Global Sources of Fine Particulate Matter: Interpretation of PM$_{2.5}$ Chemical Composition Observed by SPARTAN using a Global Chemical Transport Model

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Supporting Information

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ABSTRACT: Exposure to ambient fine particulate matter (PM$_{2.5}$) is a leading risk factor for the global burden of disease. However, uncertainty remains about PM$_{2.5}$ sources. We use a global chemical transport model (GEOS-Chem) simulation for 2014, constrained by satellite-based estimates of PM$_{2.5}$ to interpret globally dispersed PM$_{2.5}$ mass and composition measurements from the ground-based surface particulate matter network (SPARTAN). Measured site mean PM$_{2.5}$ composition varies substantially for secondary inorganic aerosols (2.4–19.7 μg/m$^3$), mineral dust (1.9–14.7 μg/m$^3$), residual/organic matter (2.1–40.2 μg/m$^3$), and black carbon (1.0–7.3 μg/m$^3$). Interpretation of these measurements with the GEOS-Chem model yields insight into sources affecting each site. Globally, combustion sectors such as residential energy use (7.9 μg/m$^3$), industry (6.5 μg/m$^3$), and power generation (5.6 μg/m$^3$) are leading sources of outdoor global population-weighted PM$_{2.5}$ concentrations. Global population-weighted organic mass is driven by the residential energy sector (64%) whereas population-weighted secondary inorganic concentrations arise primarily from industry (33%) and power generation (32%). Simulation-measurement biases for ammonium nitrate and dust identify uncertainty in agricultural and crustal sources. Interpretation of initial PM$_{2.5}$ mass and composition measurements from SPARTAN with the GEOS-Chem model constrained by satellite-based PM$_{2.5}$ provides insight into sources and processes that influence the global spatial variation in PM$_{2.5}$ composition.

INTRODUCTION

Exposure to ambient fine particulate matter (PM$_{2.5}$; aerodynamic diameter of 2.5 μm or less) is a leading risk factor for increased mortality and morbidity.$^{1,2}$ The Global Burden of Disease study attributed 4.1 million premature deaths to PM$_{2.5}$ exposure in 2016.$^6$ A strong need exists to understand the sources contributing to this PM$_{2.5}$ burden to inform mitigation efforts.$^8$ PM$_{2.5}$ formation is influenced by a range of emission sources, atmospheric transport, and atmospheric chemistry.$^5$ A chemical transport model constrained by observations offers a powerful tool to understand these sources. Until recently, long-term measurements of PM$_{2.5}$ mass and chemical composition were primarily limited to North America and Europe, with different networks using a variety of sampling techniques and standards to determine chemical composition. A global data set of ground-based PM$_{2.5}$ compositional measurements could offer valuable information to understand the sources and processes that control the spatial diversity of PM$_{2.5}$ mass and chemical composition.

The relationship between emissions and PM$_{2.5}$ loading is complex. PM$_{2.5}$ can be emitted directly as particles from combustion or mechanical processes, but it can also form and grow in the atmosphere through the condensation of low volatility products of atmospheric chemical reactions of inorganic and organic precursors.$^{5,6}$ Chemical transport models have been applied to represent this complexity through source apportionment studies aimed at characterizing the global sources contributing to PM$_{2.5}$ mass and composition,$^7$ with increasingly fine resolution.$^8$ Although insightful, simulations could benefit from stronger observational constraints to evaluate and improve accuracy and spatial representativeness.

Two observational data sets have emerged recently with information about the global distribution of PM$_{2.5}$ mass and composition, a dedicated ground-based network of PM$_{2.5}$ composition, and increasingly accurate satellite-based estimates of PM$_{2.5}$ mass. The surface particulate matter network (SPARTAN) measures ground-based PM$_{2.5}$ mass and chemical composition using consistent instrumentation and standardized chemical analysis techniques in diverse global locations with high population densities relevant for health. Measurements from SPARTAN include PM$_{2.5}$ filter samples that are analyzed for PM$_{2.5}$ mass and chemical composition including sulfate, nitrate, ammonium, black carbon (BC), crustal material, and sea salt.$^{9,10}$ Satellite-based estimates of PM$_{2.5}$ mass complement the ground-based measurement network by offering additional global constraints on PM$_{2.5}$ mass at a resolution finer than global simulations. Case studies investigating the effects of model resolution on calculated PM$_{2.5}$ mortality rates find that those calculated from coarse (2° × 2.5°) resolution are systematically lower than those calculated using finer (e.g., 0.5° × 0.66°) resolution.$^{8,11,12}$ The latest global satellite-based PM$_{2.5}$ estimates combine observations from multiple retrieval algorithms$^{3–19}$ and instruments (MODIS, MISR, SeaWiFs) weighted inversely by error with respect to ground-based AOD measurements from AERONET$^{20}$ with additional statistical constraints from ground-based PM$_{2.5}$ measurements.$^{21–23}$

We apply the GEOS-Chem global chemical transport model, constrained by satellite-derived PM$_{2.5}$ to interpret ground-based measurements of PM$_{2.5}$ mass and composition from SPARTAN to gain insight into the main sources determining the spatial distribution of PM$_{2.5}$ mass and composition. We explore the annual average influence of major emission source categories on global population-weighted PM$_{2.5}$.

