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

Reviewer #2:

Summary: The authors have substantially improved their manuscript in the revised version. I appreciate the effort the authors spent to address previous reviewer comments. I think this manuscript is now suitable for publication in ACP with a 1 major comment and few additional minor comments:

Major comment:

Lines 224-226: At coastal sites, the N_2O_5 heterogeneous reaction pathway may be enhanced due to addition reactions involved Cl-, which has a different estimated oxygen isotope mass-balance than the N_2O_5 + H_2O (surface) (check out Alexander et al., 2020). Does the model simulation use an aerosol scheme that includes N_2O_5 + Cl heterogeneous reactions? How might this impact the results and interpretation of the isotope data?

Reply: Thanks for your well-founded insights. Our Bayesian stable isotope mixing model has, to date, overlooked the contribution of the heterogeneous reaction of N_2O_5+Cl^-. Although this pathway accounts for only approximately 5% of global atmospheric NO_3^- formation, its relative significance is notably greater in coastal and marine environments, where it substantially elevates the $\Delta^{17}O$ and $\delta^{18}O$ values of produced NO_3^- (Alexander et al., 2020; Kim et al., 2023).

In response, we compiled wintertime $\delta^{18}O$-NO_3^- characteristics from inland and coastal cities across northern China (Table R1). Notably, in our urban study of Qingdao (a coastal city), $\delta^{18}O$-NO_3^- values are indeed elevated, implying that the heterogeneous N_2O_5+Cl^- pathway warrants explicit consideration. This omission likely contributes to discrepancies between the isotope model outputs and CMAQ simulations.

In future work, we would incorporate this reaction into our isotope modeling framework, thereby enhancing the analytical precision and robustness of our source apportionment.

Table R1. Concentration and isotopes of atmospheric NO_3^- in northern China during wintertime.

Season	Year	Site	Longitude (°E)	Latitude (°N)	Sample type	NO_3^- μg m^{-3}	$\delta^{15}N$ (‰)	$\delta^{18}O$ (‰)	Reference
Winter	2018	Qingdao	120.55	36.10	TSP	25.4 ±	9.5 ±	97.2	This study

					22.8	3.3	± 6.3	
2017		120.49	36.16	$PM_{2.5}$	16.3 ± 15.8	11.6 ± 3.8	85.7 ± 8.5	Xiao et al., 2025
2012	Beijing	116.38	39.98	TSP	31.3 ± 25.2	13.0 ± 3.3	-	Luo et al., 2019
2013		116.34	39.93	$PM_{2.5}$	31.3 ± 21.4	13.8 ± 5.0	98.3 ± 10.5	Zong et al., 2020
2014		116.70	40.07	$PM_{2.5}$	17.1 ± 23.0	11.9 ± 4.4	77.4 ± 14.1	Song et al., 2019
2014		116.63	40.33	$PM_{2.5}$	19.1 ± 15.6	14.9 ± 2.2	-	He et al., 2018
2015		116.39	40.00	TSP	32.3 ± 11.7	14.5 ± 2.6	95.3 ± 7.4	Dong et al., 2022
2016		116.37	39.97	$PM_{2.5}$	36.8 ± 26.4	-	86.7 ± 12.4	Fan et al., 2022
2017		116.42	40.03	$PM_{2.5}$	8.1 ± 9.8	12.8 ± 3.7	75.0 ± 13.3	Zhang et al., 2021
2017		116.38	39.98	$PM_{2.5}$	-	13.7 ± 2.7	89.4 ± 6.4	Luo et al., 2022
2018		116.37	39.97	$PM_{2.5}$	12.2 ± 4.6	12.9 ± 3.5	83.8 ± 13.4	Fan et al., 2020
2020		117.12	39.06	TSP	17.9 ± 17.0	9.4 ± 5.4	84.9 ± 10.7	Yan et al., 2023
2015	Tianjin	117.71	39.09	TSP	35.8 ± 19.1	9.7 ± 2.0	88.0 ± 12.3	Dong et al., 2022
2017		117.15	39.08	$PM_{2.5}$	13.3 ± 13.2	12.4 ± 4.0	80.8 ± 12.6	Zhang et al., 2021
2019		117.34	38.99	$PM_{2.5}$	20.3 ± 21.1	11.9 ± 6.1	86.7 ± 10.2	Zhang et al., 2022a
2021		117.42	39.56	$PM_{2.5}$	8.0 ± 6.8	6.9 ± 3.2	75.8 ± 9.2	Zhang et al., 2024
2017	Shijiazhuang	114.49	38.10	$PM_{2.5}$	18.4 ± 13.9	14.1 ± 2.6	94.2 ± 4.8	Luo et al., 2022

