to the two times it is used for the R value? Perhaps just state in the caption that the R value is significant at a $p < 0.05$ level.

Reply: Thank you for your suggestion. We have revised the figure caption to clarify the use of the star symbol. The figure now states that the * indicates R values significant at the $p < 0.05$ level. This change can be found in the caption of Figure 3 in the revised manuscript.

Figure 4: Maybe consider putting a larger label on the vertical left side for $PM_{2.5}$, NO_3^-, NH_4^+, and SO_4^{2-} to make it more clear what each row of data is representing.

Reply: Thank you for your suggestion. We have updated Figure 4 by adding larger labels on the left side to clearly indicate $PM_{2.5}$, NO_3^-, NH_4^+, and SO_4^{2-} for each row of data. This revision can be found in Figure 4 of the revised manuscript.

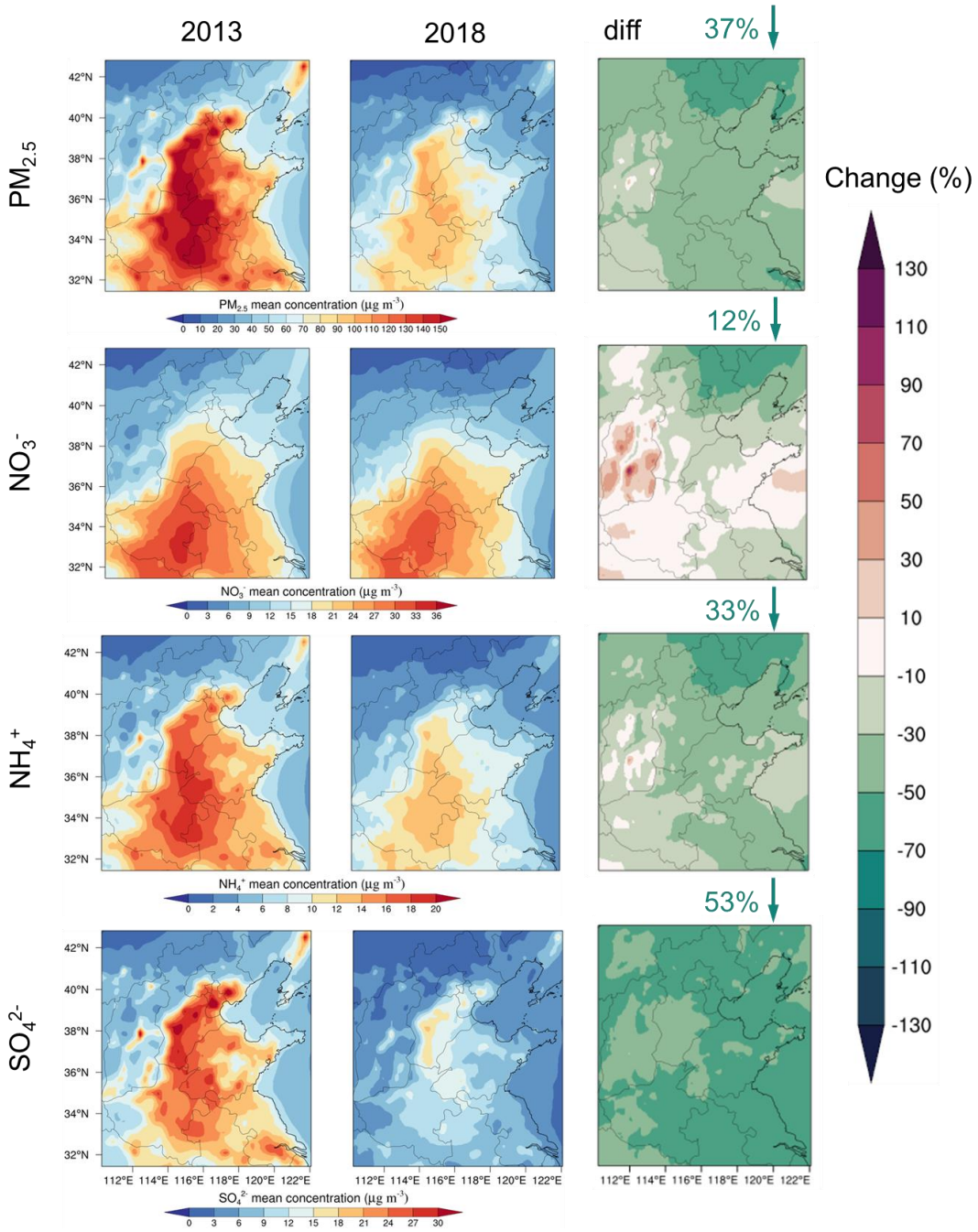

Figure 4 Spatial distribution and changes in $PM_{2.5}$ and its components in the NCP during the winters of 2013 and 2018. The up arrows indicate increases, and the down arrows indicate decreases.

Fig 5: Period missing at end of caption. This diverging color scheme is also a bit confusing as used here, because it is the same color scheme used in Fig 4 to show representative change (pos = red, neg = green), but here it is a unidirectional scale. I'd recommend a different color scheme to avoid confusion or unintentional misleading.

