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Retrospective Isotopic Analysis of Summertime Urban Atmospheric Sulfate in South Asia Using Improved Source Constraints

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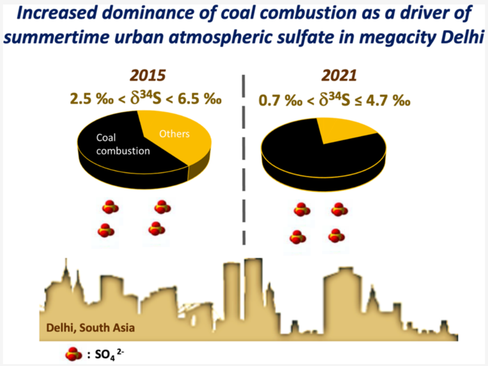
ABSTRACT: The emissions of sulfur dioxide (SO_2), a harmful atmospheric pollutant, are on the rise in South Asia. Sulfate, formed from the oxidation of SO_2, often comprises 10%−67% of aerosol mass and has a profound impact on climate, air quality/human health, and the environment. The potential drivers of sulfate-linked urban air pollution in South Asian megacities—facing a choking air pollution crisis—remain poorly understood due to a lack of systematic observations. Here, we conducted stable S-isotope ($\delta^{34}S$) fingerprinting of sulfate aerosols in summertime megacity Delhi in South Asia to evaluate the potential drivers. With newly developed region-specific isotopic endmembers in this study, a statistical source apportionment of urban atmospheric sulfate was feasible. Results show that coal combustion (80 ± 12%) and oil combustion (14 ± 11%), followed by road dust (4 ± 3%) and biomass burning (2 ± 2%), were major contributors to atmospheric sulfate in summertime Delhi. Retrospective analysis showed a marked isotopic shift in stable sulfate isotopic composition in summertime megacity Delhi wherein the average $\delta^{34}S$ value was 4 ± 1‰ in 2015 and 2 ± 1‰ in 2021, respectively. This was evidently linked to changes in the dominant fuel type as sulfate sourced from coal combustion (oil combustion) significantly increased ∼ 20% (decreased ∼ 20%) during this period. With no clear increase in the number of thermal power plants in and around Delhi, we speculate that the substantial increase in coal-derived sulfate could plausibly be linked to a rise in the informal industries such as brick production and food and agricultural product processing operations, whose SO_2 emissions remain challenging to estimate. While further observations from the region are warranted, the findings here suggest that the continued dependence on coal in developing nations of South Asia could be one of the reasons for rising SO_2 levels.



KEYWORDS: *Sulfur Dioxide, Air Pollution, Fossil Fuels, Source Apportionment, Emission Mitigation*

INTRODUCTION

The biogeochemical cycling of sulfur, an essential element for life, links the atmosphere, biosphere, hydrosphere, and lithosphere.[1] Sulfur is largely emitted as sulfur dioxide (SO_2, a reactive gas-phase hazardous environmental pollutant) both naturally from marine (as an oxidation product of DMS) and volcanic emissions and anthropogenically from biomass burning and fossil fuel combustion.[1−3] Exposure to SO_2 causes skin and eye irritation and respiratory as well as cardiovascular morbidity.[3] In the atmosphere, SO_2 is predominantly oxidized by reactions in the gas phase (with the hydroxyl radicals) or in the aqueous phase (by hydrogen peroxide and ozone) to form sulfuric acid and latter particulate sulfate.[4,5] This oxidation end-product i.e., atmospheric sulfate, is a key component of ambient particulate matter (PM); exposure to PM of aerodynamic size < 2.5 μm is estimated to annually cause ∼4.2 million premature deaths globally.[6] Sulfate comprises 10%−67% of aerosol mass in the midlatitude Northern Hemisphere and has profound impacts on the environment, notably, air pollution affecting air quality/human health, acid rain, and changing the Earth's radiative balance.[7−13] In certain cases, the in-source formation mechanism leads to the rapid growth of sulfate-linked particles in size in fresh emission plumes, enabling changes in aerosol size distribution. Such an effect can lead to differences in the depositional characteristic of the particles in the respiratory system (in the nasal, tracheobronchial, and alveolar regions) thereby affecting human health.[14]

The adverse SO_2 and consequently sulfate-driven affects are amplified in regions where the magnitudes of their columnar densities from anthropogenic sources are largest.[7−11] Such parameters are often retrieved using satellite-based remote sensing mostly relying on the flagship ozone monitoring instrument sensor (since 2005) and more recently the OMPS sensor (since 2012).[11] Cautious and rigorous analysis of long-

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term climate data records derived using these sensors unequivocally suggests a notably consistent trend in Asia, wherein East Asian SO_2 emissions are found to be declining; however, South Asian SO_2 emissions are found to be rising, particularly across the Indo-Gangetic Plain[9−11] (IGP; a global hotspot of air and environmental pollution). Megacities in the IGP often rank as one of the most polluted in the world.[12] The key driver(s) of sulfate-driven pollution in South Asian megacities remain poorly understood due to a lack of systematic observations of SO_2 and their oxidation products.[13] There is therefore an urgent need for source fingerprinting of urban atmospheric sulfate to better understand this aspect.