2017		114.64	38.01	$PM_{2.5}$	18.1 ± 14.7	12.7 ± 2.8	87.3 ± 9.3	Zhang et al., 2021
2015	Zhangjiakou	115.39	40.91	TSP	5.3 ± 3.1	6.3 ± 5.4	80.0 ± 5.2	Dong et al., 2022
2017	Jiaozuo	113.27	35.18	$PM_{2.5}$	26.9 ± 23.8	11.9 ± 2.1	87.7 ± 8.5	Zhang et al., 2021
2020		113.27	35.18	$PM_{2.5}$	108.7 ± 38.5	7.5 ± 3.3	91.6 ± 6.1	Li et al., 2022a
2017	Ji’nan	117.05	36.67	$PM_{2.5}$	20.9 ± 16.0	10.5 ± 3.7	85.3 ± 7.5	Zhang et al., 2021
2022	Zibo	118.06	36.83	$PM_{2.5}$	43.8 ± 22.9	5.6 ± 2.6	97.9 ± 4.2	Feng et al., 2023
2022	Zhoukou	114.65	33.60	$PM_{2.5}$	39.5 ± 21.8	1.5 ± 1.9	88.4 ± 5.0	Feng et al., 2023
2014	Beihuangcheng Island	120.92	38.40	$PM_{2.5}$	5.8 ± 4.1	15.9 ± 3.5	88.1 ± 10.2	Zong et al., 2017
2018	Qianliyan Island	121.63	36.45	TSP	1.9 ± 1.3	10.8 ± 3.6	84.4 ± 8.8	Zhang et al., 2022b
2018	Bohai Sea	120.32	38.38	$PM_{2.5}$	11.9 ± 8.6	9.0 ± 4.6	86.4 ± 8.2	Zong et al., 2022

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Minor Comments:

Lines 228-229: I believe Walters et al., "Summertime diurnal variations in the isotopic composition of atmospheric nitrogen dioxide at a small midwestern United States city", 2018 were the first to show this.

Reply: We appreciate the suggestion and have added a citation to Walters et al. (2018) at line 229 to acknowledge their earlier findings.

Lines 315:-317: Are there standard deviations that should be included?

Reply: Thank you for your comment. We have added the standard deviations for the data in lines 316–319 in the revised manuscript.

Modified sentence: During the winter of 2013, the average $PM_{2.5}$ concentration in the NCP reached 80.52 ± 77.13 μg/m³, with high-concentration areas mainly concentrated in the provinces of Beijing, Tianjin, southern Hebei, Henan, Shandong, and Anhui (Figure 4). By 2018, the average $PM_{2.5}$ concentration had decreased to 50.74 ± 49.26 μg/m³, representing a significant reduction of 37% ± 10%.

Lines 318: “cholars” is a typo.

Reply: The typographical error has been corrected from “cholars” to “scholars” at line 319. We have also reviewed the entire manuscript and corrected similar errors throughout.

Lines 319-321: Are these values referring to averages? What is the standard deviation of these values?

Reply: Thank you for your question. These values represent averages, and the corresponding standard deviations have been added in line 321-322 of the revised manuscript.

Modified sentence: We found that the SO_4^{2-} concentration decreased by 53% ± 5%, whereas the NO_3^- and NH_4^+ concentrations decreased by 13% ± 20% and 33% ± 13%, respectively (refer to Figure S2 for city-specific changes).

Lines 366: “hat” is a typo.

Reply: The typo “hat” has been corrected to “that” in line 367. A thorough review of the manuscript was also conducted to identify and correct similar errors throughout.