Reply: We are sorry for the confusion. We have revised Figure 5 by updating the color scheme to avoid confusion with Figure 4 and to better align it with its unidirectional scale. Additionally, we have added a period at the end of the title. This revision can be found in Figure 5 of the revised manuscript.

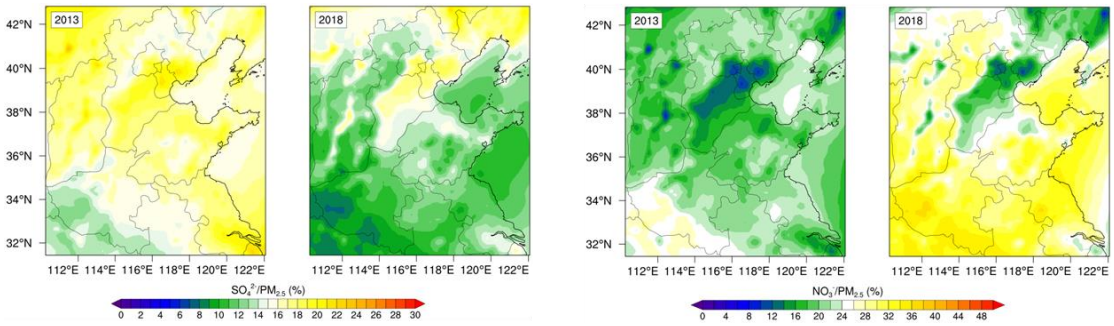

Figure 5 Spatial distributions of the nitrate and sulfate proportions in $PM_{2.5}$ in the NCP region during the winters of 2013 and 2018.

Figure 6: Humans are pretty bad at estimating angular areas. You might consider alternatives such as treemaps or waffle charts. Not required from me, but just put here for consideration. This is also a pretty simple figure, and since you have so many figures, you might consider merging it with another or whether it is necessary.

Reply: Thank you for your valuable suggestion. We believe that alternative visualizations, such as treemaps or waffle charts, can indeed improve the clarity and readability of the figure. After further review, we find that Figure 6 contributes relatively little to the overall manuscript; therefore, we have removed it.

Fig 9: The color choices could be changed to improve the visual story. For example, the OH +NO_2 on both sides would ideally both be blue, or shades of blue. And hetN_2O_5 both be orange or shades of orange. That would make it more clear that we should be directly relating them.

Reply: Thank you for your insightful suggestion. We have revised the figure according to suggestion. This revision can be found in Figure 9 of the revised manuscript.