METHODS

SPARTAN Filter Measurements and Analysis. SPARTAN is an ongoing, long-term project that measures aerosol mass, water-soluble ions, trace elements, and aerosol optical properties at globally dispersed, densely populated areas of relevance to human health. Snider et al.$^{10}$ provide an overview of SPARTAN. Instrumentation includes an AirPhoton 3-wave-length integrating nephelometer and an AirPhoton SS4i filter sampler. We focus on the latter here. The PM$_{2.5}$ is collected on a preweighed PTFE filter (2 μm pore size, SKC). Filters sample one diurnal cycle over a 9-day period beginning and ending at 09:00 local time before shipment under ambient conditions to Dalhousie University for analysis in a central laboratory. Samples have been collected for periods of 2 months to over 3 years during 2013–2017 at 11 carefully chosen, regionally diverse sites. Although initially sparse, SPARTAN is unique in covering poorly sampled regions of the world with a consistent methodology.
An extensive overview of the SPARTAN PM$_{2.5}$ sampling methodology, filter chemical analysis protocols, and the filter-based hygroscopicity parameter, $\kappa$, are provided by Snider et al.² Details on relevant SPARTAN chemical analysis procedures and the uncertainty associated with each major chemical component based on collocated measurements is presented in the Supporting Information (SI). Seasonal mean uncertainties range from 4.0% for sulfate, to 4.6% for PM$_{2.5}$, to 9.2% for nitrate. Briefly, gravimetric analysis follows USEPA protocols in a cleanroom with controlled temperature at 20–23 °C and relative humidity (RH) at 35 ± 5%. Black carbon content is estimated by surface reflectance measurements,²⁴ water-soluble ions are determined by ion chromatography,²⁵ and trace elements are determined by inductively coupled plasma-mass spectrometry.²⁵,²⁶ The residual matter (RM) component, estimated by subtracting the dry inorganic mass and particle-bound water from total PM$_{2.5}$ mass, is expected to be predominately organic.²⁷ Activities are ongoing to directly measure organics through aerosol mass spectrometry²⁷ and Fourier transform infrared (FT-IR) spectroscopy.²⁸

**GEOS-Chem Simulation.** We use the GEOS-Chem 3-dimensional chemical transport model (v11.01, http://geos-chem.org) to determine the daily distribution of PM$_{2.5}$ major chemical component mass concentrations. GEOS-Chem solves for the evolution of atmospheric aerosols and gases using assimilated meteorology from the NASA Goddard Earth Observing System (GEOS), global and regional emission inventories, and algorithms that represent the physics and chemistry of atmospheric processes. The simulation uses assimilated meteorological observations (GEOS MERRA-2) at 2° × 2.5° horizontal resolution with 47 vertical levels for the year 2014 for overlap with SPARTAN and due to emissions availability. The simulation uses anthropogenic emissions from the Emissions Database for Global Atmospheric Research (EDGAR) version 4.3 inventory²⁹ and the MIX regional anthropogenic emission inventory for 29 Asian regions and countries.³⁰

SPARTAN measurements are used to inform developments to the simulation. We include the anthropogenic fugitive, combustion, and industrial dust (AFCID) emission inventory from Philip et al.,³¹ which increased correlation ($r$) with SPARTAN fine dust concentrations in this study from 0.35 to 0.67. Simulated total PM$_{2.5}$ mass concentration is calculated at 35% RH for consistency with PM$_{2.5}$ measurement protocols. The calculation employs the kappa hygroscopicity formulation² used by SPARTAN, as described by Snider et al.,² this formulation exhibits hygroscopic growth consistent with the aerosol inorganic model (AIM)³³ and laboratory measurements.² Compared to the default GEOS-Chem model, the kappa hygroscopicity formulation decreases the bias (reduced major axis slope) of simulated PM$_{2.5}$ versus SPARTAN PM$_{2.5}$ concentrations from 1.39 to 1.29. We also include an aqueous-phase mechanism for secondary organic aerosol (SOA) formation from isoprene by Marais et al.,³⁴ that better represents SPARTAN PM$_{2.5}$ mass as shown by reduced root-mean-square-error from 14.2 to 13.3 $\mu$g/m$^3$. We perform sensitivity simulations for which emissions from individual source categories were removed to calculate the contribution of sources to PM$_{2.5}$ mass and composition by mass balance. Further details about the simulation are provided in the Supporting Information.