Lines 416-417: I wonder if some of the measurement/model mismatch could be underprediction of the N_2O_5 pathway in the model because of lack of N_2O_5 + Cl^- reactions

Reply: This is an insightful observation. Although the CMAQ model configuration includes the heterogeneous N_2O_5 + Cl^- reaction pathway, our Bayesian stable isotope mixing model has not yet incorporated this reaction. This omission may contribute to the discrepancies observed between the isotope model and CMAQ simulations in coastal regions.

Lines 419-421: What do you consider an "acceptable range"?

Reply: Thank you for your valuable comment. Acceptable range refers to the deviation between the CMAQ model simulation results and the isotope analysis contributions, assessed in the context of both our study and previously published studies. Specifically, we converted the CMAQ-simulated contributions into corresponding $\delta^{18}O$ values and compared them with the isotope analysis results, as summarized in Table R2. Most of the deviations were within ±30%, which aligns with the uncertainty range (10–30%) by the stable isotope mixing models (Moore and Semmens, 2008). Therefore, we consider deviations within ±30% to be an acceptable range in this study.

Table R2. Summary of the difference between observed and calculated $\delta^{18}O$-NO_3^- values in our study.

Location/Year	Reactions	Percentage	$\delta^{18}O$ (‰)	Cal.	Obs.	Difference
	$OH+NO_2$	56.50%	57.1			
	hetN2O5	37.00%	126.4			
Qingdao 2018	ClNO3	0.30%	135	86.9‰	97.2‰	10.3‰
	NO_3+HC	0.60%	105.8			
	hetNO2	2.40%	74.5			
	OH+NO2	77.80%	53.1			
	hetN2O5	14.30%	126.1			
Beijing 2013	ClNO3	0.10%	134.9	68.7‰	98.3‰	29.6‰
	NO3+HC	0.30%	104.6			
	hetNO2	5.40%	72.2			
	OH+NO2	85.60%	53.2			
	hetN2O5	9.90%	126			
Beijing 2018	ClNO3	0.20%	134.7	65.4‰	83.8‰	18.4‰
	NO3+HC	0.30%	104.7			
	hetNO2	2.60%	72.2			
Kim et al., 2023						7.7–20.4‰

Kim, H., Walters, W. W., Bekker, C., Murray, L. T., and Hastings, M. G.: Nitrate chemistry in the northeast US – Part 2: Oxygen isotopes reveal differences in particulate and gas-phase formation, Atmos. Chem. Phys., 23, 4203-4219, 10.5194/acp-23-4203-2023, 2023.

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Lines 450: Missing space between “to” and “the”

Reply: Thank you for pointing out the formatting issue. We have corrected the missing space between “to” and “the” in line 451-452 in the revised manuscript. Additionally, we have carefully reviewed the entire manuscript and corrected similar errors throughout.

Lines 447-451: How exactly was the backward trajectory analysis and nitrate formation analysis conducted? Does it consider all nitrate produced from the backward trajectory regions? Or does it consider nitrate mass-weighted? What about some of the nitrate formed several days upwind of the sampling location that might have undergone deposition before arriving at the site?

Reply: Thank you for the valuable questions regarding the backward trajectory and NO_3^- formation analysis. In this study, we used a backward trajectory model to trace the origin of air masses corresponding to each sample, thereby identifying potential source regions that contribute to NO_3^- formation.

Within these identified regions, all trajectory points over the relevant time periods were matched with the corresponding grid cells in the CMAQ model. We then considered all NO_3^- produced along these trajectories, analyzed and quantified their formation pathways, and averaged the results. Finally, these pathway contributions were compared with the isotope-based source apportionment derived from the collected samples.

We think that some NO_3^- formed in distant upwind regions really undergo deposition or chemical transformation during transport and may not ultimately reach the sampling site. While our trajectory analysis incorporates air mass residence time and typical atmospheric lifetimes of NO_3^- species, it does not fully account for in-transit losses such as dry/wet deposition or secondary chemical processes. This is a limitation of our current approach and may contribute to discrepancies between the model results and the isotope-based analysis.