Multiple S-isotope (^{32}S, ^{33}S, ^{34}S, and ^{36}S) analysis has proven to be useful for a wide array of applications.[15−17] In general, the isotope ratios of any two isotopes can be scaled to each other based on the mass i.e., "mass-dependent fractionation (MDF)" model.[18,19] The S-isotopic compositions vary with sources and cycling pathways e.g., in geochemical, biological, and atmospheric processes.[15−19] However, the main sulfur emissions within a specific regional reservoir possess distinctive characteristics of sulfur isotopic values, making it feasible to conduct source tracing, e.g., refs 18−21. The $\delta^{34}S$ (see the Materials and Methods section) signatures of various sources of atmospheric sulfate are disparate[1] (SI Figure S1) and, as such, can be used for determining the origin of atmospheric sulfate e.g., refs 20−24. However, an inherent issue is the broad diversity in the regional S-isotopic signatures for the two likely drivers of anthropogenic SO_2 emissions[25] i.e., coal combustion (e.g., thermal power plants) and oil combustion (e.g., vehicular emissions) (SI Table S1). "Region-specific" $\delta^{34}S$ signatures are therefore much needed to quantitatively identify potential drivers of urban sulfate-linked pollution e.g., refs 26 and 28. Such information is currently lacking for atmospheric sulfate in South Asia and has thus far led only to qualitative inferences regarding the contributing sources of sulfate-linked air pollution.[29−31] We address this issue and better optimize isotopic endmembers to attempt isotope-based source apportionment of urban atmospheric sulfate in South Asia.

To circumvent the issue of isotopic endmembers, in this study, we rely on an alternative and innovative approach of using fly ash samples collected from major thermal power plants, in the vicinity of a megacity, which reflects the ratio of different coal types and thereby sulfur sources in thermal power plants. We also tailor the isotopic endmember for oil combustion based on import statistics along with their respective sulfur content and isotopic composition. We then employ Bayesian statistical modeling in combination with these meticulously determined region-specific isotopic end-members for quantifying the dominant anthropogenetic source contributions to urban atmospheric sulfate in South Asia by using S-isotopic data for the sampling years 2021 (present study) and the only other reported summertime S-isotopic urban atmospheric sulfate data set from 2015,[29] respectively. This work thereby enables conducting a retrospective analysis (comparison of urban S-isotopic imprint in 2015 vs 2021 in South Asia) of the sulfate-linked air pollution in one of the most polluted regions in the world.

■ MATERIALS AND METHODS

Sampling. As part of a larger scientific endeavor, aiming to address a recent hypothesis involving the role of mineral dust and sulfur mass-independent fractionation,[31,33] it was imperative to sample both coarse and fine particle associated sulfate (see Discussion). As such, aerosol PM_{10} samples ($n = 44$) were collected atop a five-story residential building in the Anand Vihar area of Delhi between April-May 2021. Sampling duration was 24 h for each sample (sample collection started at 6 am and continued until 6 am of the next day local time; see SI Table S2). Samples were collected using an Envirotech Air Pollution Monitoring 550 aerosol sampler and quartz fiber filters (Millipore, Billerica, MA), operated at 1 m^3/h.

To assess the representative $\delta^{34}S$ value of a regional coal-based sulfur source, samples ($n = 7$) of fly ash (a product of coal combustion) were sourced from sellers of fly ash who source the material from four major thermal power plants (1000-2000 MW) located in Delhi and the surrounding three states of Haryana, Punjab, and Rajasthan, respectively (SI Figure S2). The proportion of coal imported into India from other countries is shown in the Supporting Information (SI Figure S2). The coal is often mixed and loaded into the boiler (personnel communication with power plant personnel). As a result, fly ash reflects the blend of different coal types and represents the regional coal-based sulfur source in thermal power plant emissions.

