Dear Editor,

We sincerely appreciate the opportunity to revise our manuscript titled "**Resolving Systematic Errors in Sulfate Source Apportionment: A Field-Validated Kinetic Isotope Fractionation Framework**". The editorial team's consideration and the reviewers' insightful comments have been invaluable in improving the quality and clarity of our work. The constructive feedback has significantly strengthened both the scientific rigor and presentation of our findings.

The manuscript has undergone rigorous revision in response to the insightful comments from both editors and reviewers, with each point carefully considered and addressed to strengthen the study's validity and clarity. The comments are in **BLACK** and our responses are in **BLUE**. Attached please find the revised version and relevant document, which we would like to submit for your kind consideration.

Once again, thank you very much for your comments and suggestions. We hope that the revisions will meet with your approval. If you have any questions, please don't hesitate to contact me at the address below.

Sincerely,

Pengxiang Qiu

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Response to Reviewer's comments

All responses and revisions in the revised manuscript are identified in **blue** text color.

Reviewer#1's comments:

1. Lines 31-32: What do the letters "a, b, c, d" in the text "$\delta^{34}S$=a, $\delta^{34}S$=b, $\delta^{34}S$=c, $\delta^{34}S$=d" represent?

Response: While regretting this initial confusion, the letters "a," "b," "c," and "d" have been entirely omitted from the revised manuscript, as these characters served no scientific purpose and were legacy remnants from an earlier draft. For more clarity, we have added/revised these sentences as following.

Page 2, Lines 45-48 in the revised manuscript:

Contemporary research has quantitatively established the sulfur isotopic signatures ($\delta^{34}S$) associated with major atmospheric oxidation routes, including transition metalion-catalyzed (TMI), ozone-mediated (O_3), nitrogen oxide-driven (NO_x), and hydrogen peroxide-initiated (H_2O_2) pathways, through systematic analysis of particulate matter samples.

2. Lines 35-38: Please clarify the distinction between complete and incomplete SO_2 oxidation frameworks.

Response: We sincerely appreciate the reviewers' valuable comments, which allow us to clarify the theoretical underpinnings of our methodology. To interpret the isotopic dynamics effectively, we established two contrasting frameworks. The Complete Oxidation (CO) Process acts as an idealized baseline, operating on the premise that all gaseous SO_2 is exhaustively converted to particulate sulfate, yielding a sulfur oxidation ratio (SOR) of 1. Consequently, this framework directly equates the calculated source isotopic signature ($\delta^{34}S$-source) to the measured sulfate value ($\delta^{34}S$-SO_4^{2-}), intentionally omitting the isotopic fractionation kinetics that govern the oxidation pathway. In contrast, the Incomplete Oxidation (InCO) Process reflects actual atmospheric conditions, specifically the reality that SO_2-to-sulfate conversion is inherently partial (SOR<1). Grounded in the Rayleigh fractionation model, this framework synchronously integrates the observed isotopic values of gaseous SO_2 and particulate SO_4^{2-}

with the corresponding SOR. By doing so, it inversely derives more realistic source isotopic signatures alongside the kinetic fractionation factors (α), a conceptual advancement that forms the core innovation of our study. For more clarity, we have added/revised these sentences as following.

Page 6, Lines 159-166 in the revised manuscript:

The Complete Oxidation (CO) Process acts as an idealized baseline, operating on the premise that all gaseous SO_2 is exhaustively converted to particulate sulfate, yielding a sulfur oxidation ratio (SOR) of 1. Consequently, this framework directly equates the calculated source isotopic signature (δ^{34}S-source) to the measured sulfate value ($\delta^{34}S\text{-}SO_4^{2-}$), intentionally omitting the isotopic fractionation kinetics that govern the oxidation pathway. In contrast, the Incomplete Oxidation (InCO) Process reflects actual atmospheric conditions, specifically the reality that SO_2-to-sulfate conversion is inherently partial (SOR<1). Grounded in the Rayleigh fractionation model, this framework synchronously integrates the observed isotopic values of gaseous SO_2 and particulate SO_4^{2-} with the corresponding SOR. By doing so, it inversely derives more realistic source isotopic signatures alongside the kinetic fractionation factors (α), a conceptual advancement that forms the core innovation of our study.

3. Lines 65-69: The uncertainties for water-soluble ions, δ^{34}S and δ^{18}O are necessary to show in this part. In addition, please add the standard materials for measurements.

Response: We sincerely appreciate the reviewer for this insightful comment regarding our analytical protocols for water-soluble ions and stable isotopes (δ^{34}S and δ^{18}O). To ensure robust data quality, the analytical precision for all major water-soluble ions was rigorously verified via replicate measurements, consistently yielding values better than 5%. For the isotopic composition, results are reported in standard delta notation relative to international reference scales, specifically, Vienna Canyon Diablo Troilite (V-CDT) for δ^{34}S and Vienna Standard Mean Ocean Water (V-SMOW) for δ^{18}O, as formulated in Eq. (1) and (2). Notably, our analytical system demonstrated high stability, with long-term reproducibility constrained to better than 0.2‰ and 0.3‰ for sulfur and oxygen isotopes, respectively[1-2].

$$\delta^{34}S(‰) = \left[\left({}^{34}S/{}^{32}S\right)_{sample}/\left({}^{34}S/{}^{32}S\right)_{reference} - 1\right] \times 1000 \quad (1)$$

$$\delta^{18}O(‰) = \left[\left({}^{18}O/{}^{16}O\right)_{sample}/\left({}^{18}O/{}^{16}O\right)_{reference} - 1\right] \times 1000 \quad (2)$$

For more clarity, we have added/revised these sentences as following.

