Author Responses (AR) to Referee Comments (RC) and resulting revisions of ms egusphere-2025-5334: "Isotopic apportionment of sulfate aerosols between natural and anthropogenic sources in the outflow of South Asia" by Sean Clarke, Henry Holmstrand, Krishnakant Budhavant, Manoj Remani, Sophie Haslett, Katerina Rodiouchkina, Ellen Kooijman, and Örjan Gustafsson

Reference: https://doi.org/10.5194/egusphere-2025-5334

We sincerely thank both reviewers for thoroughly reviewing and giving constructive feedback that is helping to clarify the significance and importance of this manuscript during revision.

All reviewer comments are included below in *black italic font* each followed by our detailed author responses, formatted as indented blue text.

Anonymous Referee #1: *Clarke et al. present new measurements of d34S(SO4) from the Maldives in South Asia, a region that is severely impacted by anthropogenic pollution. These measurements are very valuable and can help quantify the sources of sulfate in this region. Clarke et al. present a solid interpretation of their measurements. I have written some suggestions below to improve their analysis*.

We are grateful for this supportive overall assessment. We also appreciate the thoughtful and detailed review comments, which we have carefully considered below and which have helped significantly to further improve the ms.

Major comments:

- *I assume that methanesulfonic acid (MSA) is not separated through the anion-retaining mesh method described in 2.4.1. Please describe how much you expect MSA contamination to alter measured d34S(SO4).*

Author Reply:

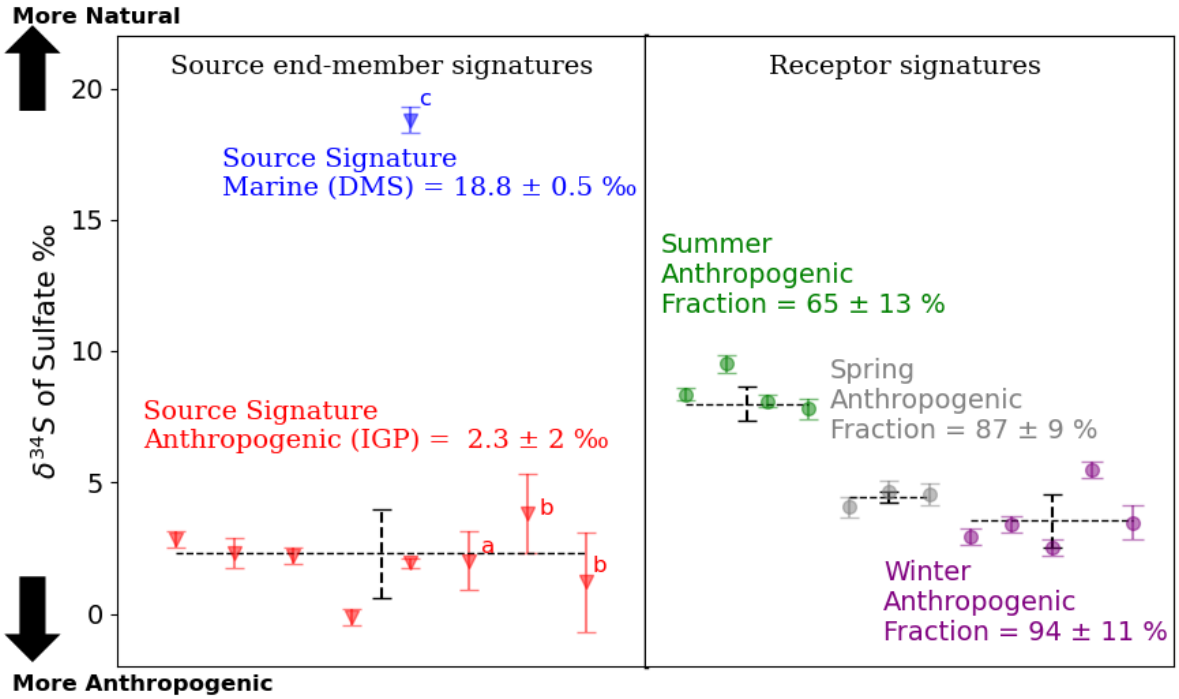
We thank the reviewer for highlighting this important aspect, however, we expect MSA contamination to have a negligible effect on measured $\delta^{34}S(SO_4^{2-})$. The isotopic composition of MSA has been reported as 17.4 ± 0.7‰ (Sanusi et al., 2006). In the Indian Ocean region, MSA concentrations are typically ~30–60 ng m^{-3} (Aswini et al., 2020), compared with sulfate concentrations on the order of ~1 - 16 µg m^{-3} during this study, implying an average MSA:SO_4 mass fraction of ≲1–6%. A simple two-endmember mass balance ($\Delta\delta \approx f\_MSA(\delta\_MSA - \delta\_SO4)$) indicates that for typical f_MSA ≲1%, any shift would be ≤~0.1–0.2‰ even under conservative isotopic contrasts for the period.