Chemical and Isotope Measurements. For the PM_{10} aerosol samples ($n = 44$), the concentration of water-soluble ions and metals ($n = 44$) and the S-isotope compositions ($n = 15$) were measured using an ion chromatography Metrohm IC (Professional 850) and triple quadrupole and a multicollector inductively coupled plasma mass spectrometer [QQQ-ICP-MS (Agilent 8900) and MC-ICP-MS (Thermo Fisher Scientific Neptune Plus)] instrument, respectively. Measurements were carried out at the University of Tours and Centre de Recherches Pétrographiques et Géochimiques, CRPG France, and the Université du Québec à Montréal, UQAM in Canada, respectively. The reported values are given as 2σ (standard deviation) of at least 5 independent measurements for a given sample (SI Table S2). The analytical error is between 0.05 and 0.1‰ 2σ. The error accounts for instrumental reproducibility. A thorough description of the procedure, measurements, analytical uncertainties, quality control, and reproducibility can be found in our previous publication.[31]

For fly ash isotopic analysis, sulfur was extracted using the Eschka method.[32] Sulfate was then extracted as $BaSO_4$ as discussed in several publications.[26,28,33−35] Briefly, the solution was first filtered and then acidified using hydrochloric acid, following which sulfate was precipitated as barium sulfate by adding a barium chloride solution. The solution was then oven-dried for approximately 48 h at 60 °C. Samples were analyzed in triplicate to assess their homogeneity. The $\delta^{34}S$ of $BaSO_4$ was analyzed using a Costech 4010 EA connected to a Delta V Plus isotope ratio mass spectrometer with a Conflo IV interface at the Iso-Analytical lab in the UK. Standardization was achieved using International Atomic Energy Agency (IAEA) standards, such as NBS-127, IAEA-SO5, and an in-house $BaSO_4$ standard. The results were reported relative to Vienna Canyon Diablo Troilite (V-CDT) in standard delta notation: $\delta^{34}S\ (‰) = [(^{34}S/^{32}S)_{sample}/(^{34}S/^{32}S)_{reference} - 1] \times 1000$.

Bayesian Statistical Source Apportionment. By combining the isotope signatures and assuming mass balance, it is possible to differentiate the relative contributions from various sources

$$\begin{Bmatrix} \delta^{34}S_{sample} \\ 1 \end{Bmatrix} = \begin{Bmatrix} \delta^{34}S_{Coal} & \delta^{34}S_{Oil} & \delta^{34}S_{Terr} & \delta^{34}S_{Bio} & \ldots \\ 1 & 1 & 1 & 1 & \ldots \end{Bmatrix} \begin{Bmatrix} f_{coal} \\ f_{oil} \\ f_{Terr} \\ f_{Bio} \\ \ldots \end{Bmatrix} \tag{1}$$

where f denotes the fractional contribution from a given source, *sample* denotes the value of the analyzed field sample, and the other isotope-values are source signatures ("Coal", "Oil", "Terr", and "Bio" corresponding to sulfate from "coal combustion", "oil combustion", "terrigenous", and "biogenic" sources, respectively). The '⋯' represents the possibility of other sources in particular those of natural origin (e.g., DMS, volcanoes) and anthropogenic origin (e.g., biomass and biofuel burning, together 'f_{Biom}') which can also be added to this mixing model depending on the likelihood. Two main complexities exist for solving this forward mixing model. The first is regarding the variability in the isotopic signatures of $\delta^{34}S$ of various source classes i.e., endmember variability (e.g., SI Figure S1, Table S1). The uncertainties in endmembers dominate the measurement uncertainties. It is recognized that in order to correctly estimate the relative source contributions and related uncertainties, the endmember variability as well as other sources of uncertainty needs to be included in the analysis.[36,37] Markov Chain Monte Carlo (MCMC)-driven Bayesian approaches have been implemented to account for multiple sources of uncertainties/variabilities.[38] Such an approach for isotope-based source apportionment has been used in multiple studies e.g., refs 34, 38, and 39. The resulting probability density functions' output from the model give a "least-biased" representation of the precision. As such, here we have estimated the relative contributions from putative sources (see Discussion) to urban atmospheric sulfate in Delhi based on this approach. Studies not employing such an approach, and attempting to source apportion atmospheric sulfate, have found it challenging to constrain the relative source contributions in the past e.g., refs 26 and 27.

