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Isotopic apportionment of sulfate aerosols between natural and anthropogenic sources in the outflow of South Asia

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S1: Mass-spectrometer settings for $\delta^{34}S$.

Instrument Settings

Mass spectrometer	Nu Plasma (II) MC-ICP-MS
Introduction	Aridus II
PFA nebulizer, ~100 µL min^{-1} uptake rate	
Nebulizer gas	37 psi
Sweep gas	5.8 L min^{-1}
Spray Chamber Temperature	110°C
Desolvator Temperature	160°C
Cones	common Ni cones
Torch	glass
Measurement mode	high resolution (slit width: 25µm, resolving power ~10000)
standard-sample bracketing (IAEA-S-1, $\delta_{34}S$ = -0.30‰$_{VCDT}$)	
sample consumption per single analysis: ~500 µL	
36 cycles, 6 seconds integration time/cycle	
washout time: 70 sec	
transfer time: 90 sec	
Sensitivity (m/z = 28)	~1.5-4 V/ppm samples and standards measured at 1.3-3 ppm Sulfur + 2.6-6 ppm Sodium (S:Na = 0.5) in 0.3 M HNO_3
Blanks (m/z = 28)	15 mV (~0.2 - 0.5 % of sample intensity)
Background	on-mass-zero measured for 60 sec in 0.3 M HNO_3 at the beginning of each run

External reproducibility

The S isotopes on the Nu Plasma II coupled with the Aridus II (Vegacenter, NRM) based on repeated analyses (n =20) on the reference solution IAEA-S-4

$\delta^{34}S$: **0.31** (2σ)

$\delta^{33}S$: **0.74** (2σ)

S2: Natural and anthropogenic Sources of Sulfate and Isotopic Attribution Uncertainty

Natural sulfate has multiple sources, including crustal, volcanic, biogenic (both terrestrial and marine), and biomass burning emissions. Volcanic emissions can be considered minor in South Asia as there is only one volcano in the region, at Barren Island (12.3° N, 93.9° E), but global outgassing could lead to a potential input (Jongebloed, Schauer, Cole-Dai, et al., 2023; Rastogi et al., 2020).

Terrestrial biogenic sources have received relatively little attention, but environments such as wetlands may emit significant amounts of sulfate. The isotopic composition of terrestrial biogenic sulfate overlaps with the depleted anthropogenic signature identified in this study, making it difficult to distinguish without additional analyses.

The ship end-member is thought to be primarily from the combustion of heavy fuel oil (HFO), with this study using a value of 3 ± 3 ‰ (Seguin et al., 2010, 2011; Wadleigh, 2004). This end-member was applied for measurements in the North Atlantic, where conditions are similar to those experienced at MCOH in summer. The ^{34}S end-member of heavy fuel oil (HFO) used by large ships can be quite depleted, with blended HFOs for East Asia averaging around 0 ± 4 ‰ (Maruyama et al., 2000). To arrive at the end-member used in this study, an enrichment during oxidation from sulfur dioxide to sulfate of about 3 ‰ would need to happen. This is consistent with measured enrichment factors at urban sites in East Asia but lower than those derived from laboratory studies (Harris et al., 2013; Lee et al., 2023). 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(δ_MSA − δ_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.

S3: Error propagation

This approach considers uncertainties in the variables; the first method only captures the deviation among samples and not the end-member uncertainties.

$$(\sigma_x^2 + \sigma_{marine}^2)^{0.5} \ / (\sigma_{anthro}^2 + \sigma_{marine}^2)^{0.5} \quad \text{(S1)}$$

σ_a σ_b

$$\frac{\sigma_x}{x} = ((\frac{\sigma_a}{a})^2 + (\frac{\sigma_b}{b})^2)^{0.5} \quad \text{(S2)}$$

S4: 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 SO42- 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.