Page 3-4, Lines 97-104 in the revised manuscript:

To ensure robust data quality, the analytical precision for all major water-soluble ions was rigorously verified via replicate measurements, consistently yielding values better than 5%. For the isotopic composition, results are reported in standard delta notation relative to international reference scales, specifically, Vienna Canyon Diablo Troilite (V-CDT) for $\delta^{34}S$ and Vienna Standard Mean Ocean Water (V-SMOW) for $\delta^{18}O$, as formulated in Eq. (1) and (2). Notably, our analytical system demonstrated high stability, with long-term reproducibility constrained to better than 0.2‰ and 0.3‰ for sulfur and oxygen isotopes, respectively.

$$\delta^{34}S(‰) = \left[\left({}^{34}S/{}^{32}S\right)_{sample}/\left({}^{34}S/{}^{32}S\right)_{reference} - 1\right] \times 1000 \quad (1)$$

$$\delta^{18}O(‰) = \left[\left({}^{18}O/{}^{16}O\right)_{sample}/\left({}^{18}O/{}^{16}O\right)_{reference} - 1\right] \times 1000 \quad (2)$$

4. Lines 66-67: The sentence "The $\delta^{34}S$ value of sulfate was determined by precipitating $BaSO_4$ via $BaCl_2$ addition, followed by selective dissolution of residual $BaSO_3$ with 1 MHCl" is vague. Please rewrite it.

Response: Acknowledging this oversight, we are deeply grateful to the reviewers for their meticulous assessment, which directly prompted a comprehensive rewriting of the corresponding descriptions to ensure absolute clarity in the revised manuscript.

For the determination of sulfate $\delta^{34}S$ values, water-soluble sulfate within the filter extracts was initially isolated as $BaSO_4$ through the addition of an excess $BaCl_2$ solution. Because the sampling matrix inevitably captures both sulfate and sulfite, the latter originating from ambient SO_2, a targeted purification protocol was introduced; specifically, treating the co-precipitate with 1 M HCl selectively dissolved any residual $BaSO_3$ while leaving the acid-insoluble $BaSO_4$ intact. Following collection via filtration, the purified precipitate was rinsed thoroughly with deionized water until completely free of chloride ions and subsequently dried. To eliminate potential organic interferences prior to

isotopic interrogation, the dried $BaSO_4$ underwent thermal treatment in a muffle furnace at 1073 K for 2 hours.

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 83-90 in the revised manuscript:

For the determination of sulfate $\delta^{34}S$ values, water-soluble sulfate within the filter extracts was initially isolated as $BaSO_4$ through the addition of an excess $BaCl_2$ solution. Because the sampling matrix inevitably captures both sulfate and sulfite, the latter originating from ambient SO_2, a targeted purification protocol was introduced; specifically, treating the co-precipitate with 1 M HCl selectively dissolved any residual $BaSO_3$ while leaving the acid-insoluble $BaSO_4$ intact. Following collection via filtration, the purified precipitate was rinsed thoroughly with deionized water until completely free of chloride ions and subsequently dried. To eliminate potential organic interferences prior to isotopic interrogation, the dried $BaSO_4$ underwent thermal treatment in a muffle furnace at 1073 K for 2 hours.

5. Lines 194-201: Wang et al. (2016) suggest that the aqueous oxidation of SO_2 by NO_2 is key to efficient sulfate formation, but is only feasible under two atmospheric conditions: on fine aerosols with high relative humidity and NH_3 neutralization or under cloud conditions. How to prove that the NO_2-mediated oxidation pathway is ubiquitous during the sampling period?

Response: We sincerely appreciate the reviewer for highlighting this critical point and directing our attention to the seminal work by Wang et al. (2020) and Wang et al (2016). We completely agree with the growing scientific consensus that the aqueous oxidation of SO_2 mediated by NO_2 is highly sensitive to aerosol liquid water content and pH, making it particularly potent during winter fog and haze conditions. Upon carefully reevaluating our data presentation in Figure 4, we realize that displaying solely the relative percentage contributions inadvertently masked the actual seasonal dynamics of this chemical pathway. While the fractional proportion of the NO_2^-mediated pathway appears visually comparable between winter and summer in our isotopic distribution, the absolute mass of sulfate generated via this route differs drastically. Our field measurements demonstrate that total particulate sulfate concentrations peak at 27.55 ±

14.36 μg/m^3 during severe haze events, which predominantly occur in winter. Consequently, when translating these relative fractions into absolute mass concentrations, the NO_2 pathway produces a substantially higher burden of particulate sulfate in winter compared to summer. This mass-based dynamic aligns perfectly with the enhanced wintertime activity reported by Wang et al. (2020) and Wang et al (2016) and the broader field-based consensus. Furthermore, the sustained relative fraction of the NO_2 pathway during the summer months in Nanjing is not an artifact of our isotopic model, but rather a direct reflection of the region's specific emission inventory. As indicated by our $[NO_3^-]/[SO_4^{2-}]$ mass ratio analysis, which yielded values spanning from 0.15 to 1.95, with a mean of 0.98 ± 0.42, mobile vehicular emissions constitute a major atmospheric driver in this region. When these continuous, high-volume NO_x emissions couple with the incomplete SO_2 oxidation regimes characteristic of our summer study site, the NO_2 pathway maintains a significant fractional foothold, even though the absolute sulfate yield remains much lower than in winter. To eliminate this apparent contradiction and integrate the reviewer's excellent insights, we have thoroughly revised the discussion section corresponding to Figure 4 to explicitly distinguish between relative pathway fractions and absolute sulfate mass yields. We formally incorporated Wang et al. (2020) and Wang et al (2016) into the text, detailing how our absolute concentration metrics strongly corroborate their lab- and field-based findings regarding enhanced wintertime NO_2 oxidation. We expanded the narrative to clarify how local vehicular NO_x emissions sustain the relative percentage of this pathway during summer, ensuring the isotopic model results are properly contextualized within the region's specific atmospheric chemistry.

Reference:

[1] Wang, G., Zhang, R., Gomez, M. E., Yang, L., Levy Zamora, M., Hu, M., Lin, Y., Peng, J., Guo, S., Meng, J., Li, J., Cheng, C., Hu, T., Ren, Y., Wang, Y., Gao, J., Cao, J., An, Z., Zhou, W., Li, G., Wang, J., Tian, P., Marrero-Ortiz, W., Secrest, J., Du, Z., Zheng, J., Shang, D., Zeng, L., Shao, M., Wang, W., Huang, Y., Wang, Y., Zhu, Y., Li, Y., Hu, J., Pan, B., Cai, L., Cheng, Y., Ji, Y., Zhang, F., Rosenfeld, D., Liss, P. S., Duce, R. A., Kolb, C. E., and Molina, M. J.: Persistent sulfate formation from

London Fog to Chinese haze, P. Natl. Acad. Sci. USA, 113, 13630–13635, https://doi.org/10.1073/pnas.1616540113, 2016.