■ RESULTS

Several factors such as an amalgam of anthropogenic activity and collocated emission sources along with the location, population density, and socioeconomic development lead to the acute air pollution crisis in Delhi located in the heart of the IGP.[40] As such, elevated SO_2 columnar densities and high PM_{10} concentrations, 90 ± 30 $\mu g/m^3$ in April and 200 ± 80 $\mu g/m^3$ in May, were found in megacity Delhi also during the summer of 2021 (SI Table S2). The sulfate concentrations varied from as much as 1 $\mu g/m^3$ to 23 $\mu g/m^3$, with $\delta^{34}S$ values ranging from 1 to 5‰ during the study period (Figure 1). The sulfate fraction in aerosol particulate matter has been reported to vary between 5% (in the Indo-Gangetic Plain) to 50% (in the remote N Indian Ocean) on average in South Asia.[40] In the present study, the average sulfate fraction in aerosol PM was 5 ± 3% on average. The ratios of non-sea salt (nss)-SO_4^{2-} to total SO_4^{2-} and nss-K^+ to total K^+ were 98 ± 4% and 97 ± 4%, respectively, suggesting a negligible marine-biogenic contribution and expectedly an overwhelming anthropogenic contribution (SI Figure S3).

Comparable average $\delta^{34}S$ values across the summer of 2021 (3 ± 2‰ in April, 2 ± 1‰ in May) suggest that sulfur sources did not differ substantially during the study period. However, we note that the overall average $\delta^{34}S$ in 2021 (2 ± 1‰) is in general lower than that reported for a similar period from Delhi in 2015 (4 ± 1‰).[30] Seasonal differences in both the dominant sources and/or oxidation process often materialize through such changes on the isotopic scale as reported elsewhere e.g., refs 21, 27, and 41. Here, an interesting aspect is that such a shift is found in the same season between different years: 2015 and 2021. As such, the marked isotopic shift in stable sulfate isotopic composition in the megacity of Delhi could in principle be linked to potential changes also in the dominant sources/processes, an aspect that has not yet been identified or reported. An interesting aspect is also that $\delta^{34}S$ values in Delhi are lower than those reported for Montreal, Beijing, and Seoul during summer, with values < 1‰ being encountered in Delhi during summer[26,28,33] and could be linked to the peculiarity of region-specific source(s) of varying isotopic compositions (SI Table S1). The $\delta^{34}S$ values of fly ash from the thermal power plants in the IGP are listed in SI Table S3. The $\delta^{34}S$ values range from 6 to 8‰. Based on the SO_2 emission quantity of each thermal power plant, the estimated weighted average $\delta^{34}S$ value of fly ash samples was 7 ± 1‰ (SI Table S3).

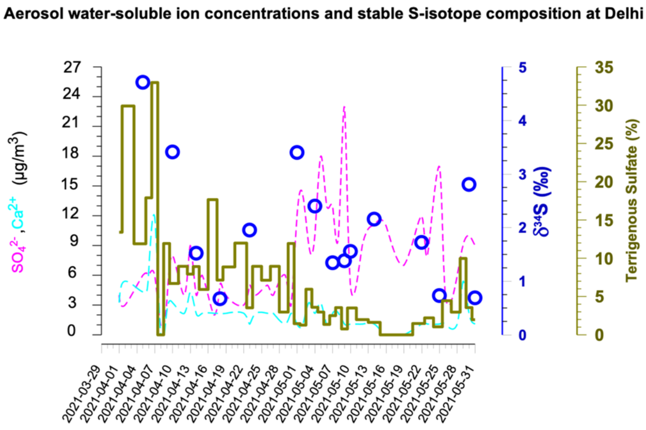

Figure 1. Temporal changes in the springtime sulfate, calcium concentrations (dotted lines), $\delta^{34}S$ (open circles), and estimated terrigenous sulfate fraction (solid line) for the samples collected at Delhi.

■ DISCUSSION

The atmospheric sulfate in an urban setting can also have a "nonurban" component.[31] As such, it is imperative to know the likelihood of such a component prior to conducting source apportionment. Recent findings, based on sulfur isotopic anomaly (from the same sampling campaign), have shown that nearly half of the atmospheric sulfate in Delhi during summertime is indeed "urban" in origin with the remaining being mineral dust-associated sulfate sourced from the neighboring Thar and Arabian deserts.[31] This makes the source apportionment of "urban atmospheric sulfate" feasible. The measurements of S-isotope compositions reported here are direct aerosol-based observations. The span of the $\delta^{34}S_{\text{sulfate}}$ values in the present study is such that it can be explained by a mixing model involving several sources: biogenic emissions, biomass/biofuel burning, terrigenous sulfate, oil combustion, and coal combustion (SI Figure S1). We note that natural sulfur sources of volcanism and DMS are irrelevant for this inland urban location.[28]

