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

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Method 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)

Method S2: Error propagation

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

$$(\sigma_x^2 + \sigma_{marine}^2)^{0.5} \ / (\sigma_{anthro}^2 + \sigma_{marine}^2)^{0.5} \quad (6)$$

σ_a σ_b

$$\frac{\sigma_x}{x} = ((\frac{\sigma_a}{a})^2 + (\frac{\sigma_b}{b})^2)^{0.5} \quad (7)$$

Text S1: 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 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).

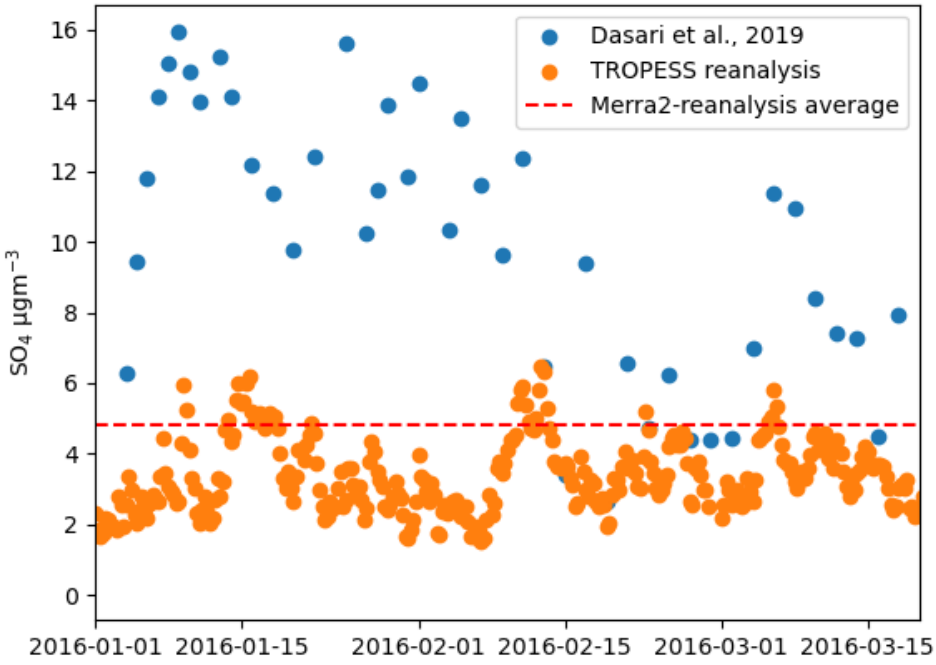

Fig. S1. Comparison between in situ measurements (SAPOEX-16; Dasari et al., 2019) and reanalysis/satellite products (TROPESS; MERRA-2;Buchard et al., 2017; Gelaro et al., 2017; Miyazaki, 2024; Randles et al., 2017). The spring average from TROPESS was approximately 1.5 µg m^{-3}, compared to this study's 4.6 ± 0.7 µg m^{-3} for spring (April).

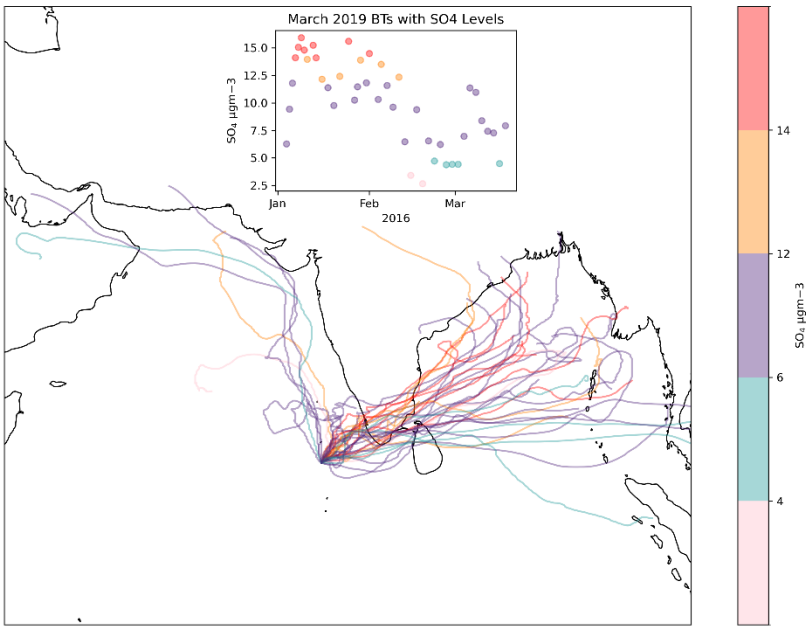

Fig. S2. Seven-day back trajectories for SAPOEX-16 campaign (January–March, Dasari et al., 2019) with color corresponding to sulfate concentration.

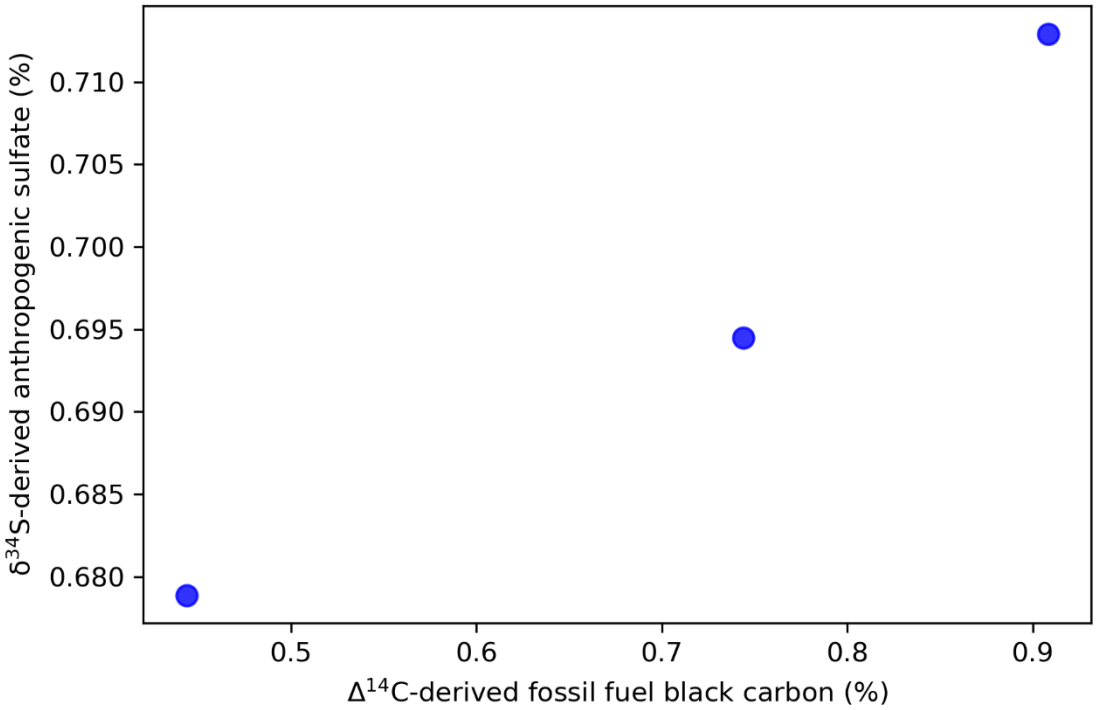

Fig. S3. Fossil fuel BC ($\Delta^{14}C$) versus anthropogenic sulfate ($\delta^{34}S$) for the summer samples (2013–2015).

Table 1: 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

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