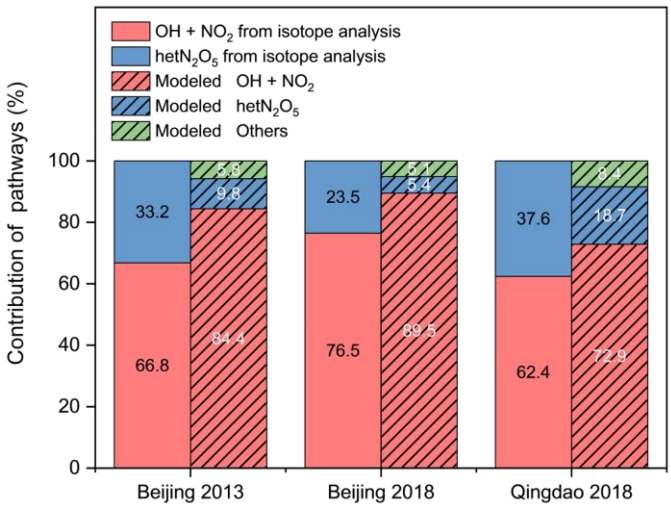

Figure 9 Comparison of the contributions of the atmospheric NO_3^- formation pathways based on the dual-isotope results and model simulations for Beijing in 2013 and 2018 and for Qingdao in 2018.

Fig 10: The legend for the dot looks like it is just connected to OH Pathway, and it should be labelled ast NO_3^- concentration or [NO_3^-] not just NO_3^-. Missing a period at end of caption. Subfigures should probably either be all in one column OR the 2018/19 Qingdao be under the 2018 Beijing chart.

Reply: Thank you for your valuable feedback. We have updated the legend to clearly label the dots as "NO_3^- concentration" and added a period at the end of the caption. Additionally, we have adjusted the layout by placing the 2018/19 Qingdao chart directly below the 2018 Beijing chart, ensuring a more logical and visually consistent arrangement. This revision can be found in Figure 8 of the revised manuscript.

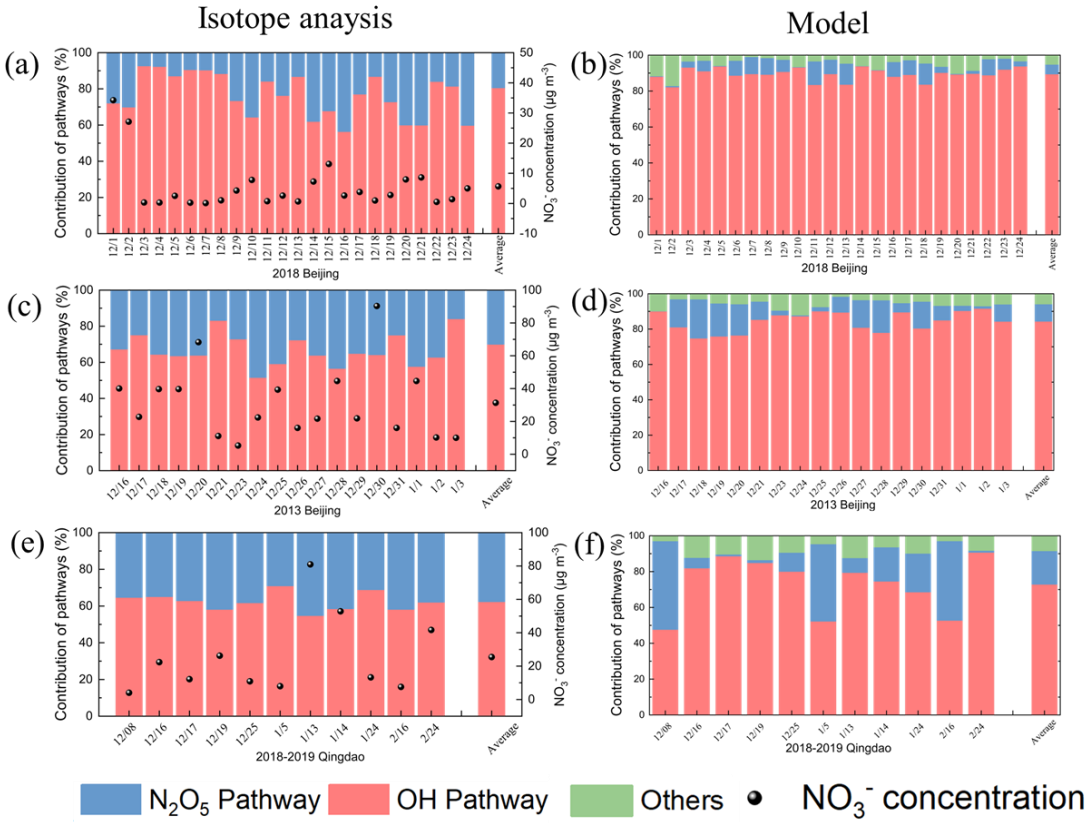

Figure 8 Time series of the contributions of the atmospheric NO_3^- formation pathways: (a, b) Beijing 2018, (c, d) Beijing 2013, and (e, f) Qingdao 2018, based on (a, c, e) dual-isotope analysis and (b, d, f) model simulations.

