

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, N₂O₅, 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 NO_x mixing ratios, and longer NO₃ radical lifetimes, which significantly promote reactions via the hetN₂O₅ pathway. In contrast, continental air masses usually exhibit higher NO_x mixing ratios and NH₃ concentrations, which are more favorable for nitrate formation through the OH + NO₂ 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.

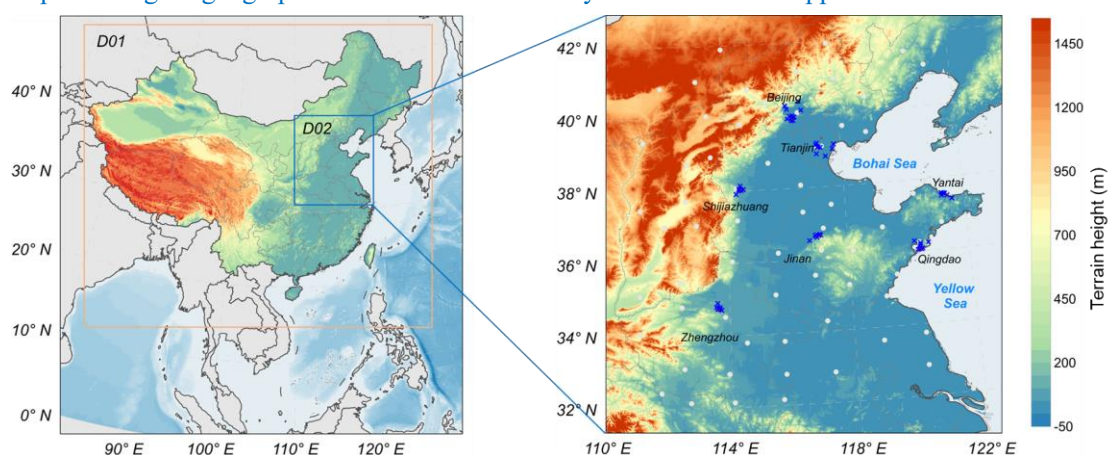
Fig. 2: Data source for terrain heights should be cited

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 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ 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 ·OH+NO₂ and hetN₂O₅ pathways because the δ¹⁸O end-member values for multiple reaction pathways were quite similar. Hence, those 5–8% of “other” pathways were attributed to the ·OH+NO₂ and hetN₂O₅ 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 δ¹⁸O for the commonly considered atmospheric NO₃⁻ 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 δ¹⁸O being too close to those of hetN₂O₅, such as in the calculations for the winter of 2018 in Qingdao, the end-member δ¹⁸O value for the hetN₂O₅ 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 ·OH+NO₂ and hetN₂O₅ the two main formation pathways when calculating atmospheric NO₃⁻ 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 NO₃⁻. 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.

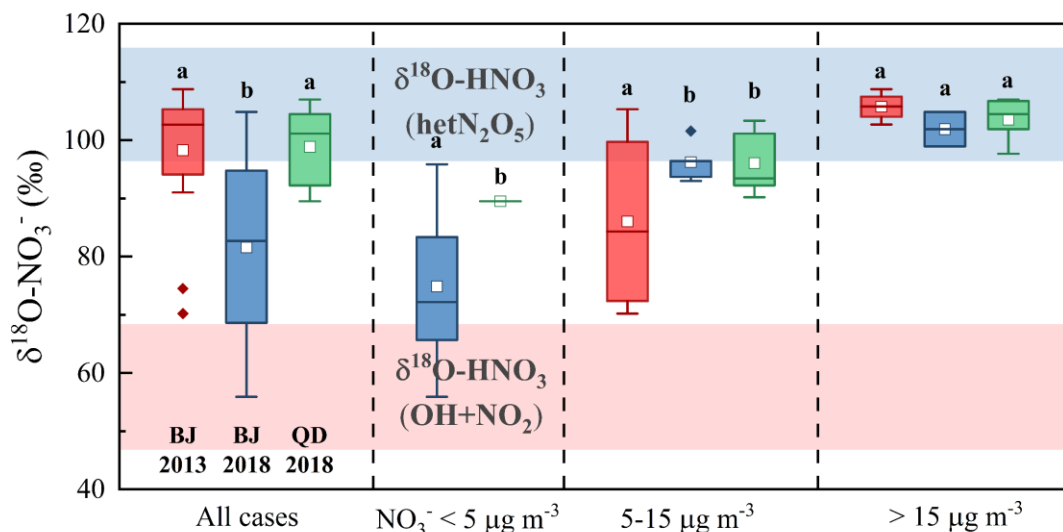


Figure R1. Boxplot of $\delta^{18}\text{O}$ of atmospheric NO_3^- collected in Beijing in the winters of 2013 and 2018 and in Qingdao in the winter of 2018 under different nitrate conditions. The shadows of red and blue indicate the ranges of $\delta^{18}\text{O}-\text{NO}_3^-$ generated via the daytime and nocturnal pathways, respectively. Categories that share common letters do not differ in significance, which is set to 0.05.

Table R1. Calculated $\delta^{18}\text{O}$ values of NO_y for each nitrate production pathway (Luo et al., 2020).

	Pathway	Expression
R1	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$\delta^{18}\text{O}-\text{NO}_2 = \phi \delta^{18}\text{O}-\text{O}_3 + (1-\phi) \delta^{18}\text{O}-\text{R}/\text{HO}_2$
R2	$\text{NO} + \text{RO}_2/\text{HO}_2 \rightarrow \text{NO}_2 + \text{O}_2$	
R3	$\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3$	$\delta^{18}\text{O}-\text{NO}_3 = 2/3 \delta^{18}\text{O}-\text{NO}_2 + 1/3 \delta^{18}\text{O}-\text{O}_3$
R4	$\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$	$\delta^{18}\text{O}-\text{N}_2\text{O}_5 = 2/5 \delta^{18}\text{O}-\text{NO}_2 + 3/5 \delta^{18}\text{O}-\text{NO}_3$
R5	$\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$	$\delta^{18}\text{O}-\text{HNO}_3 = 2/3 \delta^{18}\text{O}-\text{NO}_2 + 1/3 \delta^{18}\text{O}-\text{OH}$
R6	$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$	$\delta^{18}\text{O}-\text{HNO}_3 = 5/6 \delta^{18}\text{O}-\text{N}_2\text{O}_5 + 1/6 \delta^{18}\text{O}-\text{H}_2\text{O}$
R7	$\text{NO}_3 + \text{HC}/\text{DMS} \rightarrow \text{HNO}_3$	$\delta^{18}\text{O}-\text{HNO}_3 = \delta^{18}\text{O}-\text{NO}_3$
R8	$\text{N}_2\text{O}_5 + \text{Cl}^- \rightarrow \text{pNO}_3^-$	$\delta^{18}\text{O}-\text{HNO}_3 = \delta^{18}\text{O}-\text{N}_2\text{O}_5$
R9	$\text{ClNO}_3 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$	$\delta^{18}\text{O}-\text{HNO}_3 = 2/3 \delta^{18}\text{O}-\text{NO}_2 + 1/3 \delta^{18}\text{O}-\text{O}_3$
R10	$\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3$	$\delta^{18}\text{O}-\text{HNO}_3 = \delta^{18}\text{O}-\text{NO}_2$

Table R2. Comparison of the contributions of major atmospheric NO₃⁻ formation pathways in China

Region	City	Lon (°E)	Lat (°N)	Method	Year	Season	·OH+NO ₂	hetN ₂ O ₅ (%)	NO ₃ ·+HC	Reference
NCP	Zibo	118.0547	36.8258	Δ 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	Δ 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	δ ¹⁵ N and δ ¹⁸ O	2017-2018	Winter	17.4	61.9	20.7	Luo et al., 2023
	Tianjin	117.4177	39.5557	Δ 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	δ ¹⁵ N and δ ¹⁸ O	2017-2018	Winter	6.3	66.0	27.7	Luo et al., 2023
	Tianjin	117.3350	38.9944	δ 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	δ ¹⁸ O	2020	Winter	30.0	70.0	Li et al., 2022a	
Summer						61.0	39.0			
Beijing	116.3711	39.9744	Δ 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	δ 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	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	45.3	46.5	8.2	Zhang et al., 2021b
						Autumn	51.8	48.2		
	Shijiazhuang	114.6377	38.0128	$\delta^{18}\text{O}$	2017-2018	Winter	22.5	77.5		Luo et al., 2021
						Spring	51.5	48.5		
						Summer	71.1	28.9		
						Spring	18.8	81.2		
	Beijing	116.3400	39.9300	$\delta^{18}\text{O}$	2013-2014	Summer	41.2	58.8		Zong et al., 2020
						Autumn	17.9	82.1		
						Winter	17.3	82.7		
	Beijing	116.3667	39.9667	$\delta^{18}\text{O}$	2018	Winter	52.0	48.0		Fan et al., 2020
	Beijing	116.4167	40.0333	$\delta^{18}\text{O}$	2017-2018	Winter	48.0	52.0		Zhang et al., 2020a
	Beijing	116.3800	39.9800	$\delta^{18}\text{O}$	2013	Spring	56.5	27.2	16.3	Luo et al., 2020a
	Jinan	117.0500	36.6667	$\delta^{18}\text{O}$	2018	Summer	39.1	60.9		Zhang et al., 2020b
	Beijing	116.7000	40.0667	$\Delta^{17}\text{O}$	2015	Winter	29.5	35.1	35.6	Song et al., 2020
	Beijing	116.4167	40.0333	$\delta^{18}\text{O}$	2017-2018	Winter	47.0	53.0		Zhang et al., 2020c
						Spring	27.0	35.0	38.0	
	Beijing	116.7000	40.0667	$\Delta^{17}\text{O}$	2014	Summer	40.9	36.1	32.9	Wang et al., 2019
						Autumn	25.0	35.0	40.0	
						Winter	31.0	34.0	34.0	
	Beijing	116.6800	40.4100	$\Delta^{17}\text{O}$	2014-2015	Winter	23.5	76.5		He et al., 2018
	Dongying	118.9833	37.7500	$\delta^{18}\text{O}$	2013	Summer	47.4	52.6		Zong et al., 2018
						Spring	35.0	65.0		
Central	Wuhan	114.3000	30.5300	$\delta^{18}\text{O}$	2018-2019	Summer	69.7	30.3		Deng et al., 2024
						Autumn	34.5	65.5		

