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 #2: *Major comments:*

Lines 170–176 and Section 3.1: The discussion regarding the choice of δ^{34}S end-member values for both biogenic and anthropogenic sources should be expanded, as these choices directly affect the subsequent source apportionment.

- *Biogenic sources: Several previous studies have reported δ^{34}S values for biogenic sulfur sources ranging from approximately 17.4 to 19.7 ‰ (e.g., (Jongebloed et al., 2023; Seguin et al., 2011, and references therein). The use of lower δ^{34}S values could potentially reduce the inferred contribution of anthropogenic sources in the present analysis. Please provide clearer justification for the selected biogenic end-member values and discuss the potential sensitivity of the results to this choice.*

  Author reply

  We agree with Reviewer #2 that this discussion should be expanded and clarified. We have reassessed the use of 19.7‰ for the marine-biogenic end-member. The value used in the submitted manuscript corresponds to DMSP in aqueous solution (≈19.7‰), whereas our end-member would more accurately represent DMS in air. During conversion and transfer there is fractionation, including from DMSP → DMS (≈ −0.5‰) and during sea–air transfer (DMS(aq) → DMS(g); ≈ −0.5‰). Therefore, the value reported by Jongebloed et al. (2023) is more appropriate, as it reflects atmospheric DMS. We will revise the manuscript to use 18.8‰ as the marine-biogenic (DMS) end-member

  This revision changes the derived (biogenic (DMS) contribution as follow:

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

- Winter: 94% → 94%

Hence, only a modest change, yet the correction shall absolutely be done.

DMS end-member changed to 18.8 ‰ in revised ms

- *Anthropogenic sources: A ship emission end-member of 3 ± 3 ‰ is introduced; however, in the final source apportionment it appears that a value of 2.3 ± 1.7 ‰ was used as the anthropogenic end-member without explicitly accounting for the ship contribution. Please clarify how this value was derived and explain how ship emissions were considered (or excluded) in determining the anthropogenic end-member.*

  Author reply

  We thank Reviewer #2 for this comment and agree that our explanation was not sufficiently clear. The continental anthropogenic end-member and the ship-emission end-member are treated as distinct end-members and are not mixed in our analysis. Because these end-members are relatively similar, the source-apportionment results are only weakly sensitive to this choice. Switching between them changes the estimated anthropogenic contribution by at most ~3%.

  We separated these two end-members as we stated that the appropriate anthropogenic signature can vary spatially and seasonally. During the monsoon, air masses reaching MCOH frequently originate over the open ocean, for which a ship-emissions end-member may be more appropriate than a continental anthropogenic end-member derived from the IGP. We acknowledge that ship emissions may also influence MCOH during winter and spring; however, both top-down (MERRA-2) and bottom-up (CEDS) constraints indicate that ship emissions are minor during these periods compared to the dominant continental pollution outflow (Buchard et al., 2017; Randles et al., 2017; Hoesly et al., 2018).

  Proposed edit to ms (revised)

  The oceanic anthropogenic and continental anthropogenic end-members were treated as distinct to reflect their different origins. Ship emissions may contribute to the continental end-member, but available top-down (MERRA-2) and bottom-up (CEDS) constraints indicate that these contributions are much smaller than land-based continental emissions (Buchard et al., 2017; Randles et al., 2017; Hoesly et al., 2018). In any case, the choice of end-member changes the inferred anthropogenic contribution by at most ~3%.

- *Lines 296–311: The discrepancy between the observed BC/SO_4 ratios (0.075 ± 0.03) and the inventory-based BC/SO_2 ratio (0.097) warrants further discussion, particularly because a stated goal of this study is to provide guidance for future mitigation strategies in South Asia.*
  - *How might atmospheric processes following emission (such as SO_2 oxidation to sulfate, differential deposition of BC and sulfate, or other removal mechanisms)*

affect the BC/SO_4 ratio? After accounting for these processes, is the difference between observed and inventory-based ratios still significant? In addition, could emissions of H_2S from mangrove ecosystems influence the observed ratios? If possible, the authors are encouraged to provide suggestions on how emission inventories for this region could be improved based on these findings.