Evaluation of Plausible Sources Contributing to the $\delta^{34}S_{\text{sulfate}}$ Dynamics. Bottom-up emission inventories suggest that certain sources only account for peripheral contribution to atmospheric SO_2 emission in South Asia.[42,43] Here, we evaluate such putative contributions: Firstly, typical isotopically lighter sources biogenic sulfur compounds including H_2S with $\delta^{34}S < 0‰$[26,44] are expected to contribute to the local/regional atmospheric sulfur compositions. However, given the order(s) of magnitude difference between the anthropogenic sulfur compound reservoirs and biogenic emissions (from landfills, swamps, and so on) in megacity environments, such contributions are expectedly negligible. Here, as in studies from similar polluted environments,[28,45] and based on the weak soil microbial activity[46−48] and the low biogenic flux estimates of sulfur compounds in inland soils,[46,47] the contribution of biogenic sulfur is considered insignificant (i.e., $f_{\text{Bio}} = 0$ in eq 1). Secondly, it has been reported that K^+ accounts for a maximum of 5%, while SO_4^{2-} accounts for ∼1% in fresh biomass burning-derived particles from various biomes.[49] As such, by analyzing the water-soluble ion concentrations of the same, we estimate that biomass burning-derived sulfate (f_{Biom}) accounted for a maximum of 2% of total sulfate aerosols in megacity Delhi during summer of 2021. This is in line with estimates also from various regional and global emission inventories.[42,42] And lastly, we have independently estimated the terrigenous sulfate fraction per sample as in other studies.[26,28] Sulfates in aerosols can originate from terrigenous sources (e.g., resuspended soil dust).[26] f_{Terr} was calculated using the ratio of SO_4^{2-}-to-Ca^{2+} concentrations in regional soil (here we used a value of 0.20) to the same ratio in sampled aerosol (Figure 1). Taken together, upon elimination and estimation of the peripheral source fractions and isotopic compositions, eq 1 now becomes a determined system wherein the MCMC-driven statistical assessment allows us to then apportion the remaining source contributions, i.e., coal combustion (f_{Coal}) and oil combustion (f_{Oil}) with confidence.

Region-Specific Isotope Endmembers for Oil and Coal Combustion. Most SO_2 emissions from industry (e.g., construction and manufacturing) and transportation ultimately originate from oil combustion.[42,43,50] However, over 80% of crude oil is imported into South Asia with a major fraction of these oil imports originating from the middle East (including Saudi Arabia, UAE, and Iran, www.orfonline.org/expert-speak/indias-oil-imports/). The sulfur content in oil from these regions ranges from 1% to 2%, and their $\delta^{34}S$ value varies between −1 and −4‰ (SI Table S1). Such sulfur content is also reported in the blended oil mixes used in Asia.[25] The emission rate of SO_2 from oil combustion is relatively constant with almost no seasonal change in the consumption of petroleum.[43] Therefore, the SO_2 emissions from oil combustion in the study area are a steady source of sulfate in the aerosol that is characterized by a relatively low $\delta^{34}S$ value, here estimated to be 2 ± 1‰, in line with an independent estimate.[29] This aspect is one of the key differentiating factors between South Asian and East Asian ($\delta^{34}S_{\text{oil combustion}} \sim 20 \pm 5‰$)[26] S-isotopic compositions in atmospheric sulfate.

The contribution from coal combustion to the atmospheric sulfur pool of South Asia is expectedly of significant proportion.[42,43] The largest sectorial contribution to SO_2 emissions is from thermal power plants.[43,51] In South Asia, coal is majorly imported from Australia and Indonesia followed by South Africa accounting for over 70% of the imported coal, which is then mixed with Indian coal (SI Figure S2). The average $\delta^{34}S$ of Australian, Indonesian, South African, and Indian coal is 3‰, 14‰, 4‰, and 2‰ respectively; however, the same is not known for the blended coal mix used in the thermal power plants across the IGP. As such, an isotopic endmember cannot be simply assumed given the wide range of stable S-isotopic values.[29] We therefore rely on fly ash collected from major power plants located in Delhi and the surrounding three states. Air mass back trajectory cluster analysis shows that nearly 35% of the air mass originate/cross the surrounding regions of Punjab and Haryana, while 65% are from Rajasthan and beyond[31] (SI Figure S4). As such, the coal-fueled major thermal power plants (1000−2000 MW) in these regions could influence the urban sulfate sampled in megacity Delhi (SI Figure S5). We find a remarkable similarity in the S-isotopic composition of fly ash in these regions, suggesting a similar blend of coal mixes is perhaps used in these power plants (SI Table S3).