**Constraining the Simulation with Satellite-Based PM$_{2.5}$.** Satellite observations of AOD offer an additional constraint on the global PM$_{2.5}$ distribution at spatial scales commensurate with population density distributions.³⁵ To reduce uncertainties in PM$_{2.5}$ exposure estimates caused by model resolution,³⁶ satellite-derived PM$_{2.5}$ concentrations²¹ for the year 2014 are used to downscale GEOS-Chem PM$_{2.5}$ mass and composition from $2° \times 2.5°$ to 0.1° × 0.1° resolution following a widely used approach.³⁸⁻⁴⁰ The spatial map of the annual ratio of satellite-derived to simulated PM$_{2.5}$ concentration is applied to all simulated PM$_{2.5}$ components, thus retaining the simulated fraction and temporal variation of PM$_{2.5}$ composition.

**Supplemental Table S2** shows the Pearson’s correlation coefficient between SPARTAN measurements and PM$_{2.5}$ components from the simulation ($r$) and simulated values scaled by local satellite-derived PM$_{2.5}$ ($r_{sat}$). For most PM$_{2.5}$ components, downscaling to satellite-derived PM$_{2.5}$ increases the consistency in capturing PM$_{2.5}$ spatial diversity. Correlations tend to increase, most notably for organic mass (OM, $r_{sat} = 0.92$ vs $r = 0.64$) as well as total PM$_{2.5}$ mass ($r_{sat} = 0.93$ vs $r = 0.88$), ammonium ($r_{sat} = 0.86$ vs $r = 0.81$), and BC ($r_{sat} = 0.67$ vs $r = 0.61$). The root-mean-square-error of simulated total PM$_{2.5}$ decreased from 13.3 $\mu$g/m$^3$ to 12.8 $\mu$g/m$^3$. Prior work has similarly found that the downscaled simulation better represents observations for both mass and composition.³⁶,⁴¹ Therefore, all values of total PM$_{2.5}$ mass and chemical composition reported herein are from the downscaled simulation (scaled by the local annual ratio of PM$_{2.5}$,sat to PM$_{2.5}$,model) at 0.1° × 0.1° resolution.

**Sources Affecting PM$_{2.5}$ Mass and Composition.** Global Distribution of PM$_{2.5}$ Chemical Composition. Figure 1 shows the annual mean simulated PM$_{2.5}$ chemical composition with overlaid concentric circles depicting concentrations at SPARTAN sites. The center of each concentric circle indicates the measured value, with corresponding downscaled simulated concentration indicated by the outer ring. Differences between the outer ring and background map represent the effects of sampling the simulation for the same months as the measurements versus complete annual sampling. These seasonal sampling effects are generally much smaller than the global spatial variation, providing evidence of temporal representativeness. Inset values represent the global population-weighted mean concentration inferred from the downscaled simulation. Table 1 contains numerical values of measured and simulated concentrations for the specified sampling periods of SPARTAN sampling sites. The spatial variation of SPARTAN site-mean concentrations exceeds a factor of 5 (e.g., Kanpur, India vs Buenos Aires, Argentina) for most PM$_{2.5}$ major chemical components, as described in more detail in the following sections.

SPARTAN measurements of secondary inorganic aerosol (SIA) vary by a factor of 8 across sampling sites from 2.4 $\mu$g/m$^3$ in Ilorin, Nigeria, to 19.7 $\mu$g/m$^3$ in Beijing, China, and account for over 20% of total PM$_{2.5}$ mass at sampling sites, except Manila, Philippines (16%) and Ilorin (15%). The downscaled simulation captures the spatial heterogeneity of SIA concentrations ($r = 0.87$). SIA tends to be overestimated at SPARTAN sites, including an overestimate of nitrate concentrations in Beijing, as discussed below. SIA dominates population-weighted PM$_{2.5}$, accounting for 37% globally.

Measured concentrations of crustal material (dust) vary by an order of magnitude from <2 $\mu$g/m$^3$ (e.g., Buenos Aires) to 3–5 $\mu$g/m$^3$ in many cities (e.g., Ilorin and Rehovot, Israel), to over 5 $\mu$g/m$^3$ (Dhaka, Bangladesh; Hanoi, Vietnam; and Kanpur), and exceed 14 $\mu$g/m$^3$ in Beijing. Enhanced dust mass in Rehovot and Ilorin is expected to be predominately mineral dust, due to influence from the surrounding arid region. However, pronounced dust in urban cities throughout the South and Southeast Asia cannot be fully explained by mineral dust.
sources; elevated measured Zn:Al ratios at these sites suggest an anthropogenic component. The remaining positive bias in simulated values is driven by an overestimate in the simulated mineral dust source. Simulated dust concentrations are primarily mineral over the arid and semiarid regions of North Africa, the Middle East, and Central Asia, primarily AFCID in urban areas of Southeast Asia, and a combination of the two in Beijing. Dust contributes 29% to global population-weighted mean PM$_{2.5}$ concentrations, making it the second largest global PM$_{2.5}$ contributor.