We suggest to address this through an addition as follows: in Text S1: *Methanesulfonic acid (MSA) is not separated through the anion-retaining mesh and may in principle therefore influence measured $\delta^{34}S(SO_4^{2-})$. Methanesulfonic acid (MSA) has been reported to have $\delta^{34}S = 17.4 \pm 0.7‰$ (Sanusi et al., 2006). In the Indian Ocean region, MSA concentrations are typically ~30–60 ng m^{-3} (Aswini et al., 2020), which are small relative to sulfate (~1–16 µg m^{-3} reported in this study). Using a simple mass-balance estimate, $\Delta\delta^{34}S(SO_4^{2-}) \approx f\_MSA(\delta\_MSA - \delta\_SO4)$, the expected influence of any MSA carryover is ≤~0.1–0.2‰ for typical f_MSA ≲1%, and therefore negligible relative to analytical uncertainty.*

- *Figure 2 is confusing. I recommend splitting the source signatures and the d34S measurements into two subplots in figure 2.*

Author reply

We thank the reviewer for helping us make the graphic clearer and have now drafted the edited version below



- *Jongebloed et al. (2023) also compiled DMS-derived sulfurous compounds, including the measurements from Amrani et al. (2013) and other studies, to estimate $d34S(SO4)_{DMS}$ = 18.8 permille, which is slightly lower than the 19.7 used here. Justify why you use 19.7 – are you sure 18.8 is not a more accurate value*?

Author Reply:

We thank the reviewer and agree that we should use 18.8‰. In the original version, we effectively used the $\delta^{34}S$ value of DMSP(aq) (~19.7‰) reported by Amrani et al., 2013, rather than the more appropriate DMS-derived sulfate endmember. This choice did not fully account for the isotopic fractionations associated with conversion from DMSP to DMS (−~0.5‰) and subsequent sea–air transfer (DMS(aq) → DMS(g), −~0.5‰). Accounting for these steps lowers the expected DMS-related endmember and is consistent with the $\delta^{34}S(SO_4^{2-})_{(DMS)}$ reported by Jongebloed et al., 2023. We therefore update the mixing model using 18.8‰.

This revision changes the inferred DMS contribution:

- Summer: 67% → 65%
- Spring: 88% → 87%
- Winter: 94% → 94%

Changes in MS lines:

DMS end-member changed to 18.8 ‰

:

- *Harris et al. (2013) and others have shown that d34S(SO4) is different from d34S(SO2) due to fractionation during oxidation of SO2. Why is it justifiable to create a mixing model here that ignores this fractionation? Is it because all your source signatures are determined based on sulfate that has already been oxidized? I think this is briefly mentioned in Text S1, but should be mentioned in 1-2 sentences in the main text*.

Author reply

We thank the reviewer and agree that additional lines should be added to the ms to clairfy the effect of $\delta^{34}S(SO_2)$ → $\delta^{34}S(SO_4^{2-})$. These effects are ideally captured by measuring at source aerosols but remain an uncertainty in estimations due to the effect of oxidative pathway.

The advantage of analysing receptor-integrated source region aerosols is that they already incorporate the isotope fractionation associated with SO_2 oxidation to sulfate for the anthropogenic endmembers. We agree that this point should be highlighted in the manuscript.

Proposed addition to ms:

"*Analysing source aerosols captures isotope fractionation during SO_2 oxidation to sulfate, which can be substantial (≈3‰ enrichment in urban environments; Lee et al., 2023); see SI Text S1*."

- *The way that the anthropogenic source signature was determined is not clearly explained. This is an important and uncertain aspect of your analysis, so it should be addressed more explicitly in the main text. I assume it is determined by just taking the d34S(SO4) measurements from IGP and BCOB based on this sentence: "Samples from BCOB, which were used to represent the anthropogenic end-member of sulfate, were assumed to be predominantly anthropogenic in origin (~100 %)"*

  Author reply:

  Yes, the reviewer is correct that this sentence should be clarified. The integrated continental anthropogenic signature was calculated from $\delta^{34}S(SO_4^{2-})$ measured on aerosol filters collected in the IGP (Delhi and BCOB), which we interpret as representative of anthropogenic sulfate in the region. We note, however, that if sulfate formation pathways and oxidation conditions differ between locations or periods, the associated isotope fractionation during SO_2-to-sulfate conversion may vary; consequently, the measured $\delta^{34}S(SO_4^{2-})$ could deviate from the instantaneous source $\delta^{34}S(SO_2)$ and from a simple isotopic equilibrium assumption. This also partially motivated sampling at BCOB, located at the outflow of the IGP (downwind of Delhi), where aerosol composition is expected to reflect a more integrated IGP-region signal. We did not observe clear systematic changes in $\delta^{34}S$ with more aged air masses within our dataset.