					Winter	7.8	92.2			
					Spring	64.0	19.0	17.0		
	Shiyan	111.4000	33.2000	$\delta^{18}\text{O}$	2021	Summer	84.0	8.0	8.0	Xiao et al., 2024
						Autumn	64.0	19.0	18.0	
						Winter	25.0	38.0	37.0	
	Wuhan	104.3600	30.5200	$\delta^{18}\text{O}$	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	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	22.2	57.6	20.4	Luo et al., 2023
	Shanghai	121.4279	31.2595	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	18.3	47.9	33.8	Luo et al., 2023
	Shanghai	121.5000	31.3000	$\delta^{18}\text{O}$	2019	Summer	70.5	29.5		Huang et al., 2024
						Winter	20.7	79.3		
	Shanghai	121.5100	31.3400	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	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	$\Delta^{17}\text{O}$	2016	Winter	63.8		36.2	He et al., 2020
						Spring	62.7		37.3	
YRD	Shanghai	121.5000	31.2900	$\delta^{18}\text{O}$	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	$\Delta^{17}\text{O}$	2018	Winter	20.9	27.4	34.0	Yu et al., 2023
						Autumn	18.9	34.0	47.1	
	Hangzhou	120.1700	30.2300	$\Delta^{17}\text{O}$	2015-2016	Winter	24.1	34.8	41.1	Fan et al., 2023
						Spring	18.3	35.0	46.7	
						Summer	40.5	35.2	24.3	

Southeast	Xiamen	118.0900	24.4360	$\delta^{18}\text{O}$	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	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	17.2	43.6	39.2	Luo et al., 2023
	Nanchang	115.9333	28.6833	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	30.4	36.8	32.8	Zhang et al., 2021c
	Nanchang	115.8085	28.6832	$\delta^{18}\text{O}$	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	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017	Autumn	37.1	60.3	2.6	Xiao et al., 2020
	Ganzhou	114.7600	25.6600	$\delta^{18}\text{O}$	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	$\delta^{15}\text{N}$ and $\delta^{18}\text{O}$	2017-2018	Winter	23.5	40.8	35.7	Luo et al., 2023
	Chengdu	104.3800	30.6400	$\delta^{18}\text{O}$	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	$\delta^{18}\text{O}$	2017-2018	Autumn	85.0	15.0	Guo et al., 2021	
						Winter	74.4	25.6		
	Nanning	108.2833	22.8333	$\delta^{18}\text{O}$	2013-2014	Autumn	87.9	12.1	Li et al., 2021a	
						Winter	68.4	31.6		
	Guiyang	106.7167	26.5667	$\delta^{18}\text{O}$	2016	Winter	38.3	61.7	19.8	Luo et al., 2023
					Summer	80.2	19.8	24.7		
PRD	Guangzhou	113.3689	23.1938	$\delta^{18}\text{O}$	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	$\Delta^{17}\text{O}$	2018	Autumn	61.0	12.0	27.0	Wang et al., 2023
						Spring	48.0	52.0		
	Guangzhou	113.3600	23.1500	$\delta^{18}\text{O}$	2013-2014	Summer	66.9	33.1		Zong et al., 2020
						Autumn	33.9	66.1		
						Winter	9.7	90.3		
	Harbin	126.6333	45.7469	$\Delta^{17}\text{O}$	2022-2023	Winter	55.3	28.2	16.5	Feng et al., 2023
						Spring	65.8	25.6	8.6	
	Shenyang	123.4300	41.7700			Summer	95.3	3.0	1.7	
						Autumn	83.0	12.1	4.8	
				$\Delta^{17}\text{O}$	2015-2018	Winter	57.7	30.9	11.4	Li et al., 2022c
						Spring	40.0	34.5	25.5	
	Fushun	124.9400	41.8500			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				69.4	30.6		
	Changchun	125.4000	43.8500							
				$\delta^{18}\text{O}$	2017-2018	Winter	50.2	49.8		Zhao et al., 2021
	Harbin	126.5300	45.8400				50.1	49.9		
	Yushu	126.5300	44.8600				37.3	62.7		
						Spring	46.4	53.6		
	Harbin	120.6817	45.7539	$\delta^{18}\text{O}$	2017-2018	Summer	68.7	31.2		Sun et al., 2020
						Autumn	56.1	43.9		
						Winter	44.8	55.2		
						Summer	79.7	20.3		
	Changchun	125.4000	44.0000	$\delta^{18}\text{O}$	2017-2018	Autumn	56.1	43.9		Zhao et al., 2020
						Winter	55.9	44.1		

						Spring	58.0	42.0			
						Autumn	35.0	65.0			
Island	Beihuangcheng Island	120.9167	36.4000	$\delta^{18}\text{O}$	2015	Winter	24.0	76.0	Zong et al., 2017		
						Spring	47.0	53.0			
						Summer	68.0	32.0			
	Dongsha Island	116.7167	20.7000	$\delta^{18}\text{O}$	2013	Spring	66.8	10.2	23.0	Yang et al., 2023	
	Pengjiayu Island	122.1333	26.0500					62.1			23.4
	Bohai Sea and Yellow Sea		32 - 34	$\Delta^{17}\text{O}$	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			
Marine	Bohai Sea	38 - 40	$\delta^{18}\text{O}$			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	77.8	14.3	Liu et al., under review	
							2018	85.6	9.9		
	Tianjin	117.4812	39.0929				2013	Winter	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
						Winter	69.3	28.4	
	Shanghai	120.8662	28.0818			Spring	81.8	15.3	
						Summer	82.9	12.2	
						Autumn	86.9	11.1	
						Winter	59.2	36.1	
	Nanjing	118.6491	28.7744			Spring	73.1	5.4	
						Summer	74.7	17.9	
YRD				CMAQ	2017	Autumn	69.7	25.4	Sun et al., 2022
						Winter	66.9	27.1	
	Hefei	117.3881	28.5389			Spring	78.5	16.5	
						Summer	81.7	10.4	
						Autumn	72.5	21.8	
						Winter	68.9	26.8	
	Changzhou	119.6087	28.4776			Spring	74.9	20.9	
						Summer	78.7	14.3	

						Autumn	77.6	18.3	
						Winter	59.7	35.5	
						Spring	70.5	23.3	
						Summer	76.4	10.7	
						Autumn	73.8	21.3	
	Hangzhou	119.7671	27.1448						
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			Summer	60.4	39.6	
				WRF-Chem	2016	Winter	91.9	8.1	Li et al., 2021b
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

Chan, Y.C., Evans, M.J., He, P., Holmes, C.D., Jaeglé, L., Kasibhatla, P., Liu, X.Y., Sherwen, T., Thornton, J.A., Wang, X., Xie, Z., Zhai, S., Alexander, B., 2021. Heterogeneous nitrate production mechanisms in intense haze events in the North China Plain. *Journal of geophysical research. Atmospheres* 126, e2021JD034688. <https://doi.org/10.1029/2021JD034688>.