As discussed in the methods, SPARTAN does not yet directly measure organic aerosol content; rather, the inferred residual matter (RM) is expected to be mainly organic, based on comparison with independent organic measurements. SPARTAN RM concentrations are highest throughout Asia where values exceeding 10 $\mu$g/m$^3$ are observed at all SPARTAN sites except Manila and Singapore. The lowest RM concentrations are found in Buenos Aires (2.1 $\mu$g/m$^3$) and Rehovot (2.7 $\mu$g/m$^3$). The broad consistency in spatial variation of SPARTAN RM and simulated OM ($r = 0.92$) provides supporting evidence that SPARTAN RM is dominated by organics. Simulated OM is enhanced over broad regions of South Asia, East Asia, and tropical Africa. Prior work has found that OM is a leading global PM$_{2.5}$ chemical component for mean concentrations and trends. We similarly find that OM continues to play a major role in population-weighted PM$_{2.5}$, following SIA and dust to contribute 28%.

Sulfate accounts for over 50% of SIA at all sampling sites, except Buenos Aires (46%), and accounts for approximately 6.5 $\mu$g/m$^3$ of population-weighted PM$_{2.5}$ concentrations. SPARTAN measurements of sulfate concentrations exceed 5 $\mu$g/m$^3$ at most sites in South and East Asia, in contrast with concentrations less than 2 $\mu$g/m$^3$ in Buenos Aires and Ilorin. The simulation generally captures the spatial distribution of measured sulfate concentrations ($r = 0.78$). Observations from the OMI satellite instrument have drawn attention to the pronounced SO$_2$ concentrations from coal combustion in East and South Asia, and sensitivity simulations have shown the influence of coal burning to the large PM$_{2.5}$ burden over China. The simulation reveals the spatial scale of the sulfate enhancement associated with these SO$_2$ sources. Modest measured enhancements are found in Rehovot, with associated regional scale enhancements across the Middle East. McLinden et al. found evidence of missing SO$_2$ sources in the Middle East that could contribute to the regional sulfate burden. Low simulated concentrations across North America and Europe reflect the success of SO$_2$ emission controls over recent decades.

The spatial pattern of measured ammonium concentrations largely follows that of measured sulfate ($r = 0.96$) and nitrate ($r = 0.93$), associated with the formation of ammonium sulfate, ammonium bisulfate, and ammonium nitrate. Ammonium contributes less than 10% to measured PM$_{2.5}$ concentrations with a population-weighted mean concentration of 3.0 $\mu$g/m$^3$. IASI satellite observations have revealed pronounced NH$_3$ enhancements across East and South Asia, from agricultural systems. Simulated ammonium concentrations are significantly correlated with measurements ($r = 0.86$), although...
Table 1. PM$_{2.5}$ Mass and Composition at SPARTAN Sites from Measurements (obs) and GEOS-Chem Simulation (GC). Values Are Reported in $\mu$g m$^{-3}$ for a Laboratory RH of 30–40%, and Simulated RH of 50%.

<table>
<thead>
<tr>
<th>Site</th>
<th>Date range (mm/yyyy)</th>
<th>PM$_{2.5}$</th>
<th>SO$_{4}^{2-}$</th>
<th>NO$_{3}^{-}$</th>
<th>NH$_{4}^{+}$</th>
<th>BC</th>
<th>RM/OM$^a$</th>
<th>dat$^{-1}$</th>
<th>RM/OM$^b$</th>
<th>dat$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beijing, China</td>
<td>06/2014–01/2017</td>
<td>7.4</td>
<td>0.3</td>
<td>1.0</td>
<td>0.2</td>
<td>0.4</td>
<td>0.1</td>
<td>0.8</td>
<td>0.7</td>
<td>0.2</td>
</tr>
<tr>
<td>Rangdang, Indonesia</td>
<td>07/2016–12/2016</td>
<td>7.1</td>
<td>0.5</td>
<td>0.8</td>
<td>0.5</td>
<td>0.6</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>Manila, Philippines</td>
<td>10/2014–12/2016</td>
<td>7.4</td>
<td>0.4</td>
<td>1.0</td>
<td>0.2</td>
<td>0.6</td>
<td>0.3</td>
<td>0.7</td>
<td>0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Dhaka, Bangladesh</td>
<td>01/2016–12/2016</td>
<td>7.2</td>
<td>0.6</td>
<td>0.7</td>
<td>0.4</td>
<td>0.8</td>
<td>0.3</td>
<td>0.5</td>
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<td>Dhaka, Bangladesh</td>
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<td>Dhaka, Bangladesh</td>
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<tr>
<td>Dhaka, Bangladesh</td>
<td>01/2016–12/2016</td>
<td>7.2</td>
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<td>0.3</td>
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<td>Dhaka, Bangladesh</td>
<td>01/2016–12/2016</td>
<td>7.2</td>
<td>0.6</td>
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<td>0.3</td>
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<td>Dhaka, Bangladesh</td>
<td>01/2016–12/2016</td>
<td>7.2</td>
<td>0.6</td>
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<td>0.4</td>
<td>0.8</td>
<td>0.3</td>
<td>0.5</td>
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<tr>
<td>Dhaka, Bangladesh</td>
<td>01/2016–12/2016</td>
<td>7.2</td>
<td>0.6</td>
<td>0.7</td>
<td>0.4</td>
<td>0.8</td>
<td>0.3</td>
<td>0.5</td>
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*RM = residual matter, and OM = organic mass.