  Hence, we have revised the sentence to clarify

  The integrated continental anthropogenic signature was calculated directly from $\delta^{34}S(SO_4^{2-})$ measured on aerosol filters in the IGP (Delhi and BCOB), with samples measured in this study and from the literature, resulting in an end-member value of 2.3 ± 1.7 ‰ (see Fig. 2, Table S1; Dasari & Widory, 2024; Sawlani et al., 2019, n = 50).

- *Even in a highly polluted region, is it realistic that 100% of sulfate is anthropogenic? I wonder if this assumption results in an anthropogenic signature that is too high or too low. It would be good to test this assumption by seeing how your results would change if you assumed that the sulfate in BCOB is only 90% anthropogenic, for example.*

  Author reply

  We thank Reviewer #1 for highlighting this point. Although sulfate is unlikely to be entirely anthropogenic, it is expected to be close to 100% in this highly polluted IGP system. Our sensitivity test shows that relaxing this assumption does not change the results beyond the propagated uncertainty (shown below). Dasari & Widory, 2024 estimated contributions from biomass burning (2 ± 2%) and road dust (4 ± 3%) for the IGP/Delhi region. Biomass burning in this region is largely anthropogenically driven, but we acknowledge it represents a distinct source. The Dasari & Widory, 2024 estimates are based on PM_{10}, which have a higher dust fraction than our $PM_{2.5}$ measurements; therefore, the reported ~4% road-dust contribution can be considered an upper-bound estimate for our study. Dasari & Widory, 2024 also adopt a road-dust $\delta^{34}S$ value of 2 ± 1‰ from Sawlani et al. (2019). This value is more consistent with resuspended, pollution-

derived sulfate than with purely mineral sulfate, which is typically higher (e.g., ~+7.4‰ for gypsum-derived sulfate; Olson et al., 2021). We will incorporate these clarifications in the Supporting Information and include a sensitivity test evaluating the effect of a 5–10% non-anthropogenic sulfate fraction within the BCOB anthropogenic end-member.

Proposed addition to ms

The IGP end-member in this study was assumed to be predominantly anthropogenic. Potential crustal and biogenic contributions are expected to be minor (Dasari & Widory, 2024). Our sensitivity analysis shows that including a 5–10% non-anthropogenic sulfate fraction does not change the source apportionment beyond the propagated uncertainty (see SI Text S3).

Proposed addition to Supplementary information (SI Text S3 and SI Table 2,)

Text S3: Sensitivity analysis of non-anthropogenic inputs to the continental end-member

The source-derived "anthropogenic" end-member assumes that sulfate collected at the receptor site represents predominantly anthropogenic sulfate. In practice, this end-member may also include some contributions of SO_4^{2-} from source categories not explicitly treated in the main mixing model (e.g., biomass burning or metallurgical emissions). For the IGP/Delhi region, biomass burning has been estimated at 2 ± 2% (Dasari & Widory, 2024). This partly motivated our use of the term 'anthropogenic end-member' rather than a 'fossil-fuel end-member'."

For non-anthropogenic sources Dasari & Widory, (2024) estimated a road-dust contribution of 4 ± 3% for the IGP/Delhi region (based on PM_{10}), which is likely an upper bound relative to our $PM_{2.5}$ dataset. The road-dust $\delta^{34}S$ value used in that study (2 ± 1‰; Sawlani et al., 2019) is consistent with resuspended, pollution-derived sulfate rather than purely mineral sulfate, which is typically higher (~+7.4‰ for gypsum-derived sulfate; Olson et al., 2021).