Cheng, C., Yu, R., Chen, Y., Yan, Y., Hu, G., Wang, S., 2022. Quantifying the source and formation of nitrate in PM_{2.5} using dual isotopes combined with Bayesian

- mixing model: A case study in an inland city of southeast China. *Chemosphere* 308, 136097. <https://doi.org/10.1016/j.chemosphere.2022.136097>.
- Chuang, M., Wu, C., Lin, C., Lin, W., Chou, C.C.K., Lee, C., Lin, T., Fu, J.S., Kong, S.S., 2022. Simulating nitrate formation mechanisms during PM_{2.5} events in Taiwan and their implications for the controlling direction. *Atmos Environ* 269, 118856. <https://doi.org/10.1016/j.atmosenv.2021.118856>.
- Deng, M., Wang, C., Yang, C., Li, X., Cheng, H., 2024. Nitrogen and oxygen isotope characteristics, formation mechanism, and source apportionment of nitrate aerosols in Wuhan, central China. *Sci Total Environ* 921, 170715. <https://doi.org/10.1016/j.scitotenv.2024.170715>.
- Fan, M., Zhang, Y., Lin, Y., Hong, Y., Zhao, Z., Xie, F., Du, W., Cao, F., Sun, Y., Fu, P., 2022. Important role of NO₃ radical to nitrate formation aloft in urban Beijing: Insights from triple oxygen isotopes measured at the tower. *Environ Sci Technol* 56 (11), 6870-6879. <https://doi.org/10.1021/acs.est.1c02843>.
- Fan, M.Y., Zhang, W., Zhang, Y.L., Li, J., Fang, H., Cao, F., Yan, M., Hong, Y., Guo, H., Michalski, G., 2023. Formation mechanisms and source apportionments of nitrate aerosols in a megacity of eastern China based on multiple isotope observations. *Journal of Geophysical Research: Atmospheres* 128, e2022JD038129. <https://doi.org/10.1029/2022JD038129>.
- Fan, M.Y., Zhang, Y.L., Lin, Y.C., Cao, F., Zhao, Z.Y., Sun, Y., Qiu, Y., Fu, P., Wang, Y., 2020. Changes of emission sources to nitrate aerosols in Beijing after the clean air actions: Evidence from dual isotope compositions. *Journal of Geophysical Research: Atmospheres* 125, e2019JD031998. <https://doi.org/10.1029/2019JD031998>.
- Feng, X., Chen, Y., Chen, S., Peng, Y., Liu, Z., Jiang, M., Feng, Y., Wang, L., Li, L., Chen, J., 2023. Dominant contribution of NO₃ radical to NO₃⁻ formation during heavy haze episodes: Insights from high-time resolution of dual isotopes δ¹⁷O and δ¹⁸O. *Environ Sci Technol* 57 (49), 20726-20735. <https://doi.org/10.1021/acs.est.3c07590>.
- Fu, X., Wang, T., Gao, J., Wang, P., Liu, Y., Wang, S., Zhao, B., Xue, L., 2020. Persistent heavy winter nitrate pollution driven by increased photochemical oxidants in northern China. *Environ Sci Technol* 54 (7), 3881-3889. <https://doi.org/10.1021/acs.est.9b07248>.
- Guo, W., Luo, L., Zhang, Z., Zheng, N., Xiao, H., Xiao, H., 2021. The use of stable oxygen and nitrogen isotopic signatures to reveal variations in the nitrate formation pathways and sources in different seasons and regions in China. *Environ Res* 201, 111537. <https://doi.org/10.1016/j.envres.2021.111537>.
- He, P., Xie, Z., Chi, X., Yu, X., Fan, S., Kang, H., Liu, C., Zhan, H., 2018. Atmospheric Δ¹⁷O(NO₃⁻) reveals nocturnal chemistry dominates nitrate production in Beijing haze. *Atmos Chem Phys* 18 (19), 14465-14476. <https://doi.org/10.5194/acp-18-14465-2018>.
- He, P., Xie, Z., Yu, X., Wang, L., Kang, H., Yue, F., 2020. The observation of isotopic compositions of atmospheric nitrate in Shanghai China and its implication for reactive nitrogen chemistry. *Sci Total Environ* 714, 136727. <https://doi.org/10.1016/j.scitotenv.2020.136727>.
- Huang, W., Ye, X., Lv, Z., Yao, Y., Chen, Y., Zhou, Y., Chen, J., 2024. Dual isotopic evidence of δ¹⁵N and δ¹⁸O for priority control of vehicle emissions in a megacity of east China: Insight from measurements in summer and winter. *Sci Total Environ* 931, 172918. <https://doi.org/10.1016/j.scitotenv.2024.172918>.

- Li, M., Zhang, Z., Yao, Q., Wang, T., Xie, M., Li, S., Zhuang, B., Han, Y., 2021b. Nonlinear responses of particulate nitrate to NO_x emission controls in the megalopolises of China. *Atmos Chem Phys* 21 (19), 15135-15152. <https://doi.org/10.5194/acp-21-15135-2021>.
- Li, Q., Li, X., Yang, Z., Cui, G., Ding, S., 2021a. Diurnal and seasonal variations in water-soluble inorganic ions and nitrate dual isotopes of PM_{2.5}: Implications for source apportionment and formation processes of urban aerosol nitrate. *Atmos Res* 248, 105197. <https://doi.org/10.1016/j.atmosres.2020.105197>.
- Li, Q., Zhang, L., Wang, T., Tham, Y.J., Ahmadov, R., Xue, L., Zhang, Q., Zheng, J., 2016. Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China. *Atmos Chem Phys* 16, 14875-14890. <https://doi.org/10.5194/acp-16-14875-2016>.
- Li, X., Wu, S., Zhang, J., Schwab, J.J., 2022b. Insights into factors affecting size-segregated nitrate formation in a coastal city through measurements of dual isotopes. *Atmos Environ* 290, 119385. <https://doi.org/10.1016/j.atmosenv.2022.119385>.
- Li, Y., Geng, Y., Hu, X., Yin, X., 2022a. Seasonal differences in sources and formation processes of PM_{2.5} nitrate in an urban environment of North China. *J Environ Sci-China* 120, 94-104. <https://doi.org/10.1016/j.jes.2021.08.020>.
- Li, Z., Walters, W.W., Hastings, M.G., Song, L., Huang, S., Zhu, F., Liu, D., Shi, G., Li, Y., Fang, Y., 2022c. Atmospheric nitrate formation pathways in urban and rural atmosphere of Northeast China: implications for complicated anthropogenic effects. *Environ Pollut* 296, 118752. <https://doi.org/10.1016/j.envpol.2021.118752>.
- Liu, L., Bei, N., Hu, B., Wu, J., Liu, S., Li, X., Wang, R., Liu, Z., Shen, Z., Li, G., 2020. Wintertime nitrate formation pathways in the North China Plain: importance of N₂O₅ heterogeneous hydrolysis. *Environ Pollut* 266, 115287. <https://doi.org/10.1016/j.envpol.2020.115287>.
- Liu, L., Wu, J., Liu, S., Li, X., Zhou, J., Feng, T., Qian, Y., Gao, J., Tie, X., Li, G., 2019. Effects of organic coating on the nitrate formation by suppressing the N₂O₅ heterogeneous hydrolysis: a case study during wintertime in Beijing–Tianjin–Hebei (BTH). *Atmos Chem Phys* 19, 8189-8207. <https://doi.org/10.5194/acp-19-8189-2019>.
- Liu, Z., Liu, X., Ni, Y., Qi, J. Exploring Atmospheric Nitrate Formation Mechanisms during the Winters of 2013 and 2018 in the North China Region using Modeling and Isotopic Analysis. *Atmos Chem Phys*, under review.
- Luo, L., Kao, S., Wu, Y., Zhang, X., Lin, H., Zhang, R., Xiao, H., 2020. Stable oxygen isotope constraints on nitrate formation in Beijing in springtime. *Environ Pollut* 263, 114515. <https://doi.org/10.1016/j.envpol.2020.114515>.
- Luo, L., Liao, T., Zhang, X., Wu, Y., Li, J., Zhang, R., Zheng, Z., Kao, S., 2023. Quantifying the formation pathways of nitrate in size-segregated aerosols during winter haze pollution. *Gondwana Res* 115, 71-80. <https://doi.org/10.1016/j.gr.2022.11.015>.
- Luo, L., Pan, Y., Zhu, R., Zhang, Z., Zheng, N., Liu, Y., Liu, C., Xiao, H., Xiao, H., 2020b. Assessment of the seasonal cycle of nitrate in PM_{2.5} using chemical compositions and stable nitrogen and oxygen isotopes at Nanchang, China. *Atmos Environ* 225, 117371. <https://doi.org/10.1016/j.atmosenv.2020.117371>.