S5: Keeling-plot approach for determining the anthropogenic end-member

A Keeling plot analysis ($1/nssSO_4^{2-}$ vs. $\delta^{34}S(nssSO_4^{2-})$, Fig. S1) gave an intercept of 2.50 ± 0.36‰ (1σ), similar to our anthropogenic endmember (Fig. 1, Table. S2). However, because the intercept is sensitive to sample selection (e.g., excluding summer samples yields 1.2 ± 0.64‰), we do not use the Keeling approach here due to concerns that mixed and variable sources violate its assumptions for aerosol sulfate (Jongebloed, Schauer, Hattori, et al., 2023).

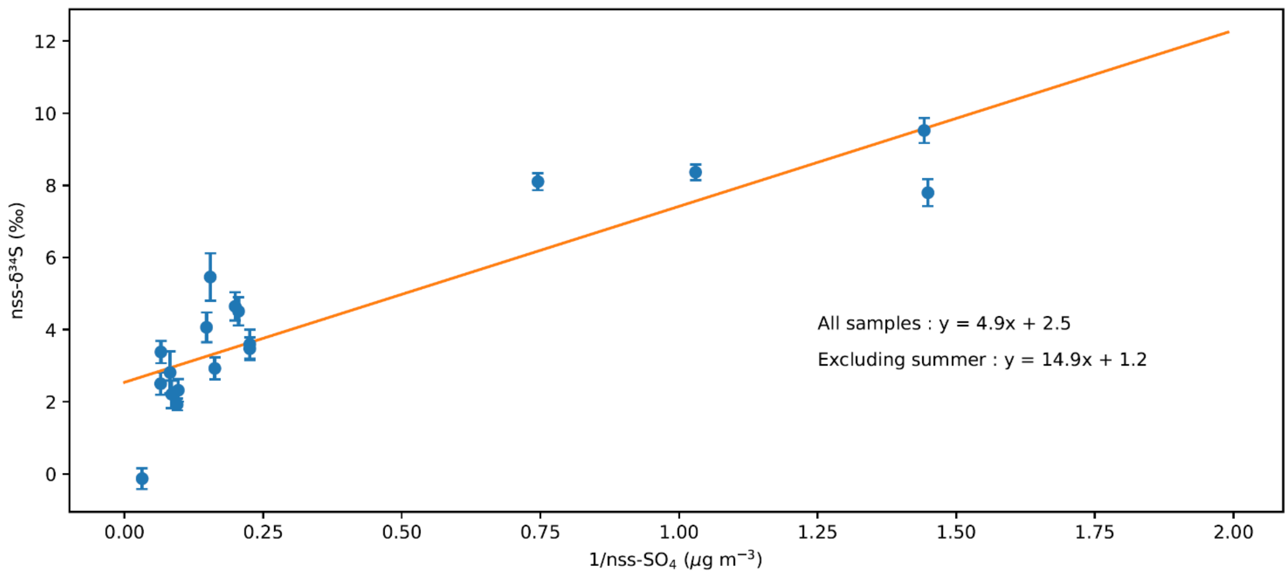

Fig. S1: Keeling plot which shows the ($1/nssSO_4^{2-}$ vs. $\delta^{34}S(nssSO_4^{2-})$). The y-intercept represents the expected anthropogenic end-member. Blue points denote the nss- $\delta^{34}S$ from this study, and the orange line denotes the linear best fit.