Sulfur isotopic fractionation and SO_2 oxidation during coal combustion ought to be considered in source apportionment. The $\delta^{34}S$ of SO_2 emitted during coal combustion is depleted by (7 ± 2)‰ (1σ) compared to the $\delta^{34}S$ of coal, while the $\delta^{34}S$ of fly ash is enriched by (2 ± 1)‰ (1σ).[15,28] An enrichment factor of (3 ± 2)‰ is used to account for the fractionation during oxidation of SO_2 into sulfate in particulate matter.[28] Taken together, a fractionation correction factor of −6 ± 3‰ is here considered for accurate source apportionment as elsewhere.[28] As a result, the average $\delta^{34}S$ value of sulfate aerosols originating from coal combustion source was (1 ± 3)‰ [i.e., 7 ± 1‰ − 6 ± 3‰], which is treated as a regional endmember for coal combustion for source apportionment calculations.

Constraining the Potential Source Contributions Using Urban S-Isotopic Signals. Combining the $\delta^{34}S$ values within a Bayesian statistical model (see the Materials and Methods section) might allow for better harnessing the information from the S-isotopic imprint in the urban atmosphere e.g., refs 31. Here, we have narrowed down four potential sources (biomass/biofuel burning, terrigenous sulfate, oil combustion, and coal combustion) which in combination could lead to the $\delta^{34}S$ values seen in Delhi (Figure 2).

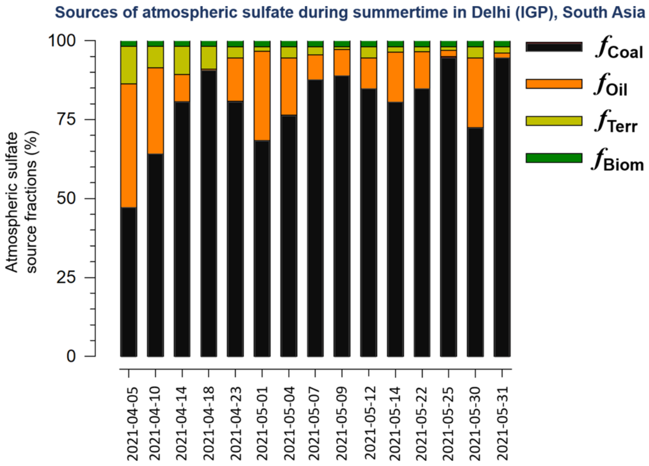

Figure 2. Atmospheric sulfate source fractions during summer of 2021 in megacity Delhi from coal combustion (f_{Coal}), oil combustion (f_{Oil}), road dust (f_{Terr}), and biomass burning (f_{Biom}).

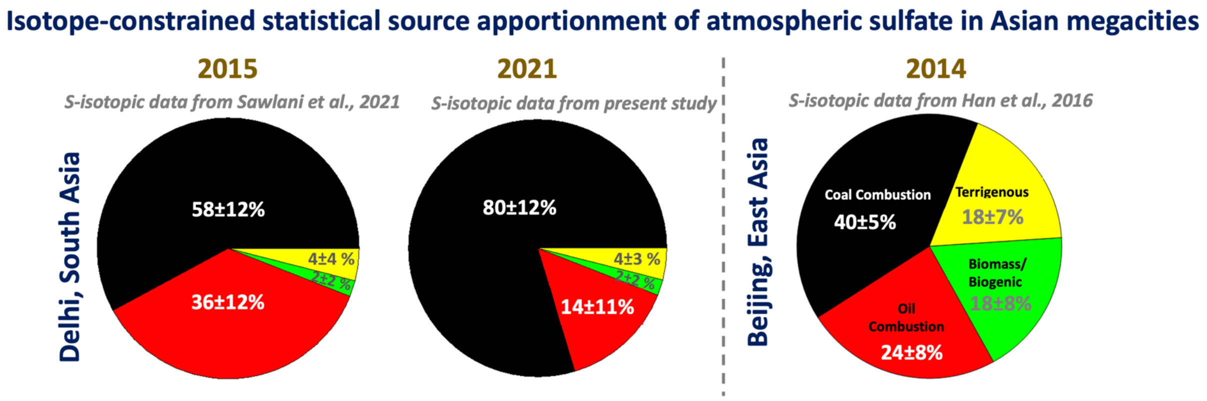

Figure 3. Comparison of the relative source fractions of atmospheric sulfate in Asian megacities computed using MCMC statistical simulations (see also SI Figure S6 for posterior probability density functions). The S-isotopic data for Delhi are available from Sawlani et al., 2021 (for the sampling year 2015) and the present study (for the sampling year 2021) and for Beijing from Han et al., 2016 (for the sampling year 2014). The data for all these studies are here processed using the Bayesian statistical model as described in the Materials and Methods section for uniformity in source apportionment calculations.