432: There is a comma splice in this sentence.

Reply: We have revised the sentence to correct this issue. In addition, we have checked the manuscript carefully to ensure proper sentence structure and improve readability in lines 518–520 of the revised version. We appreciate your careful review and valuable feedback.

Revised sentence: This hypothesis could be verified from an emission perspective. The total ammonia emissions in China increased from 9.64 to 9. 75 Tg from 2013–2015 and then gradually decreased to 9.12 Tg by 2018 (Liao et al., 2022).

Fig 13: The scaling seems poor or wrong in the difference map. The HONO concentrations only cover <2 ppb but the scaling on the difference is ±50.

Reply: We apologize for the confusion. The differential scale represents the percentage change in HONO concentration in 2018 relative to 2013. For clarity, we have adjusted the scale to ±100% to more accurately depict the range of HONO concentration variations. This revision has been implemented in Figure 11 of the revised manuscript.

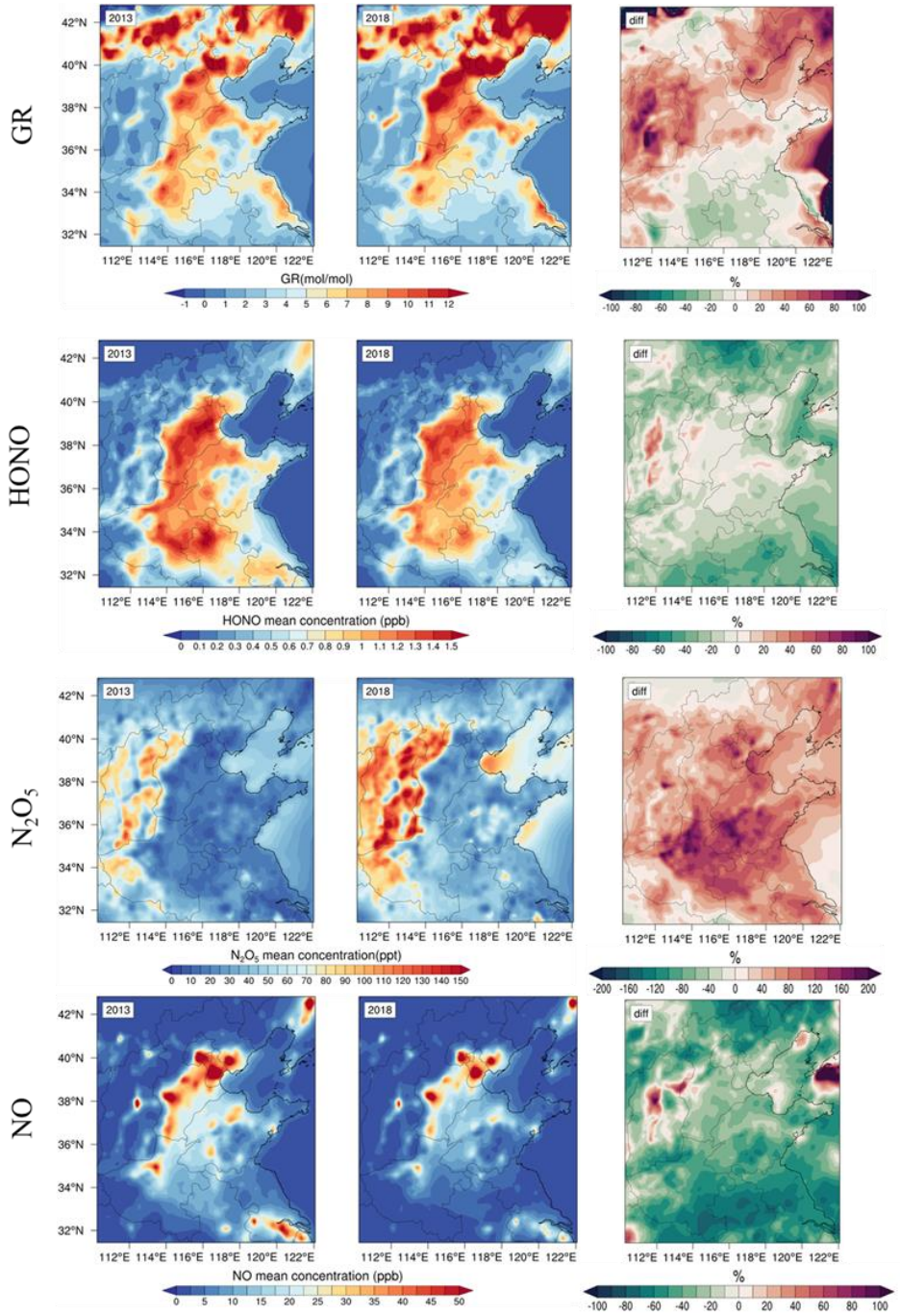

Figure 11 Spatial distributions and interannual variations in the GR, HONO, N_2O_5, and NO_x concentrations over the North China Plain during the winters of 2013 and 2018. The percentage changes (diff) represent the relative differences between 2018 and 2013.