- Luo, L., Zhu, R., Song, C., Peng, J., Guo, W., Liu, Y., Zheng, N., Xiao, H., Xiao, H., 2021. Changes in nitrate accumulation mechanisms as PM_{2.5} levels increase on the North China Plain: a perspective from the dual isotopic compositions of nitrate. *Chemosphere* 263, 127915. <https://doi.org/10.1016/j.chemosphere.2020.127915>.
- Moore, J.W., Semmens, B.X., 2008. Incorporating uncertainty and prior information into stable isotope mixing models. *Ecol Lett* 11 (5), 470-480. <https://doi.org/10.1111/j.1461-0248.2008.01163.x>.
- Qiu, X., Ying, Q., Wang, S., Duan, L., Zhao, J., Xing, J., Ding, D., Sun, Y., Liu, B., Shi, A., Yan, X., Xu, Q., Hao, J., 2019. Modeling the impact of heterogeneous reactions of chlorine on summertime nitrate formation in Beijing, China. *Atmos Chem Phys* 19 (10), 6737-6747. <https://doi.org/10.5194/acp-19-6737-2019>.
- Qu, K., Wang, X., Xiao, T., Shen, J., Lin, T., Chen, D., He, L., Huang, X., Zeng, L., Lu, K., Ou, Y., Zhang, Y., 2021. Cross-regional transport of PM_{2.5} nitrate in the Pearl River Delta, China: Contributions and mechanisms. *Sci Total Environ* 753, 142439. <https://doi.org/10.1016/j.scitotenv.2020.142439>.
- Song, W., Liu, X., Wang, Y., Tong, Y., Bai, Z., Liu, C., 2020. Nitrogen isotope differences between atmospheric nitrate and corresponding nitrogen oxides: a new constraint using oxygen isotopes. *Sci Total Environ* 701, 134515. <https://doi.org/10.1016/j.scitotenv.2019.134515>.
- 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., Hu, J., 2022. Seasonal modeling analysis of nitrate formation pathways in Yangtze River Delta region, China. *Atmos Chem Phys* 22 (18), 12629-12646. <https://doi.org/10.5194/acp-22-12629-2022>.
- Sun, X., Zong, Z., Wang, K., Li, B., Fu, D., Shi, X., Tang, B., Lu, L., Thapa, S., Qi, H., Tian, C., 2020. The importance of coal combustion and heterogeneous reaction for atmospheric nitrate pollution in a cold metropolis in China: insights from isotope fractionation and Bayesian mixing model. *Atmos Environ* 243, 117730. <https://doi.org/10.1016/j.atmosenv.2020.117730>.
- Wang, Y., Liu, J., Jiang, F., Chen, Z., Wu, L., Zhou, S., Pei, C., Kuang, Y., Cao, F., Zhang, Y., Fan, M., Zheng, J., Li, J., Zhang, G., 2023. Vertical measurements of stable nitrogen and oxygen isotope composition of fine particulate nitrate aerosol in Guangzhou city: source apportionment and oxidation pathway. *Sci Total Environ* 865, 161239. <https://doi.org/10.1016/j.scitotenv.2022.161239>.
- Wang, Y.L., Song, W., Yang, W., Sun, X.C., Tong, Y.D., Wang, X.M., Liu, C.Q., Bai, Z.P., Liu, X.Y., 2019. Influences of atmospheric pollution on the contributions of major oxidation pathways to PM_{2.5} nitrate formation in Beijing. *Journal of Geophysical Research: Atmospheres* 124, 4174-4185. <https://doi.org/10.1029/2019JD030284>.
- Wu, C., Liu, L., Wang, G., Zhang, S., Li, G., Lv, S., Li, J., Wang, F., Meng, J., Zeng, Y., 2021. Important contribution of N₂O₅ hydrolysis to the daytime nitrate in Xi'an, China during haze periods: Isotopic analysis and WRF-Chem model simulation. *Environ Pollut* 288, 117712. <https://doi.org/10.1016/j.envpol.2021.117712>.
- Xi, D., Xiao, Y., Mgelwa, A.S., Kuang, Y., 2023. Formation pathways and source apportionments of inorganic nitrogen-containing aerosols in urban environment: insights from nitrogen and oxygen isotopic compositions in Guangzhou, China. *Atmos Environ* 309, 119888. <https://doi.org/10.1016/j.atmosenv.2023.119888>.

- Xiao, C., Sun, Y., Zhao, T., Wang, G., Li, P., Zhao, Y., Chen, F., 2024. Assessment major NO_x sources to nitrate of tsp around the Danjiangkou reservoir using isotopes and a Bayesian isotope mixing model. *Atmos Pollut Res* 15 (7). <https://doi.org/10.1016/j.apr.2024.102151>.
- Xiao, H.W., Zhu, R.G., Pan, Y.Y., Guo, W., Zheng, N.J., Liu, Y.H., Liu, C., Zhang, Z.Y., Wu, J.F., Kang, C.A., Luo, L., Xiao, H.Y., 2020. Differentiation between nitrate aerosol formation pathways in a southeast Chinese city by dual isotope and modeling studies. *Journal of Geophysical Research: Atmospheres* 125, e2020JD032604. <https://doi.org/10.1029/2020JD032604>.
- Yan, X., Hu, B., Li, Y., Shi, G., 2023. Investigating atmospheric nitrate sources and formation pathways between heating and non-heating seasons in urban North China. *Environ Res Lett* 18 (3), 34006. <https://doi.org/10.1088/1748-9326/acb805>.
- Yang, J., Qu, Y., Chen, Y., Zhang, J., Liu, X., Niu, H., An, J., 2024. Dominant physical and chemical processes impacting nitrate in Shandong of the North China Plain during winter haze events. *Sci Total Environ* 912, 169065. <https://doi.org/10.1016/j.scitotenv.2023.169065>.
- Yang, S., Luo, L., Li, Y., Wang, C., Lu, B., Hsu, S., Kao, S., 2023. Dry deposition fluxes, formation mechanisms and sources of nitrate in total suspended particles in springtime on Dongsha Island, South China Sea. *Journal of Earth Environment* 14 (2), 193-206. <https://doi.org/10.7515/jee222049>.
- Yu, H., Zhang, Y., Cao, F., Zhao, Z., Fan, M., Yang, X., 2023. Fog event is possibly a source rather than a sink of atmospheric nitrate aerosols: Insights from isotopic measurements in Nanjing, China. *Appl Geochem* 155, 105721. <https://doi.org/10.1016/j.apgeochem.2023.105721>.
- Zang, H., Zhao, Y., Huo, J., Zhao, Q., Fu, Q., Duan, Y., Shao, J., Huang, C., An, J., Xue, L., Li, Z., Li, C., Xiao, H., 2022. High atmospheric oxidation capacity drives wintertime nitrate pollution in the eastern Yangtze River Delta of China. *Atmos Chem Phys* 22 (7), 4355-4374. <https://doi.org/10.5194/acp-22-4355-2022>.
- Zhang, W., Bi, X., Zhang, Y., Wu, J., Feng, Y., 2022. Diesel vehicle emission accounts for the dominate NO_x source to atmospheric particulate nitrate in a coastal city: Insights from nitrate dual isotopes of PM_{2.5}. *Atmos Res* 278, 106328. <https://doi.org/10.1016/j.atmosres.2022.106328>.
- Zhang, W., Wu, F., Luo, X., Song, L., Wang, X., Zhang, Y., Wu, J., Xiao, Z., Cao, F., Bi, X., Feng, Y., 2024. Quantification of NO_x sources contribution to ambient nitrate aerosol, uncertainty analysis and sensitivity analysis in a megacity. *Sci Total Environ* 926, 171583. <https://doi.org/10.1016/j.scitotenv.2024.171583>.
- Zhang, Z., Cao, L., Liang, Y., Guo, W., Guan, H., Zheng, N., 2021c. Importance of NO₃ radical in particulate nitrate formation in a southeast Chinese urban city: new constraints by $\delta^{15}\text{N}$ - $\delta^{18}\text{O}$ space of NO₃⁻. *Atmos Environ* 253, 118387. <https://doi.org/10.1016/j.atmosenv.2021.118387>.
- Zhang, Z., Guan, H., Luo, L., Zheng, N., Xiao, H., 2020c. Response of fine aerosol nitrate chemistry to clean air action in winter Beijing: insights from the oxygen isotope signatures. *Sci Total Environ* 746, 141210. <https://doi.org/10.1016/j.scitotenv.2020.141210>.
- Zhang, Z., Guan, H., Luo, L., Zheng, N., Xiao, H., Liang, Y., Xiao, H., 2020a. Sources and transformation of nitrate aerosol in winter 2017–2018 of megacity Beijing: Insights from an alternative approach. *Atmos Environ* 241, 117842. <https://doi.org/10.1016/j.atmosenv.2020.117842>.
- Zhang, Z., Guan, H., Xiao, H., Liang, Y., Zheng, N., Luo, L., Liu, C., Fang, X., Xiao, H., 2021b. Oxidation and sources of atmospheric NO_x during winter in Beijing

based on $\delta^{18}\text{O}$ - $\delta^{15}\text{N}$ 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 ($\delta^{18}\text{O}$ - 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 NO_x 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 NO_x 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 NO_x 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 NO_x 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 $\delta^{18}\text{O}$ and $\delta^{15}\text{N}$ 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 $\text{PM}_{2.5}$, 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 $\text{PM}_{2.5}$, 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.