To test the sensitivity of our conclusions to potential non-anthropogenic sulfate in the anthropogenic end-member, we performed a dilution/sensitivity analysis in which 5% and 10% of the anthropogenic end-member are replaced by "other" sulfate spanning a wide range of $\delta^{34}S$ values (DMS-derived, volcanic, terrestrial biogenic, and mineral dust sulfate; Table S2). The most extreme case assigns the full 10% "other" fraction to DMS-derived sulfate ($\delta^{34}S$ = +18.8‰), which is unlikely for aerosols originating from Delhi but provides an extreme upper bound on the potential effect. Across scenarios, the maximum change in inferred anthropogenic contribution is ~9 percentage points, comparable to our overall model uncertainty; therefore, our main conclusions are robust.

Table S2: Change in anthropogenic contribution when anthropogenic end-member consider non 100% anthropogenic

	100% Anthropogenic ;0% Other	**95% Anthropogenic ;5% Other**	**90% Anthropogenic ;10% Other**

Non anthropogenic contribution	Season	Percentage anthropogenic	Season	Percentage anthropogenic	Season	Percentage anthropogenic
DMS (+18.8)	Winter	94	Winter	89	Winter	85
	Spring	87	Spring	83	Spring	79
	Summer	65	Summer	61.7	Summer	59
Volcanic (+4.1)	Winter	94	Winter	93	Winter	93
	Spring	87	Spring	87	Spring	86
	Summer	65	Summer	65	Summer	65
Terrestrial biogenic (–5)	Winter	94	Winter	96	Winter	99
	Spring	87	Spring	89	Spring	92
	Summer	65	Summer	67	Summer	69
Soil dust (+7.4)	Winter	94	Winter	93	Winter	91
	Spring	87	Spring	86	Spring	84
	Summer	65	Summer	64	Summer	63

- *Another way to examine this would be to create a Keeling Plot (plot 1/nssSO4 vs. d34S(nssSO4)) of the data in Table S1. If anthropogenic sulfate is the more variable sulfate source, the y-intercept will represent the anthropogenic source signature. A Keeling Plot might not be appropriate if the other sources are too variable (see Pataki et al., 2003). I leave the decision of whether to evaluate a Keeling Plot to the authors of this study.*

Author reply

We thank reviewer #1 for this helpful suggestion. We evaluated a Keeling plot approach ($\delta^{34}S(nssSO_4^{2-})$ vs. $1/[nssSO_4^{2-}]$; Pataki et al., 2003). Using all samples yields an intercept of $2.50 \pm 0.36‰$ (1σ), which is consistent with our derived anthropogenic end-member. However, the result is sensitive to season: excluding the summer samples produces a more depleted intercept of $1.2 \pm 0.64‰$. This sensitivity suggests that variability in non-anthropogenic sources and mixed source contributions may violate the assumptions of the Keeling approach for these aerosol samples. We therefore do not adopt the Keeling-plot-derived end-member, but we report the analysis in the SI for completeness.

Proposed addition to the MS (revised ms):

We also investigated the use of a Keeling-plot to determine the anthropogenic end-member, but did not apply this approach because mixed and variable sources could bias the inferred end-member toward depleted values (see Text S3 and Fig. S3).

Proposed addition to SI

Text S2: Keeling-plot approach for determining the anthropogenic end-member:

A Keeling plot analysis ($1/nssSO_4^{2-}$ vs. $\delta^{34}S(nssSO_4^{2-})$) gives an intercept of $2.50 \pm 0.36‰$ (1σ), similar to our anthropogenic endmember (see SI Fig). However, because the intercept is sensitive to sample selection (e.g., excluding summer samples yields $1.2 \pm 0.64‰$), we do not use the Keeling approach here due to concerns that mixed and variable sources violate its assumptions for aerosol sulfate (Pataki et al., 2003, Jongebloed et al., 2023).