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?

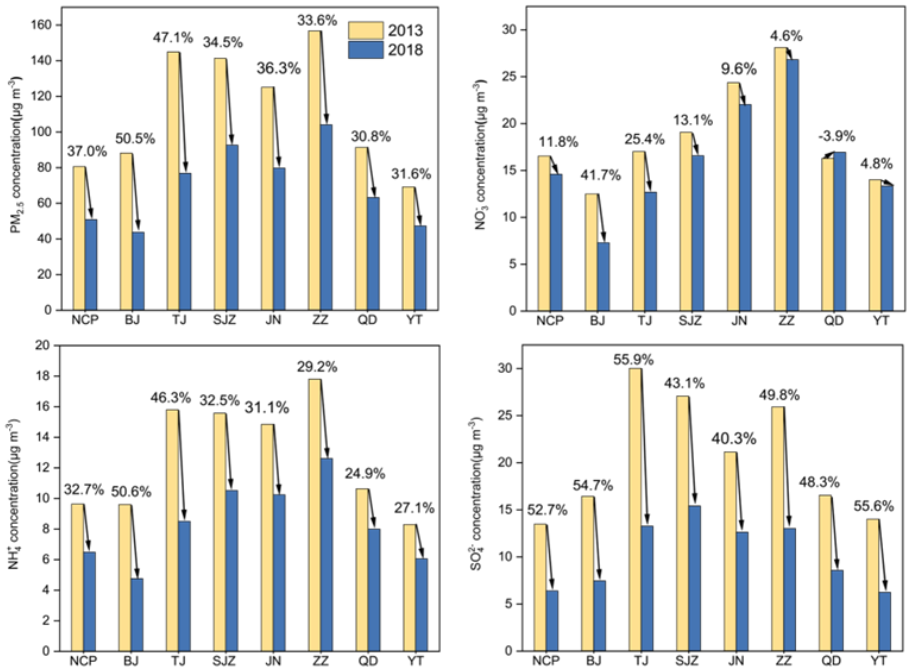

Figure R1 Concentrations of $PM_{2.5}$ and its components in seven major cities in the NCP region during the winters of 2013 and 2018

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 $\Delta^{17}O$ 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

($\Delta^{17}O$, $d^{18}O$) 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 $\delta^{18}O$ values for atmospheric oxidants such as ·OH and O_3 are shown in Table R1. We calculated the endmember $\delta^{18}O$ and $\delta^{15}N$ 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 $\delta^{18}O$-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, $\delta^{18}O$–NO_2 is significantly greater than that at night, because of the prominent $\delta^{18}O$–O_3 signal in the photochemical cycling of NO and NO_2 during the day; conversely, at night, more $\delta^{18}O$–NO_2 signals from emissions are present (Walters et al., 2016). However, numerous observational studies of $\delta^{18}O$–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 $\delta^{18}O$-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 $\delta^{18}O$-NO_2 and their impact on the generated $\delta^{18}O$–NO_3^-.