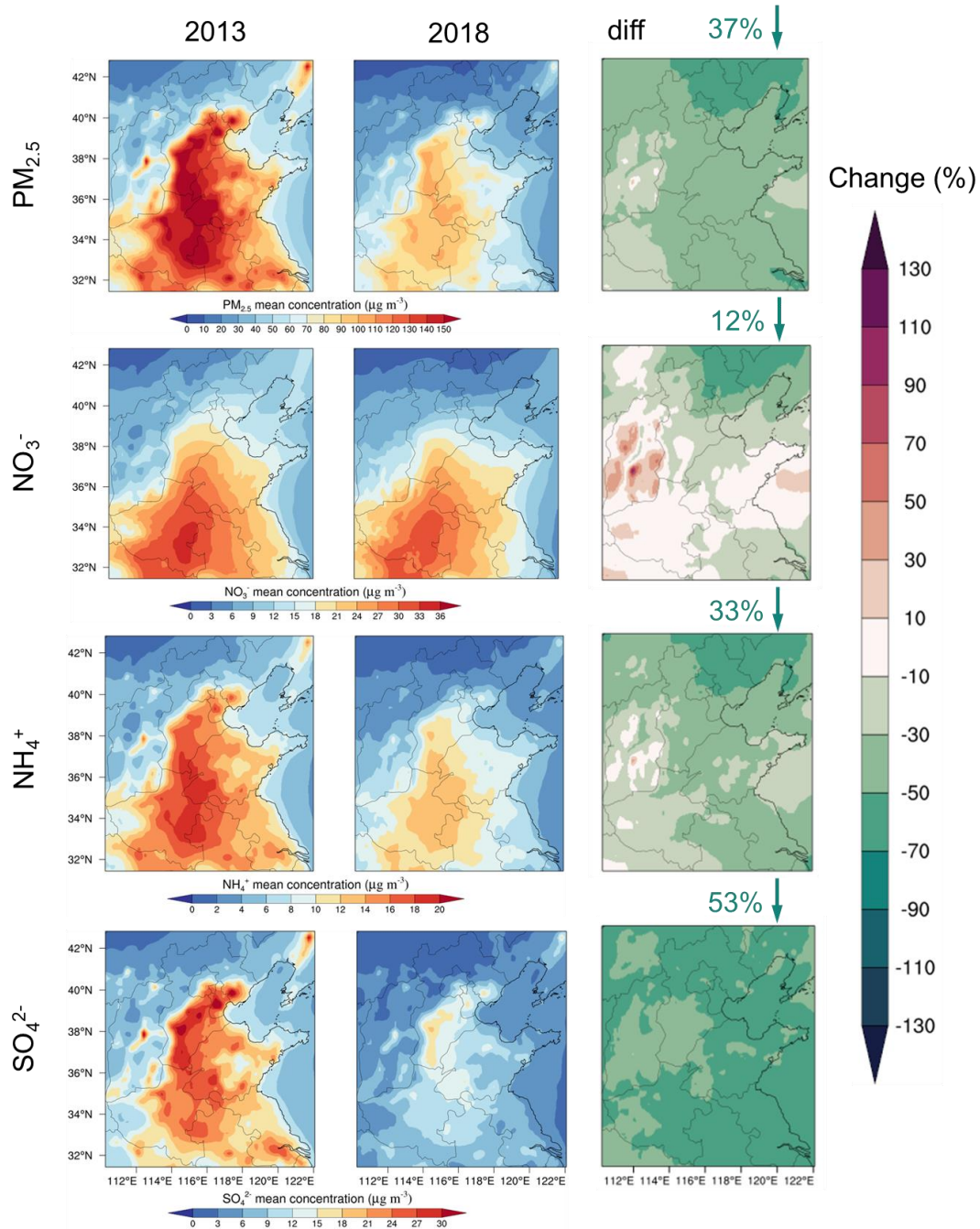


Figure 4 Spatial distribution and changes in $PM_{2.5}$ and its components in the NCP during the winters of 2013 and 2018. The up arrows indicate increases, and the down arrows indicate decreases.

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.

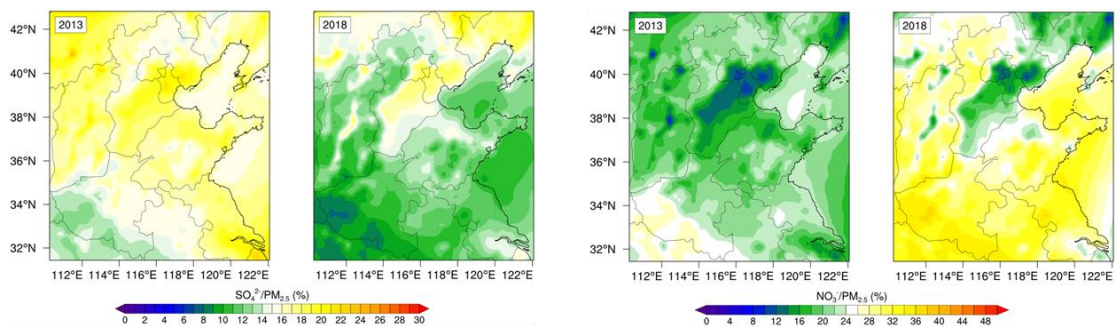


Figure 5 Spatial distributions of the nitrate and sulfate proportions in $PM_{2.5}$ in the NCP region during the winters of 2013 and 2018.

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.

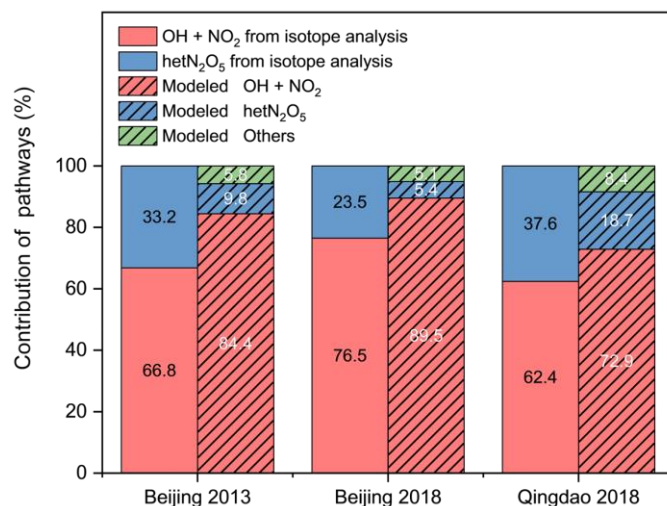


Figure 9 Comparison of the contributions of the atmospheric NO_3^- formation pathways based on the dual-isotope results and model simulations for Beijing in 2013 and 2018 and for Qingdao in 2018.

Fig 10: The legend for the dot looks like it is just connected to OH Pathway, and it should be labelled as NO_3^- concentration or $[\text{NO}_3^-]$ 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.

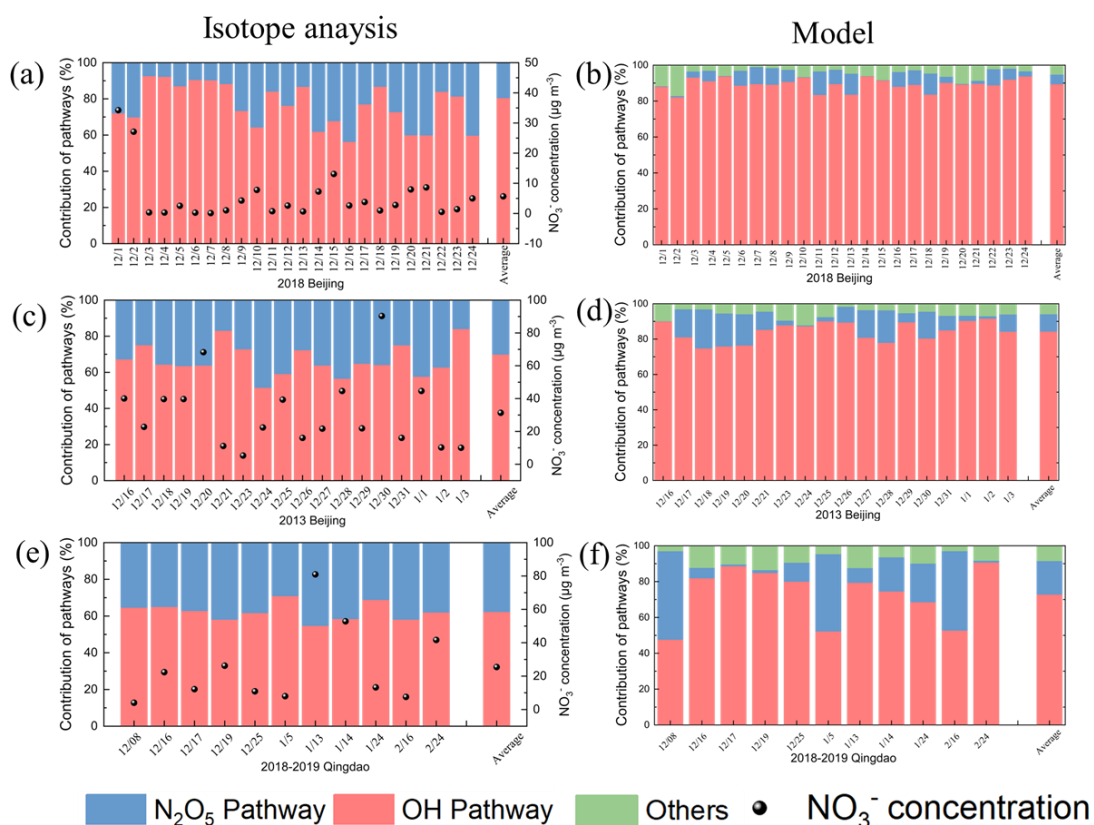


Figure 8 Time series of the contributions of the atmospheric NO_3^- formation pathways: (a, b) Beijing 2018, (c, d) Beijing 2013, and (e, f) Qingdao 2018, based on (a, c, e) dual-isotope analysis and (b, d, f) model simulations.