[2] Wang, J., Li, J., Ye, J., Zhao, J., Wu, Y., Hu, J., Liu, D., Nie, D., Shen, F., Huang, X., Huang, D., Ji, D., Sun, X., Xu, W., Guo, J., Song, S., Qin, Y., Lin, P., Turner, J., Lee, H., Hwang, S., Liao, H., Martin, S., Zhang, Q., Chen, M., Sun, Y., Ge, X., and Jacob, D.: Fast sulfate formation from oxidation of SO_2 by NO_2 and HONO observed in Beijing haze, Nat. Commun., 11, 2844, https://doi.org/10.1038/s41467-020-16683-x, 2020.

6. Lines 215-225: The concluding paragraph is effective but could be strengthened by mentioning policy implications for sulfate control.

Response: We highly appreciate the reviewer's forward-looking suggestion, under the guidance of which we have substantially enriched the concluding remarks of the revised manuscript. By explicitly articulating the practical policy implications of our findings for regional sulfate mitigation, this updated section now effectively bridges our fundamental mechanistic insights with macro-level air quality management.

For more clarity, we have added/revised these sentences as following.

Page 17, Lines 302-312 in the revised manuscript:

By transcending the idealized SO_2 oxidation assumptions that constrain conventional isotopic models, this study offers a critical advancement in atmospheric sulfate source apportionment. Integrating field-observed oxidation kinetics with optimized fractionation corrections reveals the predominance of TMI-catalyzed and NO_2-mediated pathways-chemical realities that traditional complete-oxidation frameworks systematically obscure, thereby disproportionately diminishing TMI contributions and misallocating source-specific burdens. Crucially, correcting these systematic biases exposes a profound seasonal misalignment in current emission inventories, which overestimate coal combustion by 10% while underestimating traffic emissions by 8% during summer (Figure 6b). Beyond reconciling long-standing discrepancies among isotopic, inventory-based, and transport-modeling approaches, these refinements carry immediate policy implications. Specifically, they demonstrate that effective sulfate mitigation cannot rely solely on blanket SO_2 reductions; rather, regulatory frameworks must pivot

toward multi-pollutant, seasonally differentiated strategies that dynamically target summer traffic dynamics and the co-emitted transition metals driving catalytic sulfate formation.

7. Technical corrections: Line 28, remove the number "2".

Response: While apologizing for this initial omission, we have rectified the error by entirely omitting the numeral "2" throughout the updated manuscript.

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 41-43 in the revised manuscript:

The application of stable isotope techniques in sulfate source attribution has emerged as a powerful analytical approach, leveraging the distinct isotopic fingerprints characteristic of different pollution sources and their remarkable stability during atmospheric transport.

8. Line 39: The sentence "Drawing conceptual inspiration from these insights" is vague.

Response: Appreciating the reviewer's thoughtful reminder, we have carefully recast the relevant formulations within the revised manuscript to ensure maximum clarity and scientific precision.

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 49-58 in the revised manuscript:

Advanced analytical tools, particularly Bayesian isotopic mixing and Rayleigh fractionation models, have demonstrated substantial utility in deconvoluting complex sulfate formation mechanisms. Yet, their diagnostic potential is often overshadowed by a fundamental theoretical flaw: the reliance on complete SO_2 oxidation paradigms. Because genuine atmospheric regimes rarely achieve such idealized conversion, this oversimplification severely penalizes the accuracy of sulfur transformation kinetics. Ultimately, conventional Rayleigh approaches introduce systematic uncertainties into source apportionment by neglecting the vital kinetic isotope effects and partial intermediates generated during incomplete SO_2 processing.

Building upon these insights, the present study establishes a comprehensive multi-model analytical framework that synergistically couples ambient field observations with a suite of diagnostic tools, ranging from backward trajectory analysis to Bayesian

isotope mixing and process-specific Rayleigh fractionation modeling.

9. Line 43: Please change "sulfur-oxygen isotope analysis" to "sulfur and oxygen isotope analyses".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. The "sulfur-oxygen isotope analysis" has been changed to "sulfur and oxygen isotope analyses".

For more clarity, we have added/revised these sentences as following.

Page 2, Lines 60-62 in the revised manuscript:

By applying sulfur and oxygen isotope analyses to seasonally resolved aerosol samples from Nanjing, we demonstrate significant divergence between conventional complete-oxidation Rayleigh models and our kinetic fractionation-corrected framework.

10. Line 58: Please remove "(08:00-08:00 local time)".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. (08:00-08:00 local time)" has been deleted.

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 76-77 in the revised manuscript:

Post-sampling handling included foil-wrapping (pre-combusted 723 K followed by 24-hour desiccation and dark refrigeration.

11. Line 60 and line 68: Please keep consistent with temperature units (450 ˚C V.S. 1073 K).

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. Line "450 ˚C" in line 60 has been changed to 723 K".

For more clarity, we have added/revised these sentences as following.

Page 3, Lines 73-77 in the revised manuscript:

Pre-treatment protocols involved muffle furnace combustion (723 K for 2h) followed by immersion in 2% K_2CO_3 + 2% glycerol solution for glass fiber filters. Sampling operations maintained 1.05 m^3 min^{-1} flow rates during 24-hour cycles with meteorological parameters (wind speed/direction, temperature, pressure, humidity) continuously logged. Post-sampling handling included foil-wrapping (pre-combusted 723 K

followed by 24-hour desiccation and dark refrigeration.

12. Line 191: Nanjing is in eastern China, not central. Please change "central China" to "eastern China".

Response: We sincerely appreciate the reviewers' insightful suggestions for enhancing our manuscript. "Central China" has been changed to "eastern China".

For more clarity, we have added/revised these sentences as following.