Table R1 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	

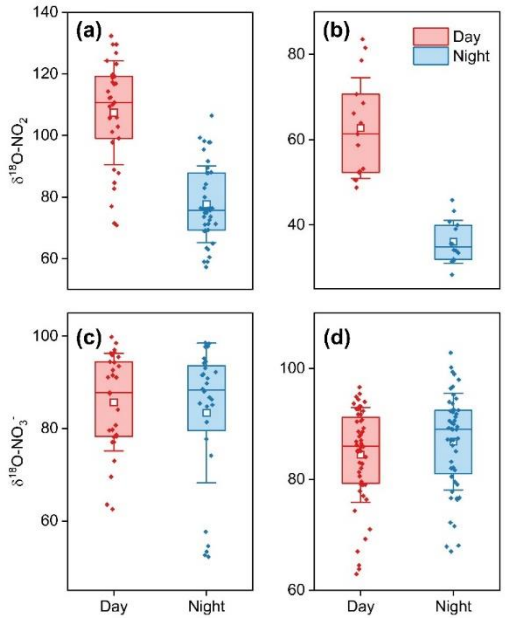

Figure R2 The diurnal values of atmospheric $\delta^{18}O\text{-}NO_2$ in Hefei winter (Zhang et al., 2025) (a) and in Nanchang summer (Cao, 2022) (b), and $\delta^{18}O\text{-}NO_3^-$ in Tianjin winter (Feng et al., 2020) (c) and in Nanjing winter (Zhang et al., 2022) (d).

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.

Luo, L., Liao, T., Zhang, X., Wu, Y., Li, J., Zhang, R., Zheng, Z., and Kao, S.: Quantifying the formation pathways of nitrate in size-segregated aerosols during winter haze pollution, Gondwana Res., https://doi.org/10.1016/j.gr.2022.11.015, 2022.

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NOx cycle and the tropospheric ozone isotope anomaly: an experimental investigation, Atmos. Chem. Phys., 14, 4935-4953, 10.5194/acp-14-4935-2014, 2014.

Michalski, G., Bhattacharya, S. K., DF Mase., 2011. Oxygen isotope dynamics of atmospheric nitrate and its precursor molecules. Springer Berlin Heidelberg.

Walters, W. W., and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope

fractionation factors involving various NO molecules, OH, and H_2O and its implications for isotope variations in atmospheric nitrate, Geochim. Cosmochim. Ac., 191, 89-101, 10.1016/j.gca.2016.06.039, 2016.
Walters, W. W., Simonini, D. S., and Michalski, G.: Nitrogen isotope exchange between NO and NO_2 and its implications for $\delta^{15}N$ variations in tropospheric NOx and atmospheric nitrate, Geophys. Res. Lett., 43, 440-448, 10.1002/2015GL066438, 2016.
Wang, Y., Cui, B., Li, D., Wang, Y., Yu, W., and Zong, H.: Stable Isotopes Reveal Water Vapor Sources of Precipitation over the Jiaolai Plain, Shandong Peninsula, China, Asia-Pac. J. Atmos. Sci., 58, 227-241, 10.1007/s13143-021-00253-2, 2022.
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 ·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 $\delta^{18}O$ 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	$NO_2 + H_2O \rightarrow HNO_3$	$\delta^{18}O\text{-}HNO_3 = \delta^{18}O\text{-}NO_2$