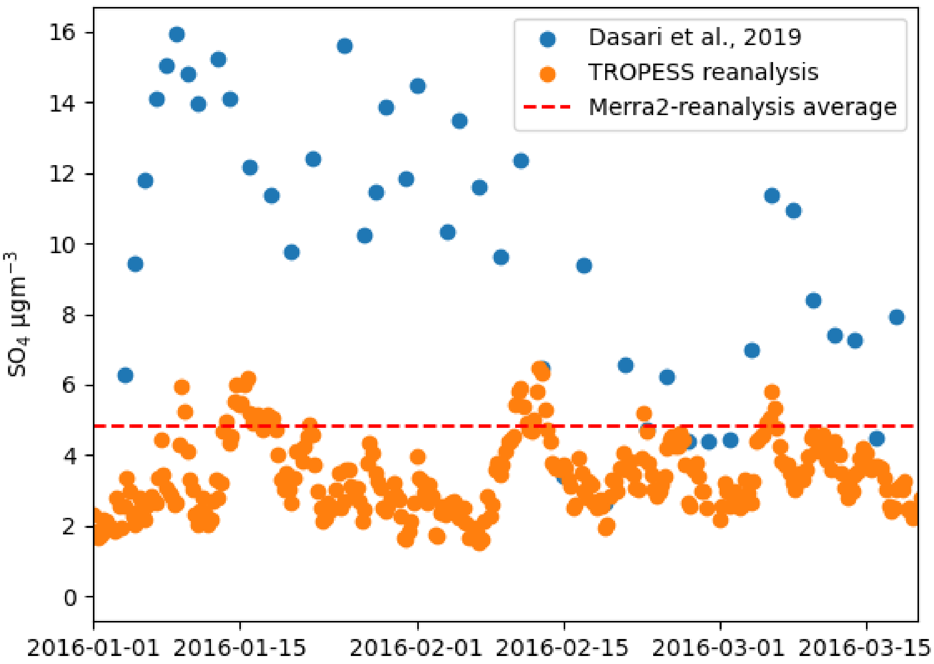

Fig. S2: Comparison between in situ measurements (SAPOEX-16; Dasari et al., 2019) and reanalysis/satellite products (TROPESS; MERRA-2;Buchard et al., 2017; Gelaro et al., 2017; Miyazaki, 2024; Randles et al., 2017). The spring average from TROPESS was approximately 1.5 µg m^{-3}, compared to this study's 4.6 ± 0.7 µg m^{-3} for spring (April).

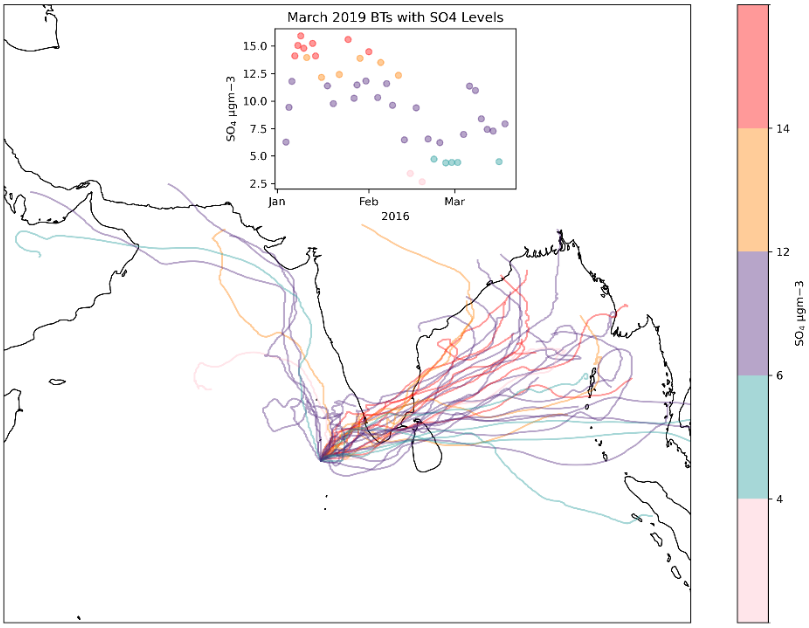

Fig. S3: Seven-day back trajectories for SAPOEX-16 campaign (January–March, Dasari et al., 2019) with color corresponding to sulfate concentration.