Impact of ammonia uptake not represented in the simulation, as discussed further below and in the Supporting Information.

The degree of spatial variation in measured nitrate reflects the availability of nitric acid and excess ammonia to form ammonium nitrate. The highest measured concentrations are observed in Beijing (4.9 $\mu$g/m$^3$), Kanpur (3.8 $\mu$g/m$^3$), and Hanoi (3.7 $\mu$g/m$^3$), whereas the lowest are in Ilorin and Singapore (0.2 $\mu$g/m$^3$). The simulation generally reproduces the distribution of measured concentrations ($r = 0.85$); however, simulated concentrations are biased high in Beijing, Kanpur, and Dhaka where stronger agricultural ammonia sources exist. These discrepancies may reflect processes related to thermodynamic equilibrium between the gas and particle phase, aerosol neutralization as discussed in the Supporting Information, and uncertainty in NH$_{4}$ emissions. As is also possible that semi-volatile ammonium nitrate is lost from the filters despite the SPARTAN sampling procedure design to limit loss of semi-volatile species such as ammonium nitrate, and despite evidence of statistically insignificant trends in PM$_{2.5}$ and ammonium nitrate mass when comparing the mass collected on the first sampled filter (45-day residence time in instrument) and the last filter sampled (negligible residence time). The simulated population-weighted mean nitrate concentration of 2.4 $\mu$g/m$^3$, driven by elevated concentrations in East Asia, South Asia, and Europe, may be overestimated.

BC concentrations vary by a factor of 7 across SPARTAN sites, with concentrations exceeding 5 $\mu$g/m$^3$ in Beijing (73 $\mu$g/m$^3$), Dhaka (5.8 $\mu$g/m$^3$), and Kanpur (5.6 $\mu$g/m$^3$) and as low as 1.0 $\mu$g/m$^3$ in Ilorin. The GEOS-Chem simulation reveals the regional nature of the BC enhancements from a variety of combustion sources in East China and the Indo-Gangetic Plain. The downscaled simulation generally captures the BC concentrations at most SPARTAN sites ($r = 0.67$), suggesting skill in capturing the heterogeneous sources of this primary PM$_{2.5}$ component at the global scale. Population-weighted mean BC concentration is an order of magnitude lower than SIA at 4%.

Sea salt concentrations are low in both the measurements and simulation, yielding a contribution to population-weighted PM$_{2.5}$ of less than 2%.

**SPARTAN Site Characteristics.** SPARTAN composition measurements also offer insight into the site-specific source attribution from sensitivity simulations. The downscaled simulation generally captures the global spatial heterogeneity of major chemical components measured by SPARTAN as summarized in Table S2. Below, we use sensitivity simulations as described in the SI to further interpret SPARTAN measurements of PM$_{2.5}$ mass and chemical composition to understand sources in regions traditionally underrepresented by measurements of PM$_{2.5}$ components. Source categories selected for investigation follow those of Lelieveld et al. as described in Table S3. The presentation is grouped by region, the left column of all Figures S3–S8 shows measured PM$_{2.5}$ composition at the indicated SPARTAN site. The simulated chemical composition summed across all source sectors (Sens. Sim.) can exceed the downscaled simulated chemical composition (Sim.) due to nonlinearity in aerosol processes, primarily affecting nitrate, ammonium, and SOA. The agricultural source is most strongly influenced by this process and is likely overestimated both here and in other studies that exclude specific sources.
East Asia. Figure S3 shows the measured PM$_{2.5}$ composition and source attribution at two SPARTAN sites located in East Asia: Hanoi, Vietnam and Beijing, China. Measured PM$_{2.5}$ composition is dominated by RM (likely OM), followed by dust and sulfate. Residential energy use dominates the OM component of PM$_{2.5}$ through the burning of solid fuels for domestic cooking, space heating, and industrial purposes.55 Bonjour et al.56 estimate approximately 50% of the 2010 population in Vietnam and China burned solid fuels for domestic use. Open fires and other sources also contribute to OM in Hanoi due to transport of seasonal biomass burning plumes from Southeast Asia and the oxidation of biogenic volatile organic compounds (VOCs). SPARTAN measurements indicate that dust accounts for 22% of PM$_{2.5}$ in Beijing and 17% in Hanoi. In Beijing we find contributions from both mineral and anthropogenic dust, consistent with prior work.9,31,57 Simulated dust concentrations in Hanoi are driven by urban sources and underestimate the observations. Sulfate concentrations are influenced primarily by emissions from industry and power generation. Numerous studies have reported that decreasing SO$_2$ emissions from power generation in East Asia are being influenced primarily by emissions from industry and power generation.55,58,59 Ma et al.60 estimate that coal combustion contributes to 40% of the total PM$_{2.5}$ in Chinese cities. Ammonium concentrations are mostly from agricultural NH$_3$ and affected by formation with sulfate and nitrate. Agricultural activity has the largest impact on nitrate concentrations due to the limiting role that ammonia can play in ammonium nitrate formation.6,60,61 The positive bias in simulated nitrate and ammonium in Beijing could reflect loss of semivolatile species from measurements, errors in simulated thermodynamic partitioning, or missing processes.62,63 The bias is exacerbated by the sensitivity simulations due to nonlinear chemistry, when excluding specific sources, likely leading to an overestimate of the role of agriculture. Hanoi exhibits a minor increase in OM when emissions from agriculture are removed due to increased aerosol acidity, as this ammonia source neutralizes acidic components. Industrial sources of NO$_x$ (NO + NO$_2$) also contribute to nitrate formation in East Asia.60 BC has two primary source categories: residential energy and industrial activity; the negative bias could reflect heterogeneity of this primary source. Overall, each of the investigated source categories are active in East Asia and contribute to the complex PM$_{2.5}$ mixture measured by SPARTAN.