The source contribution from biomass/biofuel burning to atmospheric pollutants in Delhi varies seasonally between summer and winter due to the influx of biomass burning aerosols from crop-residue burning in upwind Punjab.[29,52] However, this source is of peripheral importance during summer,[40] noted also when comparing the observations and the isotopic endmembers. Reported wintertime maximum δ^{34}S (6‰) is much closer to the isotopic endmembers of C3-biomass and biofuel burning in Delhi (ranging between 6‰ and 9‰).[29] As such, we estimate the maximum contribution from biomass burning to be 2% (see Discussion above). Given that f_{Terr} is calculated independently, the source contribution of terrigenous sulfate is known for each observation. The δ^{34}S values of sulfate in road dust have been reported to be 2 ± 1‰.[29] The relative source contributions of the remaining sources (oil combustion and coal combustion) can be apportioned upon teasing apart their combined isotopic signal ($\delta^{34}\mathrm{S}_{\mathrm{observed}} - [f_{\mathrm{Terr}} \times \delta^{34}\mathrm{S}_{\mathrm{Terr}}]$). Such an exercise reveals that coal combustion (80 ± 12%), followed by oil combustion (14 ± 11%) and road dust (4 ± 3%), was a major contributor to atmospheric sulfate in summertime Delhi in 2021.

Notably, on three occasions, the δ^{34}S values were <1‰. Such isotopic shifts can be linked to changes in sources, oxidation processes, or meteorology.[45] The possibility of isotopically light biological sulfur emissions can be invoked to account for isotopically light sulfur observed during such occasions. However, as discussed earlier, such influences are rather less likely in a megacity environment. Laboratory experiments have shown that oxidation reaction of S(IV) catalyzed by iron results in a depletion of heavy sulfur isotope with $\alpha = 0.9894 \pm 0.0043$ at 19 °C, which is currently the only pathway that produces depletion of ^{34}S in sulfate aerosols relative to SO_2.[21] An influx of mineral dust-associated sulfate to Delhi during summer of 2021 has been found in our previous study, and therefore, such a shift can be linked to process-based changes;[31] however, the expected magnitude is much higher than observed here[21,45] and more likely to explain seasonal shifts in δ^{34}S values rather than on a daily scale. A third possibility is linked to changes in air masses which has often been the factor for changes observed in urban δ^{34}S values. The three occasions coincide with air masses originating from west-central India and beyond.[31] This region has relatively more thermal power plants than the two of the upwind states of Delhi (Haryana and Punjab) (SI Figure S5). It is therefore likely that sulfate from coal combustion-dominated air mass plumes was encountered in Delhi during such occasions, an aspect also witnessed in South Korean and Chinese cities.[28,45]

Retrospective Analysis of Atmospheric Sulfate in South Asian and East Asian Capital Megacities. Given that summertime S-isotopes were measured for atmospheric sulfate sampled in the same city, i.e., northern Delhi in 2015 and 2021, we take the opportunity to conduct a retrospective analysis. The term "retrospective" is used to highlight the aspect that we compared the isotopic signatures of atmospheric sulfate from Delhi in these two years (2015 vs 2021). It should be noted that there have been no S-isotope-based field investigations of urban atmospheric sulfate aerosols between the years 2016 and 2020 in South Asia; as such, we can only compare the results from years 2015 (from Sawlani et al., 2019) and 2021 (this study).

Data from overlapping summer periods of 2021 and 2015 for South Asian sulfate were both processed using the Bayesian statistical source apportionment model, as described in the Materials and Methods section. This allows for a direct "quantitative" comparison of the relative source contributions in South Asia and a significant observation-based ground truthing. To further the retrospective nature of our analysis, we also added the S-isotopic data from 2014 (from Han et al., 2016) for East Asian sulfate and processed in a similar manner as above to also compare the sulfate sources in the two of the most polluted cities in the world: Delhi vs Beijing (Figure 3).