Page 15, Lines 273-275 in the revised manuscript:

An alternative α calculation (formula 9) generated a mean of 2.8 ± 1.7‰ (range: -0.2 to +6.1‰), higher than Guangzhou (<1.5‰) but lower than Beijing (4.2 ±1.2‰) with elevated α in eastern China attributable to temperature-dependent fractionation increases.

13. References:

Several references have incomplete DOIs (e.g., Han et al., 2022 has a PNAS DOI that doesn't match the journal)

Response: We sincerely appreciate the reviewers' insightful suggestions for improving the references. Han et al., 2022- the complete reference information has been supplemented.

Han, X., Lang, Y., Guo, Q., Li, X., Ding, H., and Li, S.: Enhanced oxidation of SO_2 by H_2O_2 during haze events: constraints from sulfur isotopes, J. Geophys. Res. Atmos., 127, e2022JD036960, https://doi.org/10.1029/2022JD036960, 2022.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 368-369 in the revised manuscript:

Han, X., Lang, Y., Guo, Q., Li, X., Ding, H., and Li, S.: Enhanced oxidation of SO_2 by H_2O_2 during haze events: constraints from sulfur isotopes, J. Geophys. Res. Atmos., 127, e2022JD036960, https://doi.org/10.1029/2022JD036960, 2022.

14. Mang et al., 2018- check author names

Response: We sincerely appreciate the reviewers' insightful suggestions for improving the references. Lin, M., Zhang, X., Li, M., Xu, Y., Zhang, Z., Tao, J., Su, B., Liu, L., Shen, Y., and Thiemens, M. H.: Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean

atmospheres, Proc. Natl. Acad. Sci., 115, 8541–8546, https://doi.org/10.1073/pnas.1803420115, 2018.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 394-396 in the revised manuscript:

Lin, M., Zhang, X., Li, M., Xu, Y., Zhang, Z., Tao, J., Su, B., Liu, L., Shen, Y., and Thiemens, M. H.: Five-S-isotope evidence of two distinct mass-independent sulfur isotope effects and implications for the modern and Archean atmospheres, Proc. Natl. Acad. Sci., 115, 8541–8546, https://doi.org/10.1073/pnas.1803420115, 2018.

15. Sinha, 2013 – incomplete reference (missing journal, volume, pages)

Response: We sincerely appreciate the reviewers' insightful suggestions for improving the references. Sinha, 2013-the complete reference information has been supplemented.

Harris, E., Sinha, B., Hoppe, P., and Ono, S.: High-precision measurements of ^{33}S and ^{34}S fractionation during SO_2 oxidation reveal causes of seasonality in SO_2 and sulfate isotopic composition, Environ. Sci. Technol., 47, 12174–12183, https://doi.org/10.1021/es402824c, 2013a.

For more clarity, we have added/revised these sentences as following.

Page 20, Lines 376-378 in the revised manuscript:

Harris, E., Sinha, B., Hoppe, P., and Ono, S.: High-precision measurements of ^{33}S and ^{34}S fractionation during SO_2 oxidation reveal causes of seasonality in SO_2 and sulfate isotopic composition, Environ. Sci. Technol., 47, 12174–12183, https://doi.org/10.1021/es402824c, 2013a.

Reviewer#2's comments:

This study is interesting and novel. It does provide a new perspective towards sulfate source apportionment, accounting for newer pathways for sulfate formation. I suggest the authors to comment on the following and make necessary changes in the manuscript:

1. Role of primary sulfates: I think this aspect has been overlooked. It needs to be quantified as the works of Daie et al. (2019) and Song et al., (2024) reveal nearly half of atmospheric sulfate could be attributed to primary sulfate. Once the authors attribute this fraction, the remaining can be attributed to secondary and as such Fig. 6 needs to show this division clearly with a separate sub-figure.

Response: We thank the reviewer for the insightful comment. In the revised manuscript, we have thoroughly refined the seasonal and process-specific partitioning of primary and secondary sulfates. To address the well-known underestimation of primary sulfate emissions, a factor that partially accounts for the missing sulfate phenomenon often encountered in chemical transport modeling, our refined mass-balance framework parameterizes anthropogenic primary sulfate (n_{ap}) as 3% of total anthropogenic sulfur emissions. Under the reasonable assumption that ambient SO_2 and secondary sulfate precursors are predominantly of anthropogenic origin, the molar concentrations of the various sulfate fractions are resolved through a coupled system of equations:

$$n_{ps} = n_{ss} + n_{ts} + n_{ap} \quad (1)$$

$$n_{ap} = 3\% \times \left(n_{SO_2} + n_{sas}\right) \quad (2)$$

$$n_{sas} = n_{tos} - n_{ss} - n_{ts} - n_{ap} \quad (3)$$

where n_{tos}, n_{ps}, and n_{sas} represent the molar concentrations of total, primary, and secondary atmospheric sulfate, respectively, with the primary fraction further resolved into sea-salt (n_{ss}), terrestrial (n_{ts}), and anthropogenic primary (n_{ap}) components. To constrain these natural backgrounds, we employed companion tracer concentrations and mass ratios; specifically, sea-salt sulfate was quantified from soluble Na^+ assuming a purely marine origin (n_{ss}=k[Na^+], where k=[SO_4^{2-}]/[Na^+]=0.25), while

terrestrial sulfate was evaluated based on crustal Ca^{2+} abundances (0.18×[Ca^{2+}]). Building upon this physical allocation, the stable sulfur isotope signatures ($\delta^{34}S$) are integrated via an isotopic mass-balance framework to isolate the secondary formation pathways:

$$\delta^{34}S_{obs} = f_{ss} \times \delta^{34}S_{ss} + f_{ts} \times \delta^{34}S_{ts} + f_{ap} \times \delta^{34}S_{ap} + f_{sas} \times \delta^{34}S_{sas} \quad (4)$$

$$f_{ps} = f_{ss} + f_{ts} + f_{ap} \quad (5)$$

Here, $\delta^{34}S_{obs}$ denotes the bulk observed $\delta^{34}S$-SO_4^{2-} value, while the terms prefixed with *f* represent the corresponding molar fractions of each discrete source relative to the total sulfate burden, matched with their respective endmember isotopic signatures ($\delta^{34}S_{ss}$, $\delta^{34}S_{ts}$, $\delta^{34}S_{ap}$, and $\delta^{34}S_{sas}$). Derived from these calculations, the anthropogenic contribution to the ambient sulfate burden is quantified at 19% during winter and 8% during summer, with these refined values and their accompanying discussions now fully integrated into the revised text.