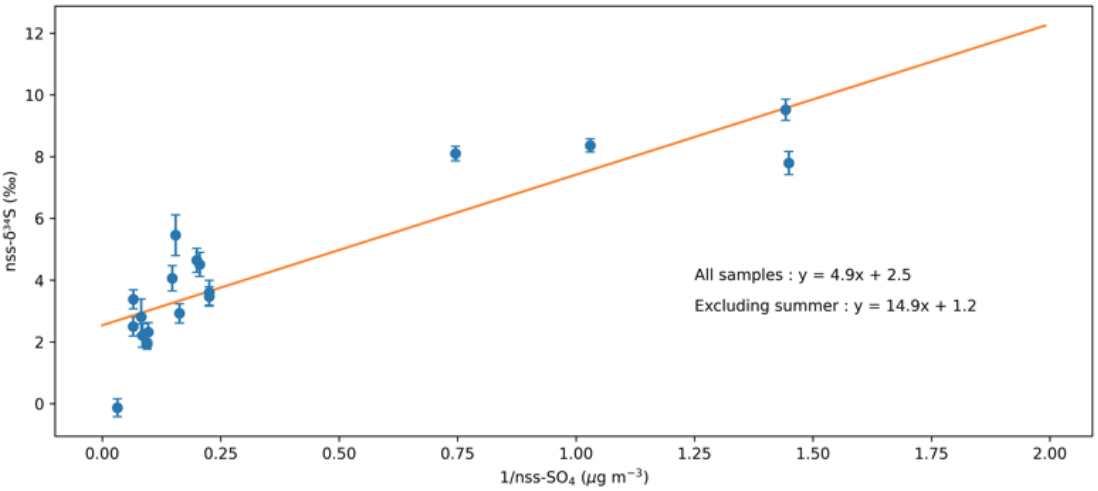


Fig. S3:

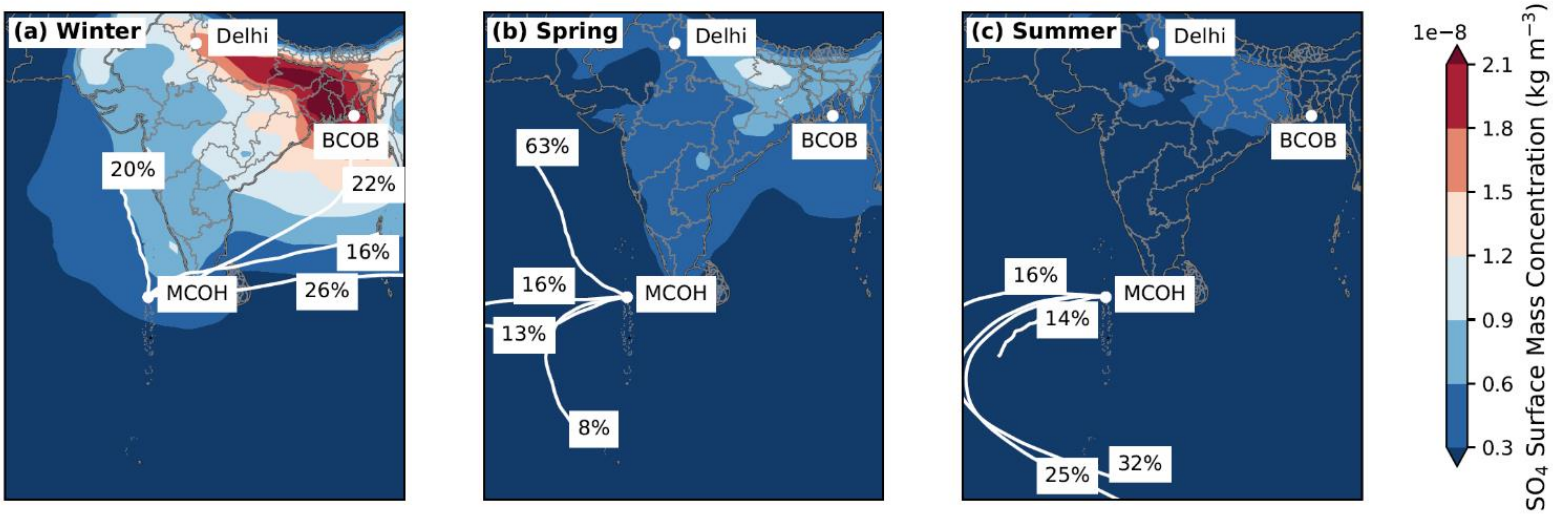
Keeling which shows the ($1/nssSO_4^{2-}$ vs. $\delta^{34}S(nssSO_4^{2-})$)

Minor comments:

- *Figure 1: the labels of the seasons (winter, autumn, summer) don't align with the caption (winter, spring, summer), unless if I'm missing something.*

Author reply

Thank you for catching this error. It should read spring and will be fixed.



- *This sentence needs a citation at the end: The ship end-member had a δ34S of 3 ± 3 ‰ taken from studies that measured δ34-SO4 and δ34-SO2 in the North Atlantic,*

which is thought to be representative of remote air masses with strong ship emissions from heavy fuel oil. Perhaps (Seguin et al., 2010, 2011; Wadleigh, 2004)?

Author reply

Agreed the sentence will be updated to have the references as stated in the first section of results

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Sanusi, A. A., Norman, A. L., Burridge, C., Wadleigh, M., & Tang, W. W. (2006). Determination of the S isotope composition of methanesulfonic acid. *Analytical Chemistry*, *78*(14). https://doi.org/10.1021/ac0600048