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 $\pm 100\%$ to more accurately depict the range of HONO concentration variations. This revision has been implemented in Figure 11 of the revised manuscript.

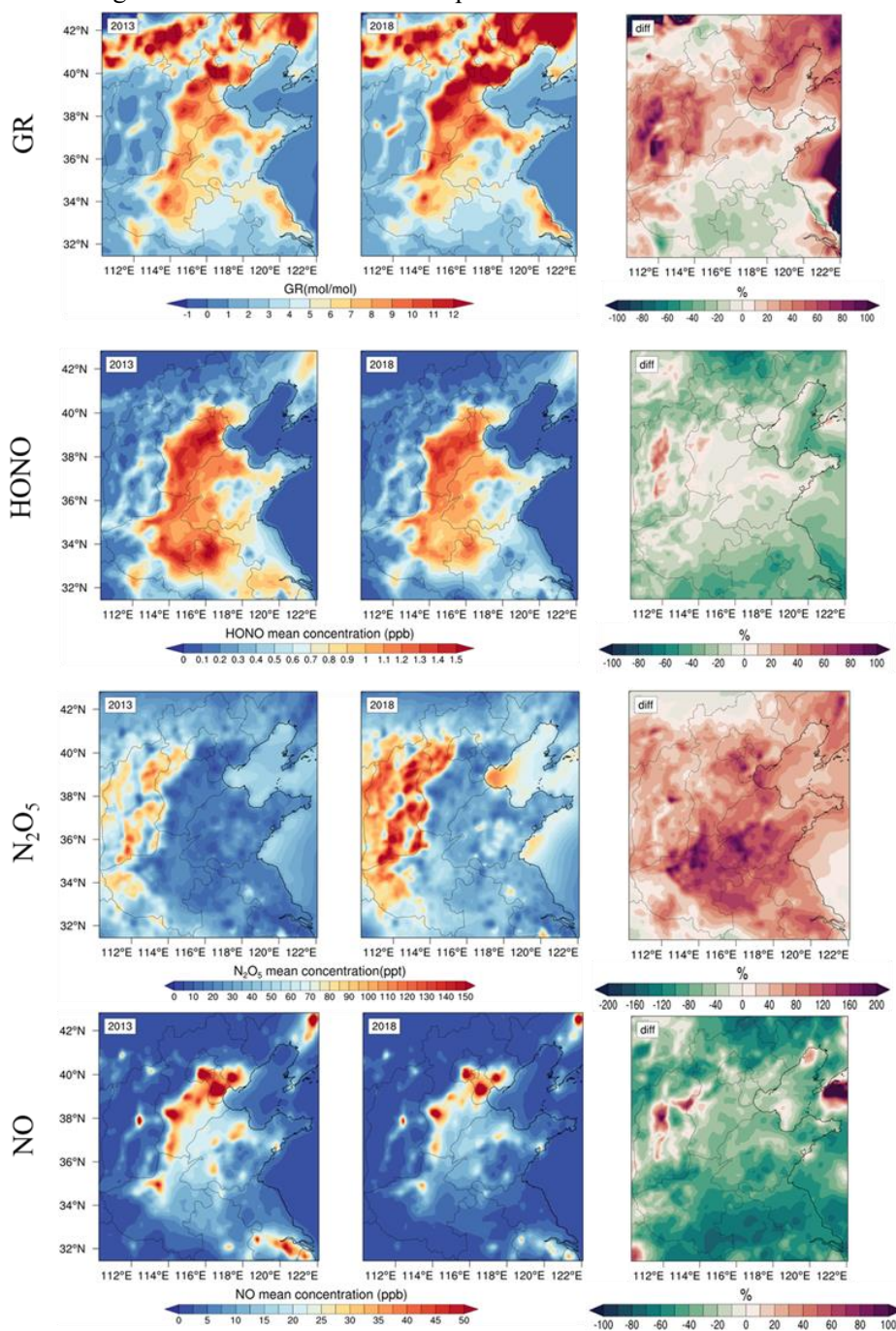


Figure 11 Spatial distributions and interannual variations in the GR, HONO, N_2O_5 , and NO_x concentrations over the North China Plain during the winters of 2013 and 2018. The percentage changes (diff) represent the relative differences between 2018 and 2013.

Supporting Information

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

Zhenze Liu^{1,2}, Jianhua Qi^{1,2}, Yuanzhe Ni¹, Likun Xue³, Xiaohuan Liu^{1,2}

¹ Key Laboratory of Marine Environment and Ecology, Ministry of Education, Ocean University of China, Qingdao 266100, China

² Laboratory for Marine Ecology and Environmental Science, Qingdao Marine Science and Technology Center, Qingdao 266237, China

³ Environment Research Institute, Shandong University, Qingdao, Shandong, 266237, China

Correspondence to: Jianhua Qi (qjianhua@ouc.edu.cn), Xiaohuan Liu (liuxh1983@ouc.edu.cn)

Text S1

Our isotope blank measurements followed the same procedure as the sample isotope analysis. Specifically, in the sample measurements, after purging with high-purity nitrogen, 20 nmol of nitrogen was added to the headspace vial containing the *Pseudomonas aureofaciens* (ATCC13985) strain. For the blank measurements, no sample was added, and after 24 hours, 10 M NaOH was directly injected to quench the reaction before the analysis. The peak area in the chromatogram represents the absolute amount of N₂O reduced by the strain, and the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values correspond to the $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of the sample. The peak area for the samples was around 10, while the peak areas for the two blank measurements were only 0.371 and 0.336, indicating an influence on the isotope values of less than 5%, which is negligible and thus not considered.

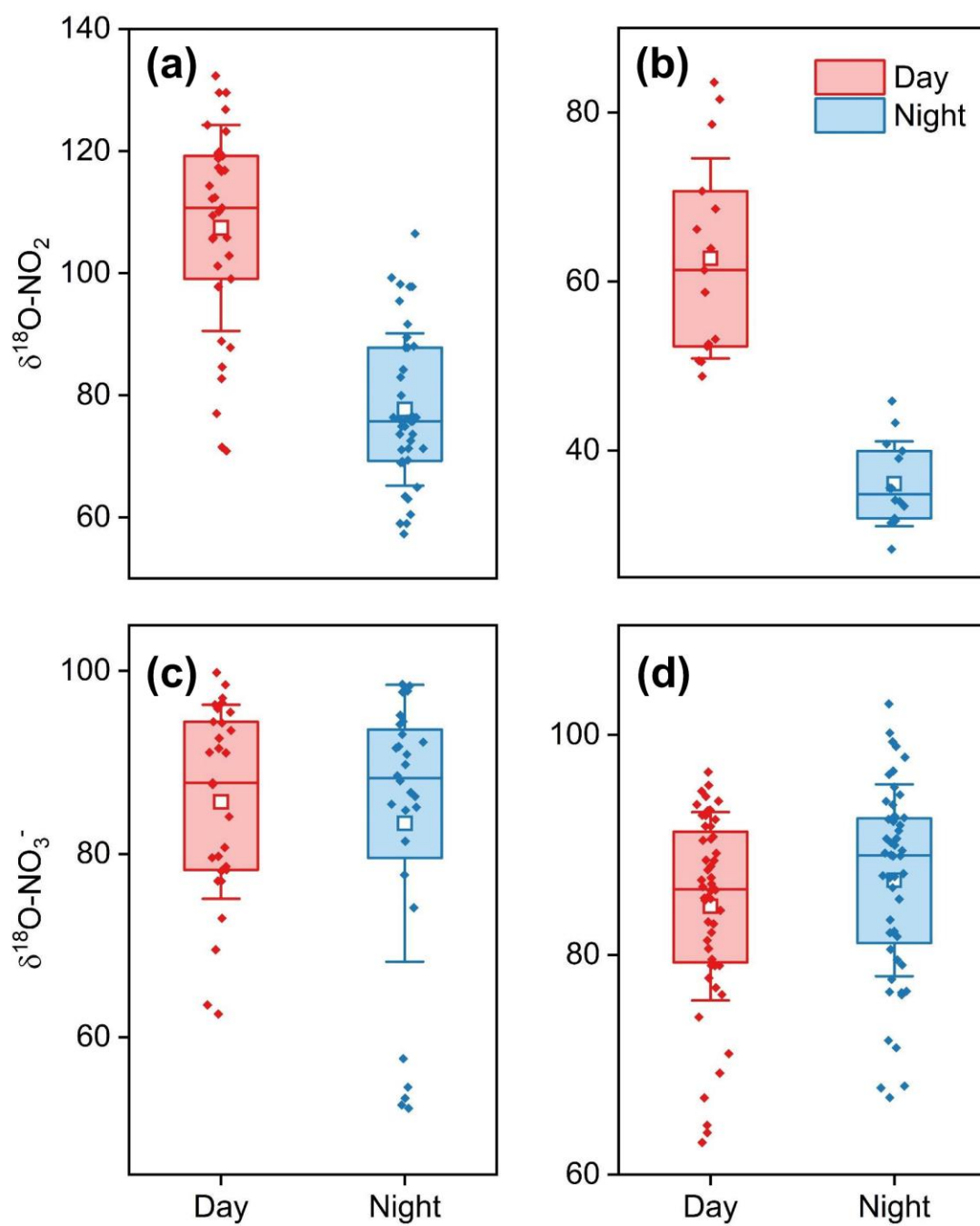


Figure S1 The diurnal values of atmospheric $\delta^{18}\text{O-NO}_2$ in Hefei winter (Zhang et al., 2025) (a) and in Nanchang summer (Cao, 2022) (b), and $\delta^{18}\text{O-NO}_3^-$ in Tianjin winter (Feng et al., 2020) (c) and in Nanjing winter (Zhang et al., 2022) (d).