For more clarity, we have added/revised these sentences as following.

Page 6-7, Lines 167-189 in the revised manuscript:

2.7 Estimation of primary sulfate and secondary sulfate

The underestimation of primary sulfate emissions can partially account for the phenomenon known as missing sulfates. The anthropogenic primary sulfate is estimated as 3% of anthropogenic sources of sulfur emissions in the model. Assuming all the detected concentrations of SO_2 and precursors of secondary sulfate are anthropogenic, we can deduce Eq. (17). Considering the influence of anthropogenic sulfate sources on primary sulfate, the method for estimating primary sulfate can be expressed as follows:

$$n_{ps} = n_{ss} + n_{ts} + n_{ap} \quad (16)$$

$$n_{ap} = 3\% \times \left(n_{SO_2} + n_{sas}\right) \quad (17)$$

$$n_{sas} = n_{tos} - n_{ss} - n_{ts} - n_{ap} \quad (18)$$

where n_{tos}, n_{ps}, and n_{sas} represent the molar concentrations of total, primary, and secondary atmospheric sulfate, respectively, with the primary fraction further resolved into sea-salt (n_{ss}), terrestrial (n_{ts}), and anthropogenic primary (n_{ap})

components. To constrain these natural backgrounds, we employed companion tracer concentrations and mass ratios; specifically, sea-salt sulfate was quantified from soluble Na^+ assuming a purely marine origin (n_{ss}= k[Na^+], where k=[SO_4^{2-}]/[Na^+]=0.25), while terrestrial sulfate was evaluated based on crustal Ca^{2+} abundances (0.18×[Ca^{2+}]). Building upon this physical allocation, the stable sulfur isotope signatures ($\delta^{34}S$) are integrated via an isotopic mass-balance framework to isolate the secondary formation pathways:

$$\delta^{34}S_{obs} = f_{ss} \times \delta^{34}S_{ss} + f_{ts} \times \delta^{34}S_{ts} + f_{ap} \times \delta^{34}S_{ap} + f_{sas} \times \delta^{34}S_{sas} \quad (19)$$

$$f_{ps} = f_{ss} + f_{ts} + f_{ap} \quad (20)$$

Here, $\delta^{34}S_{obs}$ denotes the bulk observed $\delta^{34}S$-SO_4^{2-} value, while the terms prefixed with *f* represent the corresponding molar fractions of each discrete source relative to the total sulfate burden, matched with their respective endmember isotopic signatures where f_{ps}, f_{ss}, f_{ts}, f_{ap}, and f_{sas} are the proportion of primary sulfate, sea salt sulfate, terrestrial sulfate, anthropogenic primary sulfate, and secondary sulfate, respectively ($\delta^{34}S_{ss}$, $\delta^{34}S_{ts}$, $\delta^{34}S_{ap}$, and $\delta^{34}S_{sas}$).

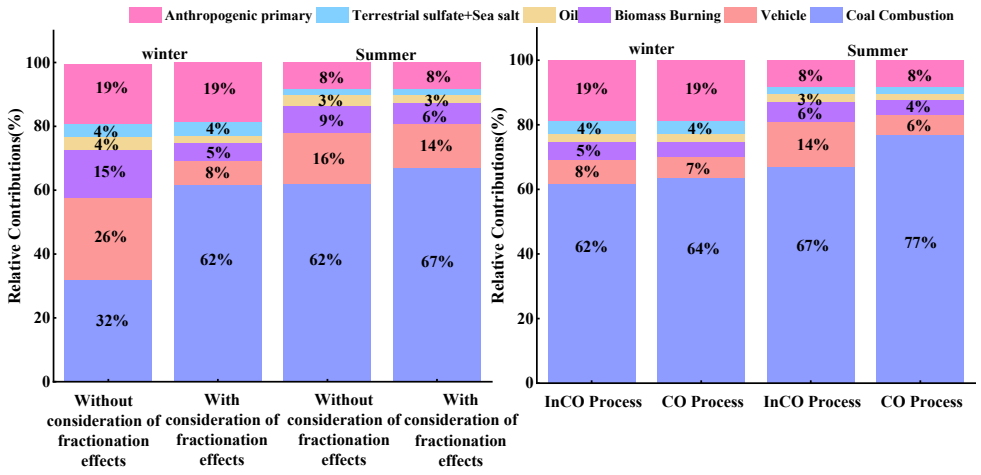

Figure 7. (a) Seasonal variations of source apportionments to sulfate aerosols in Nanjing. (b) Source apportionments of sulfate aerosols in Nanjing resolved by the SIAR model with consideration of fractionation effects under InCO Process and CO Process.

For more clarity, we have added/revised these sentences as following.

Page 16, Lines 293-299 in the revised manuscript:

Neglecting fractionation effects distorts source contributions, yielding winter estimates of 19% (anthropogenic primary sulfate) ,4% (Terrestrial sulfate and Sea salt), 32%

(coal), 4% (oil), 15% (biomass), and 26% (vehicle), alongside summer values of 8%, 2%, 62%, 3%, 9%, and 16% (Fig. 7a) respectively-results that inaccurately emphasize traffic emissions contrary to regional emission inventories and chemical transport modeling. Incorporating fractionation factors resolves this discrepancy, aligning sulfate sources with inventory data where coal combustion dominates annually, while idealized complete-oxidation models underestimate summer vehicle contributions by 8% and overestimate coal combustion proportions (about 10%) by comparable margins despite minimal winter deviations.

Reference:

[1] Ding, X., Li, Q., Wu, D., Wang, X., Li, M., Wang, T., Wang, L., and Chen, J.: Direct observation of sulfate explosive growth in wet plumes emitted from typical coal-fired stationary sources, Geophys. Res. Lett., 48, e2020GL092071, https://doi.org/10.1029/2020GL092071, 2021.