South Asia. Figure S4 shows the measured PM$_{2.5}$ composition and source attribution at two SPARTAN sites located in South Asia: Kanpur, India, and Dhaka, Bangladesh. Overall consistency is found across the two simulated source attributions. Kanpur is situated in the Indo-Gangetic plain where significant agricultural and industrial activity occur55,64 and stagnant air in winter enhances particulate matter concentrations.65–67 Dhaka is influenced by air masses transported from the Indo-Gangetic plain68 as well as strong local emission sources. The residential energy use source category is the largest simulated contributor to PM$_{2.5}$ in Kanpur and Dhaka, by substantially influencing OM and BC. An estimated 58% of the population in India and 91% of the population in Bangladesh in 2010 burned solid fuels for domestic heating and cooking.56 Sulfate concentrations are most heavily influenced by the power generation and industry source categories. Generally, there has been an increase in SO$_2$ emissions from India, driven by rapid economic development.5,59 Fioletov et al.70 found that coal-fired power plants account for nearly all major SO$_2$ emission sources seen by the OMI spacecraft instrument in India, with growth of a factor of 2 over 2005–2014, and a factor of 3 in the Chhattisgarh and Odisha regions, located south of the Kanpur site and west of the Dhaka site. The main fuel for the iron and steel industry is coal, resulting in SO$_2$ emissions from this sector as well.55,58 Current legislation does not require the installation of fuel gas desulfurization in either the industrial or power generation sectors.55,58 Elevated observed ammonia concentrations contribute to measured ammonium sulfate, and the sensitivity of ammonium to emissions from industry and power generation. Dust is a notable contributor to measured PM$_{2.5}$ in South Asia, accounting for 11% of total PM$_{2.5}$ in Dhaka and 8% in Kanpur due to both anthropogenic and natural sources. Previous studies (e.g., refs 63,71–76) have found evidence of desert dust transport from the western Thar Desert, Northeast Africa, and the Gulf region. The overestimation of the dust contribution to PM$_{2.5}$ by the simulation highlights the need for further development of the AFCID inventory and mineral dust simulation.

Southeast Asia. Figure S5 shows the measured PM$_{2.5}$ composition and source attribution at three SPARTAN sites in Southeast Asia: Bandung, Indonesia; Manila, Philippines; and Singapore. At all three sites, measured PM$_{2.5}$ is dominated by RM/OM, sulfate, and BC. The residential energy use source category has the largest impact on OM concentrations in Bandung and Manila through the burning of solid fuels in domestic cooking and heating; at least 50% of the population in Indonesia and the Philippines was estimated to burn solid fuels for domestic cooking in 2010.56 The negative biases in simulated OM and BC contributions suggest the contribution from the residential energy use combustion source may be underestimated. Open fires dominate OM concentrations in Singapore where seasonal biomass burning events throughout Southeast Asia significantly impact ground-level air quality.77–79 The OM simulation bias in Singapore could reflect mismatch in representing long-range transport of biomass burning emissions for the measurement period. Significant contributions to sulfate concentrations arise from the industry and power generation source categories from SO$_2$ emissions due to burning of high-sulfur containing fossil fuels in boilers, limestone kilns, furnaces, and power plants. A minor source of sulfate is the other source category as atmospheric oxidation of oceanic DMS80 and in Bandung, nearby volcanos.81 The overestimation of sulfate and ammonium in Manila, which is not found at the other two sites in this region, implies uncertainty in local emissions. The low measured and simulated nitrate concentrations at all three sites reflect ambient temperatures that thermodynamically limit NH$_4$NO$_3$ formation. The dust component of PM$_{2.5}$ in Southeast Asia is dominated by anthropogenic dust from industry, power generation, and transport in this region.