- *Finally, as noted above, uncertainties associated with the choice of $\delta^{34}S$ end-member values may further propagate into the estimated BC/SO_4 ratios and should be acknowledged.*

Author reply

We agree with reviewer #2 that these issues are important and would be relevant for mitigation guidance. However, a quantitative treatment of that topic is beyond the scope of this paper and would require a chemical transport model. This includes post-emission atmospheric processing (oxidation of SO_2 to sulfate and differential deposition/removal of BC and sulfate) as well as potential reduced-sulfur inputs (e.g., mangrove H_2S).

This comment however prompted us to compare BC to anthropogenic sulfate rather than to total nssSO_4^{2-}, since BC is predominantly anthropogenic. This yields BC/SO_4^{2-}_anth = 0.082 ± 0.03 (spring and winter), which is closer to the inventory-based BC/SO_2 ratio (0.097). We note that the quoted ±0.03 reflects measurement variability only and does not include additional uncertainty propagated from the $\delta^{34}S$ end-member constraints.

Evaluating why these ratios differ quantitatively remains challenging. As the reviewer notes, differential transport and removal of BC and sulfate, as well as additional terrestrial sulfur inputs, could play a role. Black carbon at MCOH has been reported to have a longer atmospheric lifetime than more hygroscopic species (e.g., Budhavant et al., 2020). Preferential removal of sulfate during transport would therefore be expected to increase BC/SO_4^{2-} in situ relative to the emission-inventory ratio. In contrast, unaccounted biogenic sulfur inputs from mangroves (e.g., reduced-sulfur emissions that oxidize to sulfate) would add sulfate without co-emitted BC and thus decrease BC/SO_4^{2-}.

Proposed text to be added to the revised ms ():

When we compare to the in situ anthropogenic sulfate fraction (BC/anthro-SO_4^{2-}), the agreement improves (0.082 ± 0.03; spring and winter). The quoted uncertainty reflects measurement variability only and does not include additional uncertainty propagated from the $\delta^{34}S$ end-member constraints. Notably, the inventory-based ratio is closer to our in-situ constraint than the MERRA-2 estimate. The emission-inventory ratio does not include biogenic sulfur inputs, which could lower BC/SO_4^{2-}, nor does it account for preferential removal of hygroscopic sulfate during transport, which could act in the opposite direction by increasing BC/SO_4^{2-} (Krishnakant et al., 2020).

Specific comments:

- Line 113: Please provide information on the IC column used for ion quantification.’

Author Reply

The analytical details on analytical columns have been added to the Methods section: cation (Dionex IonPAc CS12A) anion (Dionex IonPac AS22 fast)

Line 118: Please explicitly state whether the sulfate-to-sodium ratio refers to a mass ratio or a molar ratio.

Author Reply:

We thank reviewer #2 and agree that this should be stated. The ratio is mass ratio. This is now explicitly stated in the revised Methods section.

- Lines 130–132: Please specify the chemical forms of the solutions used for adding Si and Na. For example, were these added in acidic (e.g., H_3SiO_4) and alkaline (e.g., NaOH) forms, respectively? Although readers can consult Rodiouchkina (2018) for methodological details such as solution concentrations, the simplified procedure presented here is difficult to follow from an analytical chemistry perspective without this clarification.

  Author Reply

  We agree that these details should be included and the ms will be revised accordingly.

  Silicon (Si) was added to all solutions as ammonium hexafluorosilicat ($(NH_4)_2SiF_6$**.**) at a concentration ratio of 1:1 (S:Si, µg mL^{-1}:µg mL^{-1}) for internal standardization. Additionally, sodium (Na) was added as sodium carbonate (Na_2CO_3) at a molar ratio of 2 (Na/S) to all measurement solutions.

Line 159: Replacing "%nssSO_4" with "F_nssSO_4" would improve readability and maintain consistency with other equations in the manuscript (e.g., F_biomass in Eq. (3) and F_DMS-SO_4 in Eq. (5)).

Author Reply :

Reviewer #2 is correct. Line corrected and will say F_nnsSO_4

References

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