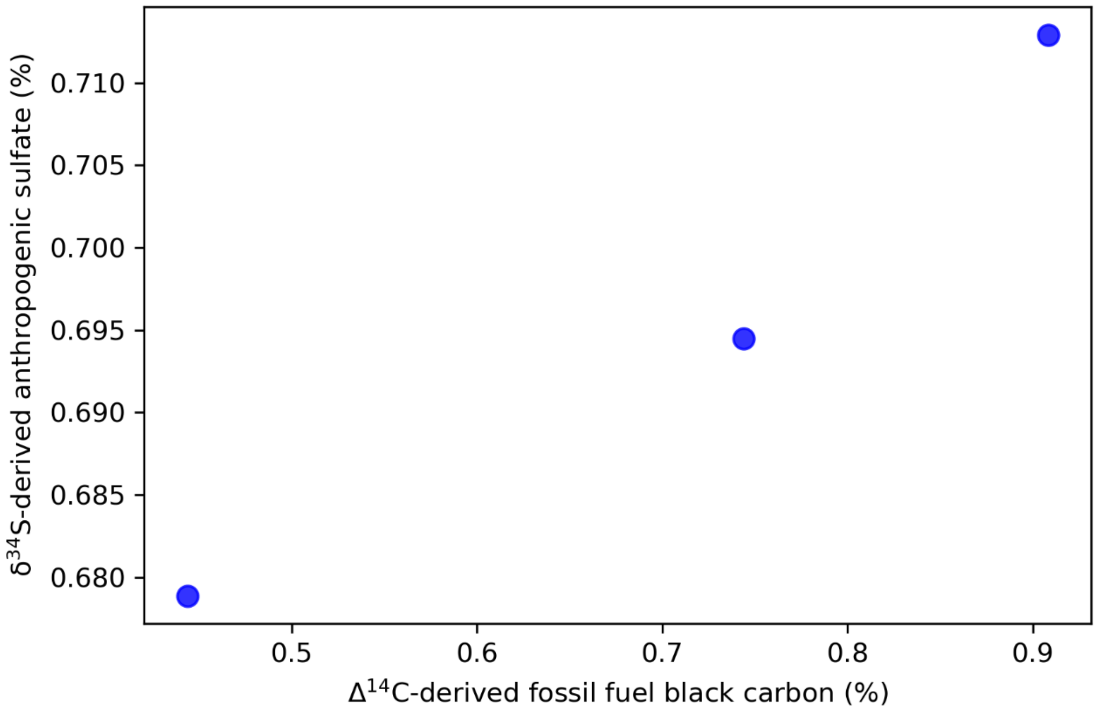

Fig. S4: Fossil fuel BC ($\Delta^{14}C$) versus anthropogenic sulfate ($\delta^{34}S$) for the summer samples (2013–2015).