Sub-Saharan Africa. Figure S6 shows the measured PM$_{2.5}$ composition and source attribution in Ilorin, Nigeria, and Pretoria, South Africa. Both sites have measured PM$_{2.5}$ concentrations below 20 mg m$^{-3}$ that are mostly composed of residual (organic) mass, dust, and sulfate. Pronounced mineral dust concentrations in Ilorin arise from the Sahara Desert, where seasonal Harmattan trade winds advect fine dust to West Africa.82 Both sites are influenced by the open fires and residential energy use source categories. Ilorin is downwind of seasonal biomass burning events in west Africa,83 whereas open fires in central Africa affect South Africa.84 The burning of solid fuels (e.g., biofuel and coal) for domestic stoves and heaters accounts for the influence of the residential energy category on
organic, sulfate, and BC concentrations. In 2010 an estimated 74% of households used solid fuels for domestic cooking in Nigeria. Other sources of OM in PM$_{2.5}$ are biogenic VOCs from regional vegetation. Unlike many other SPARTAN sites, the industry and power generation source categories have minimal influence on PM$_{2.5}$ concentrations in Ilorin. However, power generation and industry are leading contributing source categories to sulfate in the industrialized city of Pretoria, although uncertainty in these emissions may lead to an overestimation.

**Buenos Aires, Argentina.** Figure S7 shows the measured PM$_{2.5}$ composition and source attribution in Buenos Aires, Argentina. Distinct from other SPARTAN sites, sensitivity simulations suggest most PM$_{2.5}$ arises from other, mostly natural, sources. SPARTAN measurements corroborate this conclusion, with 21% of PM$_{2.5}$ from sea salt, 20% from organics, and 16% from mineral dust. Mineral dust from the arid desert region to the northwest of the city influences the dust content of PM$_{2.5}$ at this site. Substantial cropland to the west and tree covered areas to the north provide a source of secondary organic aerosol from oxidation of biogenic emissions of VOCs such as isoprene and other monoterpenes. The flux of oceanic DMS influences sulfate; however, this source appears overestimated as indicated by the measurement-simulation differences. Industry and power generation are also notable sources of sulfate in Buenos Aires. Open fires from deforestation activity in the Amazon produce plumes that affect air quality in Argentina. Organic content increases when ammonia emissions from agriculture are removed due to increased aerosol acidity.

**Rehovot, Israel.** Figure S8 shows the measured PM$_{2.5}$ composition and source attribution at the Middle East site in Rehovot, Israel. Other, mostly natural, sources are the leading source category in this region, dominated by mineral dust; SPARTAN measurements indicate that 26% of PM$_{2.5}$ is dust, and also suggest that the simulation is overestimating this source. Power generation has the largest anthropogenic impact on PM$_{2.5}$ concentrations and is the leading source of sulfate at this site. The Middle East is among the largest SO$_2$ emitting regions in the world from oil fields and refineries. Transport of air masses from Europe have been shown to influence ground-level concentrations (e.g., refs 87, 88). Ammonium is found to be sensitive to sources of sulfate, suggesting elevated background NH$_3$; Clarisse et al. reported NH$_3$ columns well above background level in the Nile River Delta, southwest of the sampling site. Simulated ammonium is again higher than measurements. Elevated temperatures thermodynamically inhibit formation of particulate nitrate. The negative bias in simulated OM and BC suggests a missing combustion source.

**Global PM$_{2.5}$ Source Categories.** Overall, the general consistency of the simulation with measured PM$_{2.5}$ composition supports the applicability of using sensitivity simulations to explore the influence of source categories to global population-weighted PM$_{2.5}$. The most prominent exceptions are positive bias in ammonium nitrate and dust, implying that sensitivities to agricultural and crustal sources should be interpreted with caution. Figure 2 shows the impact of seven source categories to PM$_{2.5}$ as determined from sensitivity simulations that separately exclude each source. Values inset show the global population-weighted mean PM$_{2.5}$ concentrations from each source. The sum
of PM$_{2.5}$ concentrations from the seven source sectors exceeds the global mean PM$_{2.5}$ concentration (36.9 vs 32.6 μg/m$^3$) due to nonlinearity in modeled aerosol processes.