Text S2

In most studies, the tropospheric $\delta^{15}\text{N-NO}_x$ was often assumed as 0‰ following Walters and Michalski (2016), Luo et al. (2023) and Deng et al. (2024). In addition, the tropospheric $\delta^{18}\text{O-H}_2\text{O}_{(g)}$ in Beijing in winter was determined as -27.9‰ in Wen et al. (2010), and in Qingdao, it was determined as -18.6‰ in Wang et al. (2022). The tropospheric $\delta^{18}\text{O-NO}_x$ ranged from 112‰ to 122‰ (Michalski et al., 2014; Walters and Michalski, 2016). The f_{NO_2} values in Beijing and Qingdao were 0.655 (Luo et al., 2023) and 0.786 (Lian et al., 2022) in winter, respectively.

$$\begin{aligned}\delta^{15}\text{N} - \text{NO}_3^- &= \gamma \times [\delta^{15}\text{N} - \text{NO}_3^-]_{\text{OH}} + (1 - \gamma) \times [\delta^{15}\text{N} - \text{NO}_3^-]_{\text{N}_2\text{O}_5} \\ &= \gamma \times [\delta^{15}\text{N} - \text{HNO}_3]_{\text{OH}} + (1 - \gamma) \times [\delta^{15}\text{N} - \text{HNO}_3]_{\text{N}_2\text{O}_5}\end{aligned}\quad (\text{S1})$$

$$\begin{aligned}\delta^{18}\text{O} - \text{NO}_3^- &= \gamma \times [\delta^{18}\text{O} - \text{NO}_3^-]_{\text{OH}} + (1 - \gamma) \times [\delta^{18}\text{O} - \text{NO}_3^-]_{\text{N}_2\text{O}_5} \\ &= \gamma \times [\delta^{18}\text{O} - \text{HNO}_3]_{\text{OH}} + (1 - \gamma) \times [\delta^{18}\text{O} - \text{HNO}_3]_{\text{N}_2\text{O}_5}\end{aligned}\quad (\text{S2})$$

$$\begin{aligned}[\delta^{15}\text{N} - \text{HNO}_3]_{\text{OH}} &= \delta^{15}\text{N} - \text{NO}_2 \\ &= 1000 \times \left[\frac{(^{15}\alpha_{\text{NO}_2/\text{NO}} - 1)(1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + (^{15}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2})} \right] + \delta^{15}\text{N} - \text{NO}_x\end{aligned}\quad (\text{S3})$$

$$[\delta^{15}\text{N} - \text{HNO}_3]_{\text{N}_2\text{O}_5} = 1000 \times (^{15}\alpha_{\text{N}_2\text{O}_5/\text{NO}_2} - 1) + \delta^{15}\text{N} - \text{NO}_x \quad (\text{S4})$$

$$\begin{aligned}[\delta^{18}\text{O} - \text{HNO}_3]_{\text{OH}} &= \frac{2}{3} \times [\delta^{18}\text{O} - \text{NO}_2]_{\text{OH}} + \frac{1}{3} \times [\delta^{18}\text{O} - \text{OH}]_{\text{OH}} \\ &= \frac{2}{3} \times \left[\frac{1000 \times (^{18}\alpha_{\text{NO}_2/\text{NO}} - 1) \times (1 - f_{\text{NO}_2})}{(1 - f_{\text{NO}_2}) + (^{18}\alpha_{\text{NO}_2/\text{NO}} \times f_{\text{NO}_2})} + [\delta^{18}\text{O} - \text{NO}_x] \right] \\ &\quad + \frac{1}{3} \times \left[(\delta^{18}\text{O} - \text{H}_2\text{O}_{(g)}) + 1000 \times (^{18}\alpha_{\text{OH}/\text{H}_2\text{O}_{(g)}} - 1) \right]\end{aligned}\quad (\text{S5})$$

$$[\delta^{18}\text{O} - \text{HNO}_3]_{\text{N}_2\text{O}_5} = \delta^{18}\text{O} - \text{NO}_2 + 1000 \times (^{18}\alpha_{\text{N}_2\text{O}_5/\text{NO}_2} - 1) \quad (\text{S6})$$

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

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

Components	Values (‰)	References
O_3	From 80 to 130	Michalski et al., 2011
O_2	23.5	Kroopnick and Craig; 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
$\cdot\text{OH}$ in Beijing winter	From -72.4 to -64.9	$\delta^{18}\text{O}\text{-OH} = \delta^{18}\text{O}\text{-H}_2\text{O}_{(\text{g})} + 1000(^{18}\alpha_{\text{XY}} - 1)$
$\cdot\text{OH}$ in Qingdao winter	From -61.2 to -57.8	(Walters and Michalski, 2016)

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

		A	B	C	D
$^{15}\alpha_{A/B}$	N ₂ O ₅ /NO ₂	0.69398	-1.9859	2.3876	0.16308
	NO ₂ /NO	3.8834	-7.7299	6.0101	-0.17928
$^{18}\alpha_{A/B}$	NO/NO ₂	-0.04129	1.1605	-1.8829	0.74723
	·OH/H ₂ O _(g)	2.1137	-3.8026	2.5653	0.5941
	N ₂ O ₅ /NO ₂	-0.54136	0.13073	1.2477	-0.1272

Table S3 Equations for calculating the statistical evaluation indices

Statistical index	Formula
1. Mean Bias	$MB = \frac{1}{N} \sum_1^N (Sim - Obs)$
2. Root Mean Square Error	$RMSE = \sqrt{\frac{1}{N} \sum_1^N (Sim - Obs)^2}$
3. Index of agreement, IOA	$IOA = 1 - \frac{\sum_{i=1}^N (Sim - Obs)^2}{\sum_{i=1}^N (Sim - Obs + Obs - \overline{Obs})^2}$
4. Normalized Mean Bias	$NMB = \frac{1}{N} \sum_1^N \left(\frac{Sim - Obs}{Obs} \right)$
5. Normalized Mean Error	$NME = \frac{1}{N} \sum_1^N \left \frac{Sim - Obs}{Obs} \right $
6. Correlation coefficient (R)	$R = \frac{1}{N} \sum_{i=1}^N \left[\frac{(Sim - \overline{Sim})(Obs - \overline{Obs})}{S_p S_o} \right]$ $S_p = \left[\frac{1}{N} \sum_{i=1}^N (Sim - \overline{Sim})^2 \right]^{\frac{1}{2}}$ $S_o = \left[\frac{1}{N} \sum_{i=1}^N (Obs - \overline{Obs})^2 \right]^{\frac{1}{2}}$

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

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

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

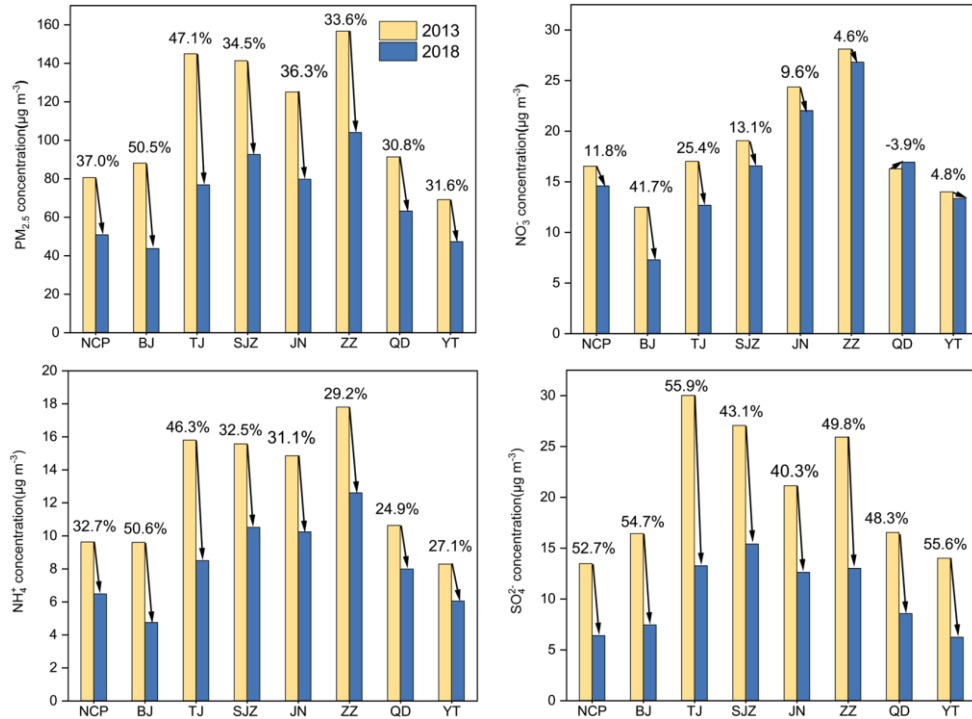


Figure S2 Concentrations of PM_{2.5} and its components in seven major cities in the NCP region during the winters of 2013 and 2018