Table S1: Samples used to derive the anthropogenic IGP end-member

Date	Location	$\delta^{34}S$ (‰)	Author
10/02/2016	Delhi	4	Sawlani et al., 2019
10/05/2016	Delhi	4.5	Sawlani et al., 2019
10/08/2016	Delhi	6	Sawlani et al., 2019
10/12/2016	Delhi	5.5	Sawlani et al., 2019
10/15/2016	Delhi	5.6	Sawlani et al., 2019
10/18/2016	Delhi	3.5	Sawlani et al., 2019
10/24/2016	Delhi	4.6	Sawlani et al., 2019
10/26/2016	Delhi	3	Sawlani et al., 2019
10/27/2016	Delhi	2.5	Sawlani et al., 2019
10/28/2016	Delhi	2.6	Sawlani et al., 2019
10/29/2016 (D)	Delhi	2.8	Sawlani et al., 2019
10/29/2016 (N)	Delhi	1.2	Sawlani et al., 2019
10/30/2016 (D)	Delhi	1.5	Sawlani et al., 2019
10/30/2016 (N)	Delhi	−1.3	Sawlani et al., 2019
10/31/2016 (D)	Delhi	1.7	Sawlani et al., 2019
10/31/2016 (N)	Delhi	−1	Sawlani et al., 2019
11/01/2016 (D)	Delhi	3.2	Sawlani et al., 2019
11/01/2016 (N)	Delhi	1.3	Sawlani et al., 2019
11/02/2016 (D)	Delhi	1.3	Sawlani et al., 2019
11/02/2016 (N)	Delhi	-0.4	Sawlani et al., 2019
11/03/2016 (D)	Delhi	4.5	Sawlani et al., 2019
11/03/2016 (N)	Delhi	4.1	Sawlani et al., 2019
11/04/2016 (D)	Delhi	2.3	Sawlani et al., 2019
11/04/2016 (N)	Delhi	2	Sawlani et al., 2019
11/05/2016 (D)	Delhi	-0.8	Sawlani et al., 2019
11/05/2016 (N)	Delhi	-0.2	Sawlani et al., 2019
11/06/2016 (D)	Delhi	-0.7	Sawlani et al., 2019
11/06/2016 (N)	Delhi	-1	Sawlani et al., 2019
11/07/2016 (D)	Delhi	4	Sawlani et al., 2019
11/07/2016	Delhi	0.6	Sawlani et al., 2019
05/04/2021	Delhi	4.71	Dasari & Widory, 2024
10/04/2021	Delhi	3.41	Dasari & Widory, 2024
14/04/2021	Delhi	1.52	Dasari & Widory, 2024
18/04/2021	Delhi	0.67	Dasari & Widory, 2024
23/04/2021	Delhi	1.95	Dasari & Widory, 2024
01/05/2021	Delhi	3.4	Dasari & Widory, 2024
04/05/2021	Delhi	2.4	Dasari & Widory, 2024
07/05/2021	Delhi	1.34	Dasari & Widory, 2024
09/05/2021	Delhi	1.38	Dasari & Widory, 2024
10/05/2021	Delhi	1.55	Dasari & Widory, 2024
14/05/2021	Delhi	2.16	Dasari & Widory, 2024
22/05/2021	Delhi	1.72	Dasari & Widory, 2024
25/05/2021	Delhi	0.73	Dasari & Widory, 2024
30/05/2021	Delhi	2.8	Dasari & Widory, 2024
31/05/2021	Delhi	0.69	Dasari & Widory, 2024

Batch 116; 16/01/2016	BCOB	2.83	This study
Batch 117; 17/01/2016	BCOB	2.52	This study
Batch 118; 19/01/2016	BCOB	2.4	This study
DEL_SPX-16_24hrs_25JAN_2016	Delhi	-0.07	This study
DEL_SPX-16_night_27FEB_2016	Delhi	1.98	This study

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

Non anthropogenic contribution	100% Anthropogenic; 0% Other		95% Anthropogenic; 5% Other		90% Anthropogenic; 10% Other	
	Season	Percentage anthropogenic	Season	Percentage anthropogenic	Season	Percentage anthropogenic
DMS (+18.8 ‰)[a]	Winter	94	Winter	89	Winter	85
	Spring	87	Spring	83	Spring	79
	Summer	65	Summer	61.7	Summer	59
Volcanic (+4.1 ‰)[b]	Winter	94	Winter	93	Winter	93
	Spring	87	Spring	87	Spring	86
	Summer	65	Summer	65	Summer	65
Terrestrial biogenic (−5 ‰)[c]	Winter	94	Winter	96	Winter	99
	Spring	87	Spring	89	Spring	92
	Summer	65	Summer	67	Summer	69
Soil dust (+7.4 ‰)[d]	Winter	94	Winter	93	Winter	91
	Spring	87	Spring	86	Spring	84
	Summer	65	Summer	64	Summer	63

a = (Amrani et al., 2013); b = (Jongebloed, Schauer, Cole-Dai, et al., 2023); c = (Kamyshny et al., 2014); d = Olson et al., 2021 . Note: Kamyshny et al. (2014) reports a broad range of possible values. For the purposes of this sensitivity test, −5 ‰ was selected as a rough approximation of the mean. The full range of isotopic compositions is large and lies outside the scope of this paper.

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