[2] Alexander, B., Park, R.J., Jacob, D.J., Gong, S., Transition metal-catalyzed oxidation of atmospheric sulfur: global implications for the sulfur budget. J. Geophys. Res. Atmos. 114, D02309, https://doi.org/10.1029/2008JD010486, 2009.

[3] He, P., Alexander, B., Geng, L., Chi, X., Fan, S., Zhan, H., Kang, H., Zheng, G., Cheng, Y., Su, H., Liu, C., and Xie, Z.: Isotopic constraints on heterogeneous sulfate production in Beijing haze, Atmos. Chem. Phys., 18, 5515–5528, https://doi.org/10.5194/acp-18-5515-2018, 2018.

[4] Zheng, M., Song, D., Zhang, D., Cao, Y., and Fan, H.: Using sulfur isotopes to constrain the sources of sulfate in $PM_{2.5}$ during the winter in Jiaozuo City, Atmos. Environ., 332, 120618, https://doi.org/10.1016/j.atmosenv.2024.120618, 2024.

[5] Dasari, S. and Widory, D.: Retrospective isotopic analysis of summertime urban atmospheric sulfate in South Asia using improved source constraints, ACS ES&T Air, 1, 357–364, https://doi.org/10.1021/acsestair.3c00060, 2024.

[6] Dasari, S., Paris, G., Saar, B., Pei, Q., Cong, Z., and Widory, D.: Sulfur isotope anomalies ($\Delta^{33}S$) in urban air pollution linked to mineral-dust-associated sulfate,

Environ. Sci. Technol. Lett., 9, 604–610, https://doi.org/10.1021/acs.estlett.2c00312, 2022.

2. Terrigenous sulfate/mineral dust: Please refer to Dasari et al., 2022 ES&T L and 2024 ES&T Air (which should be cited as these are also relevant works to this study) wherein the role of long-range transported mineral dust/terr-sulfate has been shown as an important factor. The authors need to apportion this source, too.

Response: In response to the reviewers' constructive comments, terrigenous sulfate emissions have been rigorously accounted for in our updated budget matrix. The corresponding descriptions in the revised manuscript have been systematically updated to reflect these new calculation results, thereby providing a more accurate representation of localized precursor contributions.

For more clarity, we have added/revised these sentences as following.

Page 16, Lines 286-288 in the revised manuscript:

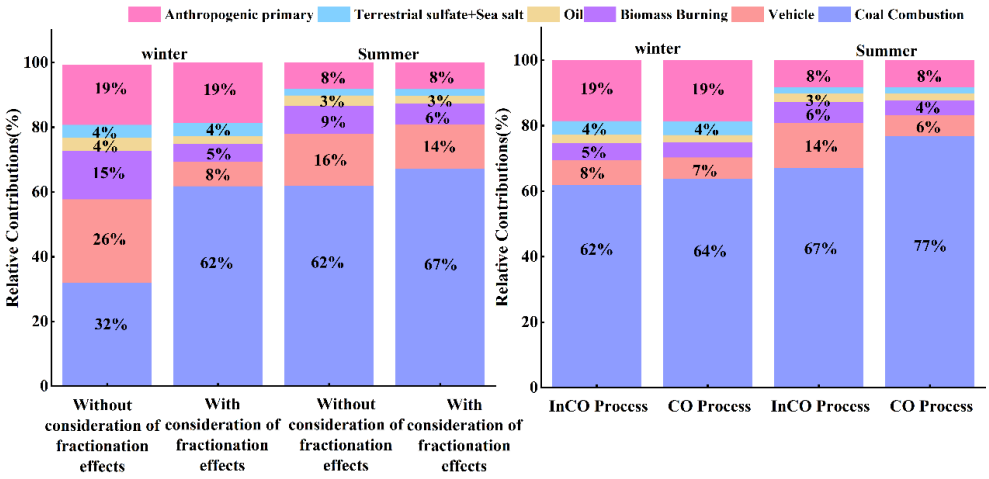

Figure 7. (a) Seasonal variations of source apportionments to sulfate aerosols in Nanjing. (b) Source apportionments of sulfate aerosols in Nanjing resolved by the SIAR model with consideration of fractionation effects under InCO Process and CO Process.

Reference:

[1] Dasari, S., Paris, G., Saar, B., Pei, Q., Cong, Z., and Widory, D.: Sulfur isotope anomalies ($\Delta^{33}S$) in urban air pollution linked to mineral-dust-associated sulfate, Environ. Sci. Technol. Lett., 9, 604–610, https://doi.org/10.1021/acs.estlett.2c00312, 2022.

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[3] Zheng, M., Song, D., Zhang, D., Cao, Y., and Fan, H.: Using sulfur isotopes to constrain the sources of sulfate in $PM_{2.5}$ during the winter in Jiaozuo City, Atmos. Environ., 332, 120618, https://doi.org/10.1016/j.atmosenv.2024.120618, 2024.

3. Cluster analysis vs. footprint analysis: Please note the AMBTs can show the air masses arriving from a certain region, the footprint of the contributing regions can be very different. Please refer to Dasari et al., 2020 ES&T for this distinction. As such, solely banking on the AMBTs isnt proof enough of the regional source contributions. The authors should convincingly show that the footprint analysis matches the AMBTs.

Response: We sincerely thank the reviewer for highlighting this critical methodological distinction and for directing our attention to the highly relevant work by Dasari et al. (2020). We completely agree with the fundamental premise that while Air Mass Backward Trajectories (AMBTs) effectively delineate atmospheric transport pathways, they do not inherently capture the emission footprint or the actual residence time of pollutants over contributing regions. Consequently, relying exclusively on AMBTs leaves a gap in definitively proving regional source contributions.

To address this insightful critique and comprehensively validate our regional source apportionment, we have significantly expanded our spatial analysis framework. In the revised manuscript, we have introduced rigorous FLEXPART footprint modeling (Figure 4) alongside Concentration Weighted Trajectory (CWT) mapping (Fig. S5). By systematically comparing these advanced diagnostics with our original trajectory clusters (Fig. S4), we can now convincingly demonstrate that the emission footprints perfectly match the AMBTs.