In 2015, the δ^{34}S values varied from 3‰ to 7‰.[30] As no ancillary data on water-soluble ions are available from the study in 2015, we assume that biomass burning and terrigenous sulfate contributions to total urban atmospheric sulfate remained the same between 2015 and 2021. Following this, we conducted source apportionment in the same manner as that done here. While coal combustion (58 ± 12%) was still the major contributor to urban atmospheric sulfate in Delhi, the relative proportions between oil vs coal combustion were much different than in 2021 (Figure 3, see also SI Figure S6). The fraction of sulfate derived from oil combustion in 2015 (36 ± 12%) was nearly three times as much higher than in

2021. Intuitively, this suggests that the dependence on coal combustion has significantly increased over the past half a decade in and around Delhi. In comparison, atmospheric sulfate in the East Asian megacity Beijing is also but relatively less dominated by coal combustion (Figure 3). While through the middle part of the last decade, the East Asian SO_2 emission trend has displayed a downturn implying the control on coal-related emissions through efficient policies; such a trend is yet to be realized with regards to SO_2 emissions in South Asia.[9−11] Directives under the National Clean Air Program, NCAP, launched in South Asia in 2019 (https://moef.gov.in/wp-content/uploads/2019/05/NCAP_Report.pdf; accessed 2023.12) implicate the reliance on coal and propose actions for phasing out coal. This is in line with the findings here that coal combustion could be one of the key contributors to sulfate driven air pollution in general in the Asian region.

While there is a clear increase in the number of thermal power plants in the neighboring state of Rajasthan, no significant changes occurred in Delhi and the upwind states of Punjab and Haryana (https://cea.nic.in/wp-content/uploads/installed/2022/03/installed_capacity.pdf). We speculate that the substantial increase in coal-derived sulfate could plausibly be linked to a rise in the “informal industries” around Delhi.[43] The informal industry sector includes brick production (in traditional kiln technologies like Bull’s trench kilns and clamp kilns) and food and agricultural product processing operations (like drying and cooking operations related to sugarcane juice, milk, food grain, jute, silk, tea, and coffee).[43] These traditionally rely on coal as one of fuel sources as it a cheaper alternative to the relatively highly priced liquid fuels such as diesel and kerosene.[43,53] Such industries are often located in peri-urban regions and contribute to the urban air pollution.[53] The mapping of these industries and related emissions involves major uncertainties, and as such, their emissions can largely remain underrepresented in the emission inventories.[43,53]

Taken together, the findings suggest that sulfate-linked air pollution, affecting both air quality and human health, in megacity Delhi could largely be driven by coal combustion. While desulfurization technologies are being implemented in thermal power plants, progress remains slow as per recent reports.[54] The continued dependence on coal for developing nations in South Asia could be the reason for rising SO_2 emissions. Such a rising trend in SO_2 emission (and thereby sulfate loadings) has recently been modelled to increase the aerosol-induced direct and indirect effects leading to a significant reduction in the summer monsoon in the South Asian landmass.[54] Agriculture plays a major role in this region’s economy, and an increasing frequency of droughts linked to sulfate-linked pollution can be catastrophic for the region.[55] The findings here implicate coal combustion as the major source of atmospheric sulfate. Mitigating and rather phasing out coal through investment in alternate and renewable energy could prove immensely beneficial to both air quality and regional climate, as this would significantly reduce the aerosol sulfate burden in the region. Such a scenario has been reported in modeling simulations by decreasing SO_2 emissions.[54,56] We echo the directives of the NCAP 2019 wherein there is an urgent need for policies and actions curtailing the key driver of sulfate emissions, i.e., coal combustion in South Asia.

While this study focused on summertime alone, systematic year-round observations for sulfur isotopes of atmospheric sulfate covering all seasons from several urban regions are therefore needed to provide a more concise view of the dominant sources of atmospheric sulfate in the region. This would also allow for validating chemistry-transport/climate models incorporating $\delta^{34}S$ tracers in simulations.[54] This is imperative for reducing the model-observation discrepancies in sulfate aerosol dynamics, particularly in South Asia where rising SO_2 levels pose an existential threat to several of the sustainable development goals.[54,55]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestair.3c00060.

> Figures S1−S5, Isotopic signatures of sulfate for various sources, sampling locations of fly ash from power plants and coal import statistics for India, estimation of the influence of marine emissions, air mass back trajectory analysis, and map with location of thermal power plants, respectively; Tables S1−S3, region-specific isotopic signatures of sulfur in coal and oil combustion, sampling details, and details of fly ash isotopic values, respectively (PDF)

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Author Contributions

S.D. conceived the study; S.D. designed the research with D.W.; S.D. contributed to chemical and isotopic measurements; S.D. and D.W. analyzed the data; S.D. drafted the paper and wrote the paper with input from D.W.

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Notes

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