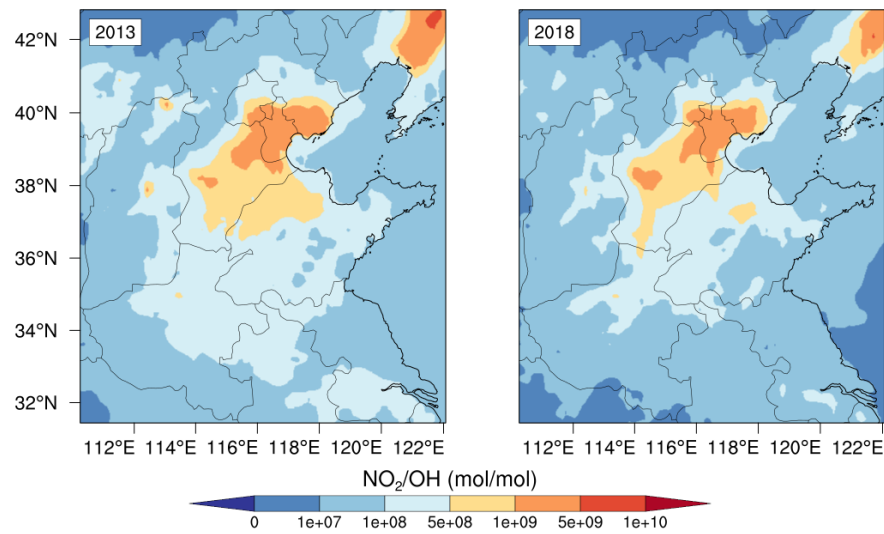


Figure S3 Spatial distribution of the NO₂/OH molar ratio in the NCP region during the winters of 2013 and 2018

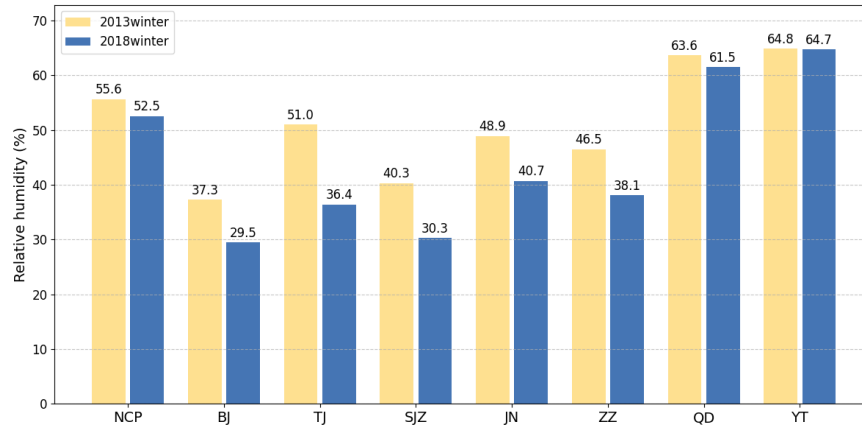


Figure S4 Relative humidity in the NCP and seven major cities (2013, 2018)

Reference

- Cheng, M., Tang, G., Lv, B., Li, X., Wu, X., Wang, Y., and Wang, Y.: Source apportionment of PM_{2.5} and visibility in Jinan, China, *Journal of Environmental Sciences*, 102, 207-215, doi:10.1016/j.jes.2020.09.012, 2021.
- Deng, M., Wang, C., Yang, C., Li, X., and Cheng, H.: Nitrogen and oxygen isotope characteristics, formation mechanism, and source apportionment of nitrate aerosols in Wuhan, Central China, *Science of The Total Environment*, 921, 170715, doi:10.1016/j.scitotenv.2024.170715, 2024.
- Dong, Z., Su, F., Zhang, Z., and Wang, S.: Observation of chemical components of PM_{2.5} and secondary inorganic aerosol formation during haze and sandy haze days in Zhengzhou, China, *J Journal of Environmental Sciences*, 88, 316-325, doi:10.1016/j.jes.2019.09.016, 2020.
- Fan, M.-Y., Zhang, Y.-L., Lin, Y.-C., Cao, F., Zhao, Z.-Y., Sun, Y., Qiu, Y., Fu, P., and Wang, Y.: Changes of Emission Sources to Nitrate Aerosols in Beijing After the Clean Air Actions: Evidence From Dual Isotope Compositions, *Journal of Geophysical Research: Atmospheres*, 125, e2019JD031998, doi:10.1029/2019JD031998, 2020.
- Lian, C., Wang, W., Chen, Y., Zhang, Y., Zhang, J., Liu, Y., Fan, X., Li, C., Zhan, J., Lin, Z., Hua, C., Zhang, W., Liu, M., Li, J., Wang, X., An, J., and Ge, M.: Long-term winter observation of nitrous acid in the urban area of Beijing, *Journal of Environmental Sciences*, 114, 334-342, doi:10.1016/j.jes.2021.09.010, 2022.
- Luo, L., Wu, S., Zhang, R., Wu, Y., Li, J., and Kao, S.-j.: What controls aerosol $\delta^{15}\text{N}-\text{NO}_3^-$? NO_x emission sources vs. nitrogen isotope fractionation, *Science of The Total Environment*, 871, 162185, doi:10.1016/j.scitotenv.2023.162185, 2023.
- Michalski, G., Bhattacharya, S. K., and Girsch, G.: NO_x cycle and the tropospheric ozone isotope anomaly: an experimental investigation, *Atmos. Chem. Phys.*, 14, 4935-4953, doi:10.5194/acp-14-4935-2014, 2014.
- Song, W., Wang, Y.-L., Yang, W., Sun, X.-C., Tong, Y.-D., Wang, X.-M., Liu, C.-Q., Bai, Z.-P., and Liu, X.-Y.: Isotopic evaluation on relative contributions of major NO_x sources to nitrate of PM_{2.5} in Beijing, *Environmental Pollution*, 248, 183-190, doi:10.1016/j.envpol.2019.01.081, 2019.
- Walters, W. W. and Michalski, G.: Theoretical calculation of nitrogen isotope equilibrium exchange fractionation factors for various NO_y molecules, *Geochimica et Cosmochimica Acta*, 164, 284-297, doi:10.1016/j.gca.2015.05.029, 2015.

Walters, W. W. and Michalski, G.: Theoretical calculation of oxygen equilibrium isotope fractionation factors involving various NO_y molecules, OH, and H₂O and its implications for isotope variations in atmospheric nitrate, *Geochimica et Cosmochimica Acta*, 191, 89-101, doi:10.1016/j.gca.2016.06.039, 2016.

Wang, X., Zhou, Y., Cheng, S., and Wang, G.: Characterization and regional transmission impact of water-soluble ions in PM_{2.5} during winter in typical cities, *China Environmental Science*, 36, 2289-2296, 2016.

Wang, Y., Cui, B.-l., Li, D.-s., Wang, Y.-x., Yu, W.-x., and Zong, H.-h.: Stable Isotopes Reveal Water Vapor Sources of Precipitation over the Jiaolai Plain, Shandong Peninsula, China, *Asia-Pacific Journal of Atmospheric Sciences*, 58, 227-241, doi:10.1007/s13143-021-00253-2, 2022.

Wei, X., Gao, m., and Tong, j.: Characterization of water-soluble ions of PM_{2.5} in Zhengzhou, *Chinese journal of quantum*, 36, 495-499, 2019.

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, doi:10.1029/2009JD012408, 2010.

Yao, Q., Liu, Z., Han, S., Cai, Z., Liu, J., Hao, T., Liu, J., Huang, X., and Wang, Y.: Seasonal variation and secondary formation of size-segregated aerosol water-soluble inorganic ions in a coast megacity of North China Plain, *Environmental Science and Pollution Research*, 27, 26750-26762, doi:10.1007/s11356-020-09052-0, 2020.

Zhou, J., Duan, J., Wang, J., Liu, H., LI, M., and Jin, W.: Analysis of pollution characteristics and sources of PM_{2.5} during heavy pollution in Shijiazhuang city around New Year's Day 2019, *Environmental Science*, 41, 39-49, doi:10.13227/j.hjx.201906085, 2020.

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 ¹⁵N and ¹⁸O isotope ratios, *Sci. Total Environ.*, 708, 134797, doi:10.1016/j.scitotenv.2019.134797, 2020.

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 $\Delta^{17}\text{O}(\text{NO}_3^-)$ 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 ($\delta^{15}\text{N}$, $\delta^{18}\text{O}$, and $\Delta^{17}\text{O}$) of Winter NO_2 in a Megacity in Central China, *Environ. Sci. Technol.*, 59, 3634-3644, 10.1021/acs.est.4c07724, 2025.

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

Michalski, G., Bhattacharya, S. K., and Girsch, G.: NO_x 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.