Page 13, Lines 246-249 in the revised manuscript:

Besides, by synergistically combining AMBTs (Fig. S4), CWT (Fig. S5) analysis, and FLEXPART footprint modeling (Fig. 4a, 4b), our integrated framework now successfully bridges the gap between empirical trajectory data and actual emission source strengths. This robust spatial validation explicitly supports our overarching objective to

resolve long-standing discrepancies in atmospheric sulfate source attribution.

Page 5-6, in the Supplementary Information:

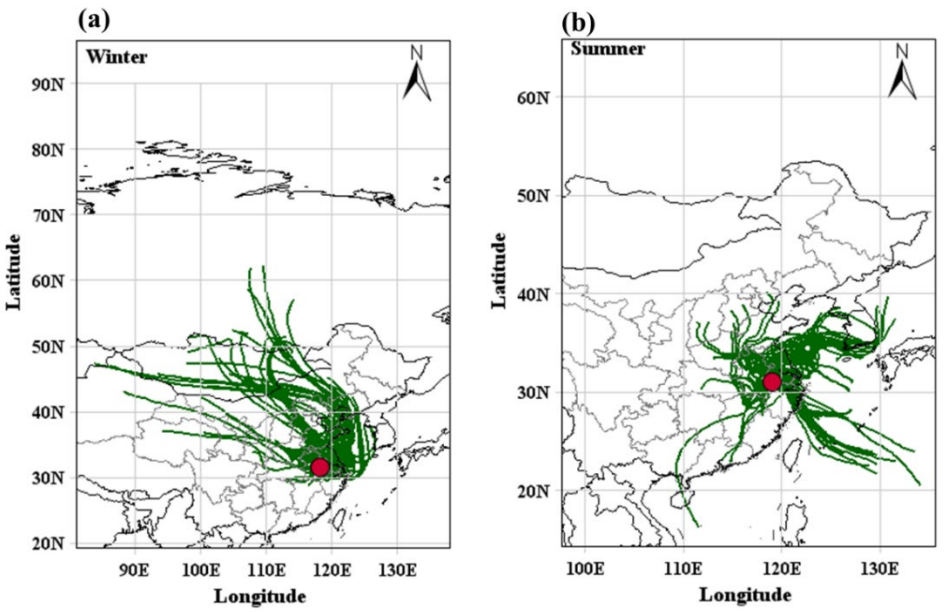

Figure S4. Air mass clusters (a) Winter, (b) Summer.

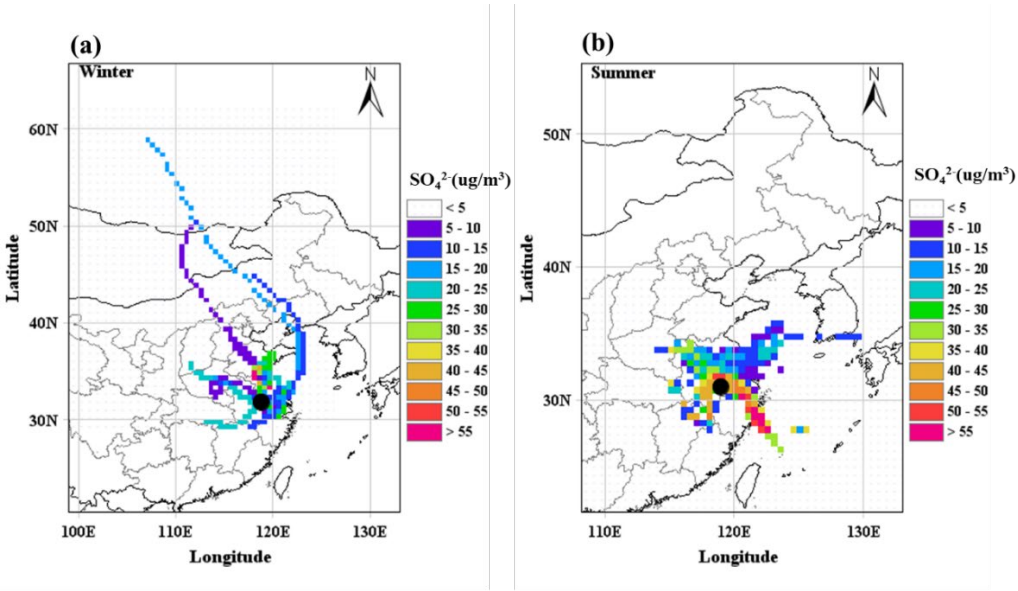

Figure S5. The Concentration weighted trajectory (CWT) maps for sulfate (SO_4^{2-}) mass concentrations (μg m^{-3}) at Nanjing during (a) Winter and (b) Summer are shown, respectively. Color scale represents the SO_4^{2-} mass concentrations.

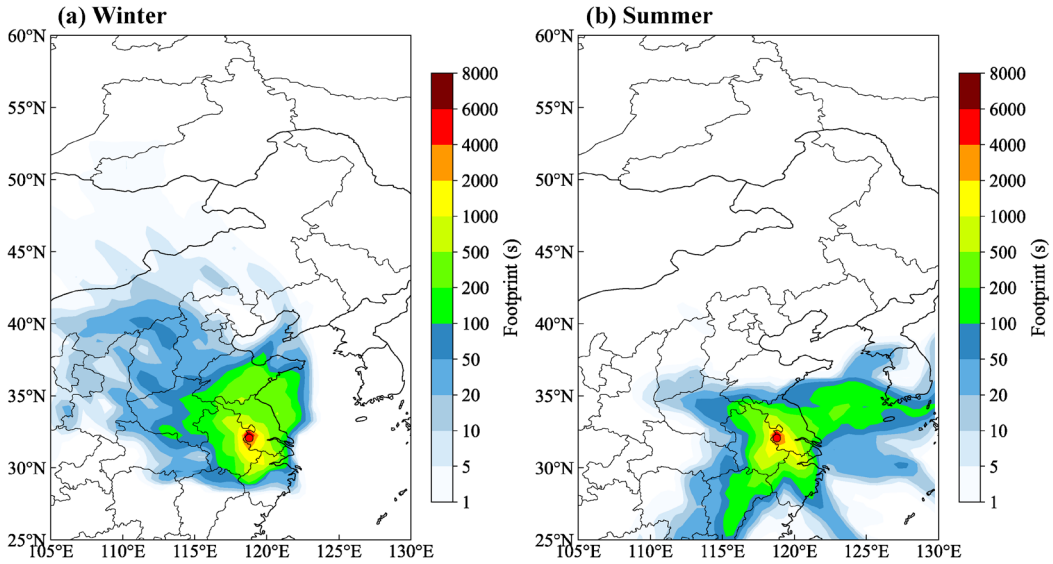

Figure 4. Footprints of sulfate aerosols at the receptor site during the (a) winter and (b) summer computed by the FLEXPART model. The color scale denotes the residence time (s) of sulfate aerosols in the grid cell.