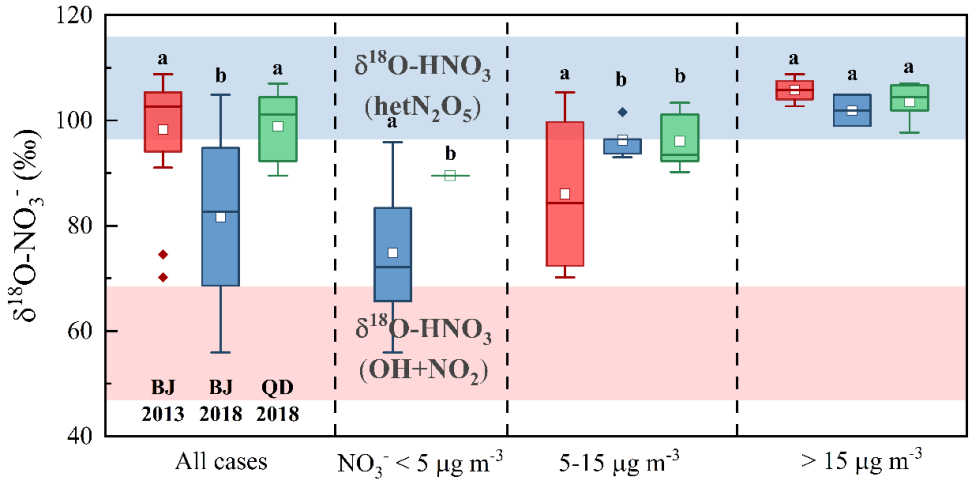

Figure R3. Boxplots of $\delta^{18}O$ of atmospheric NO_3^- collected in Beijing in the winters of 2013 and 2018 and in Qingdao in the winter of 2018 under different nitrate conditions. The shadows of red and blue indicate the ranges of $\delta^{18}O$–NO_3^- generated via the daytime and nocturnal pathways,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

Xiao H W, Chen T S, Zhang Q J, et al. Changes in the Dominant Contributions of Nitrate Formation and Sources During Haze Episodes: Insights From Dual Isotopic Evidence[J]. Journal of Geophysical Research: Atmospheres, 2025, 130(2): e2024JD042175.

Li T, Li J, Sun Z, et al. High contribution of anthropogenic combustion sources to atmospheric inorganic reactive nitrogen in South China evidenced by isotopes[J]. Atmospheric Chemistry and Physics, 2023, 23(11): 6395-6407.

Luo L, Pan Y, Zhu R, et al. Assessment of the seasonal cycle of nitrate in PM2.5 using chemical compositions and stable nitrogen and oxygen isotopes at Nanchang, China[J]. Atmospheric Environment, 2020, 225: 117371.

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]

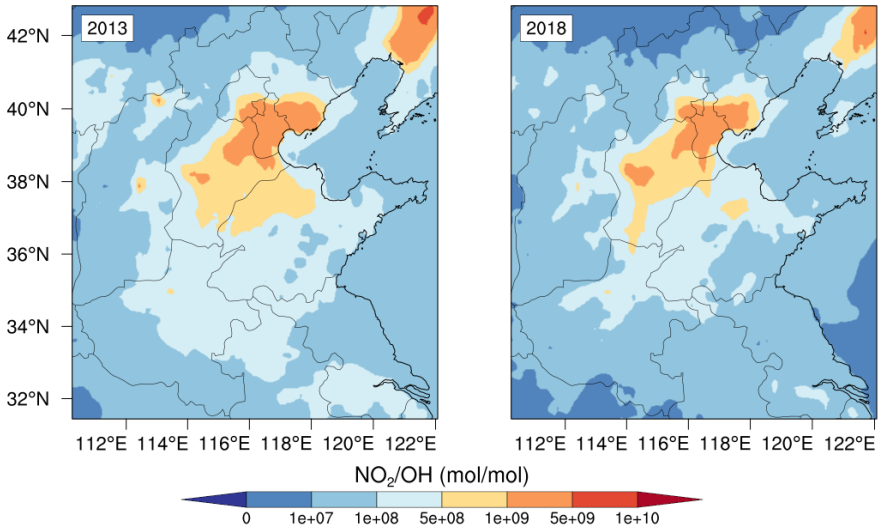

Figure 4 Spatial distributions of the NO_2/OH molar ratio in the NCP region during the winters of 2013 and 2018

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).