4. NO_2 mediated pathway: Growing evidence suggest this pathway is more active in winter foggy/hazy conditions Wang et al., 2020 Nat. Comm. However, here the authors suggest this pathway is key with contribution in winter and summer nearly the same. This is contradictory to growing body of research (both lab-based and field-based). I suggest the authors reconsider the literature findings and convincingly show this and rethink Fig. 4.

Response: We sincerely appreciate the reviewer for highlighting this critical point and directing our attention to the seminal work by Wang et al. (2020). We completely agree with the growing scientific consensus that the aqueous oxidation of SO_2 mediated by NO_2 is highly sensitive to aerosol liquid water content and pH, making it particularly potent during winter fog and haze conditions. Upon carefully reevaluating our data presentation in Fig 4, we realize that displaying solely the relative percentage contributions inadvertently masked the actual seasonal dynamics of this chemical pathway. While the fractional proportion of the NO_2-mediated pathway appears visually comparable between winter and summer in our isotopic distribution, the absolute mass of sulfate generated via this route differs drastically. Our field measurements demonstrate that total particulate sulfate concentrations peak at 27.55 ± 14.36 μg m^{-3} during severe haze events, which predominantly occur in winter. Consequently, when translating

these relative fractions into absolute mass concentrations, the NO_2 pathway produces a substantially higher burden of particulate sulfate in winter compared to summer. This mass-based dynamic aligns perfectly with the enhanced wintertime activity reported by Wang et al. (2020) and the broader field-based consensus. Furthermore, the sustained relative fraction of the NO_2 pathway during the summer months in Nanjing is not an artifact of our isotopic model, but rather a direct reflection of the region's specific emission inventory. As indicated by our $[NO_3^-]/[SO_4^{2-}]$ mass ratio analysis, which yielded values spanning from 0.15 to 1.95, with a mean of 0.98 ± 0.42, mobile vehicular emissions constitute a major atmospheric driver in this region. When these continuous, high-volume NO_x emissions couple with the incomplete SO_2 oxidation regimes characteristic of our summer study site, the NO_2 pathway maintains a significant fractional foothold, even though the absolute sulfate yield remains much lower than in winter. To eliminate this apparent contradiction and integrate the reviewer's excellent insights, we have thoroughly revised the discussion section corresponding to Figure 4 to explicitly distinguish between relative pathway fractions and absolute sulfate mass yields. We formally incorporated Wang et al. (2020) into the text, detailing how our absolute concentration metrics strongly corroborate their lab- and field-based findings regarding enhanced wintertime NO_2 oxidation. We expanded the narrative to clarify how local vehicular NO_x emissions sustain the relative percentage of this pathway during summer, ensuring the isotopic model results are properly contextualized within the region's specific atmospheric chemistry.

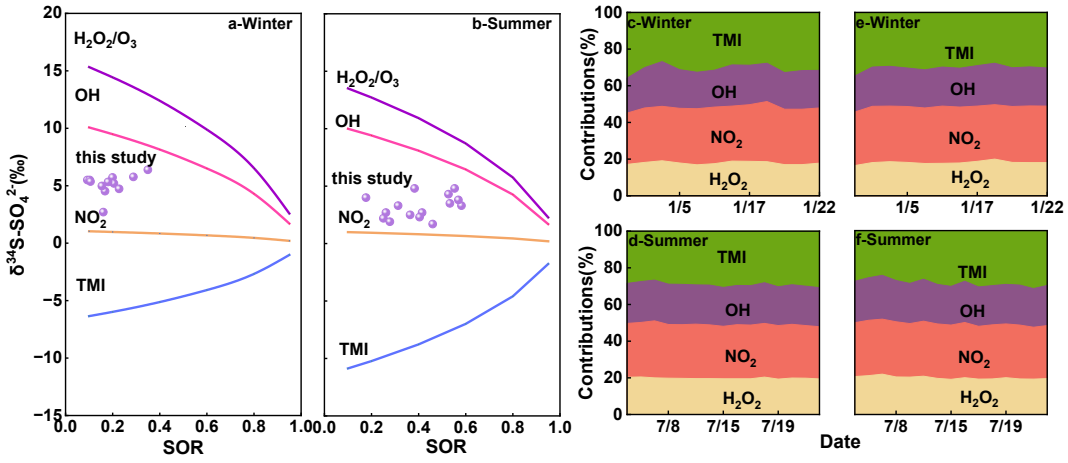

Figure 5. (a, b) Rayleigh fractionation models for secondary SO_4^{2-} formation in

different seasons. (c, d, e, f) Relative contributions of primary, OH, TMI, NO_2, and H_2O_2/O_3 pathways to secondary SO_4^{2-} generation across different seasons. (c, d) represents the fractionation effects under InCO Process; (e, f) represents the fractionation effects under CO Process.

5. Referencing is poor and needs to be updated to correct format and form. Please also add relevant regional works from other parts of the world to address the issue with d34S-based source apportionment of sulfate.

Response: We sincerely appreciate the reviewer's constructive feedback. We have updated and corrected the format and form of the references.

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6. While the study is interesting, there are many caveats (e.g, with pathway attribution) as such some wording like 'paradigm shift' seem unncessary. I suggest the authors to reconsider such wordings.

Response: We are deeply grateful for the reviewer's constructive feedback, which has prompted a comprehensive linguistic refinement of the entire manuscript to ensure maximum clarity and scientific readability.