Six primarily anthropogenic categories contribute 76% of global PM$_{2.5}$ exposure. The residential energy use sector has the largest anthropogenic contribution, responsible for 21% (7.9 μg/m$^3$) of population-weighted PM$_{2.5}$. This residential category primarily includes small combustion sources for domestic heating, cooking, and waste disposal. These biofuel sources, diesel generators and burning of household waste, produce a large amount of indoor and outdoor carbonaceous PM$_{2.5}$ with implications for human health.\textsuperscript{7,41,89,90} The contribution of this source category to outdoor PM$_{2.5}$ is most pronounced in the populous areas of South Asia, East Asia, and Africa. Lacey et al.\textsuperscript{39} found that the elimination of solid fuel cookstoves over a 20-year period could avoid 22.5 million premature deaths associated with outdoor PM$_{2.5}$ between the years 2000 and 2100.

Industry is the second largest anthropogenic source category, contributing to 18% (6.5 μg/m$^3$) of population-weighted PM$_{2.5}$. Emissions from the industry source category include manufacturing of iron, steel, pulp, and paper, as well as oil refineries and fuel production. Industry contributes significantly to PM$_{2.5}$ in China and India and has a notable impact near major urban areas in the Americas, Europe, and Southeast Asia. The impact is highest in emerging economies and industrialized countries, in part due to international trade.\textsuperscript{91,92}

The four remaining anthropogenic categories are responsible for 37% of population-weighted PM$_{2.5}$. Power generation, although not the leading source in any one region, makes a prominent contribution of 15% to global population-weighted PM$_{2.5}$. Emissions of SO$_2$ and NO$_x$ from fossil fuel fired power plants are readily oxidized in the atmosphere to sulfate and nitrate, leading to enhanced PM$_{2.5}$ concentrations, especially in South Asia, East Asia, and North America. Agriculture, primarily NH$_3$ and NO$_x$ from fertilizer and domesticated animals, contributes 9% to global-population weighted PM$_{2.5}$. Agriculture is the leading source category in most of Europe and one of the leading sources over much of China and parts of India, similar to the findings of Lelieveld et al.\textsuperscript{7} The PM$_{2.5}$ contribution from agricultural activity is largest where both a large nitric acid burden exists from NO$_x$ emissions and where excess ammonia is available. The positive biases found in simulated ammonium nitrate suggest the sensitivity of PM$_{2.5}$ to this source may be overestimated. Transportation emissions contribute 8% of global population-weighted PM$_{2.5}$ through emissions of NO$_x$,BC, and SO$_2$; the most heavily influenced regions are East Asia, Southeast Asia, and the Indo-Gangetic plain. Emissions of carbonaceous aerosol and gaseous organic compounds from open fires comprise only 5% of population-weighted mean PM$_{2.5}$ concentrations. However, open fires can dominate PM$_{2.5}$ mass in large parts of the tropical and boreal forests.

All sources not clearly controlled by mitigation strategies, primarily natural in origin, are lumped into a single “Other sources” category described in Table S3. This combined Other category contributes 24% of population-weighted PM$_{2.5}$. Sources include mineral dust that dominates PM$_{2.5}$ in arid and semiarid regions of North Africa, the Middle East, Central Asia, and Australia. The size distribution of lofted dust aerosols extends from the coarse mode into the fine mode of PM$_{2.5}$ that can remain suspended and undergo long-range transport.\textsuperscript{93,94} This dust source may be overestimated. Sources of biogenic organic compounds, NO$_x$ from soil, and microbial activity of oceanic dimethyl sulfide contribute to a diffuse PM$_{2.5}$ background.

**DISCUSSION**

This initial interpretation of globally dispersed ambient PM$_{2.5}$ mass and composition measurements from SPARTAN with the GEOS-Chem model, with development motivated by SPAR-TAN measurements and constrained by satellite-based estimates of PM$_{2.5}$, identified a promising level of agreement along with areas for further model development. To our knowledge, this is the first global source attribution study that includes either constraints from satellite observations or comparison with global PM$_{2.5}$ composition measurements. Consistency between simulated and observed PM$_{2.5}$ composition adds confidence in utilizing the sensitivity simulations to identify the ambient PM$_{2.5}$ sources with prominent influence on population-weighted PM$_{2.5}$. The pronounced global contributions from residential energy use (21%), industry (18%), and power generation (15%) warrant further attention.

However, site-specific discrepancies between measured and simulated components such as nitrate/ammonium in Beijing and Kanpur, sulfate/ammonium in Manila and Buenos Aires, and dust in Ilorin and Rehovot provide insight into local biases in simulated PM$_{2.5}$ composition. It is possible that previous global source attribution studies (e.g., refs 7, 95, and 96) exhibit biases as well. Evidence of incomplete sulfate neutralization at SPARTAN sites, which is not captured in the simulation, requires additional investigation as this may partially explain the overestimate of simulated ammonium and nitrate concentrations. Although improvements to the dust simulation and emissions have been implemented in recent model versions (e.g., refs 31, 97), further attention is needed to mineral and AFCID emission inventories to address regional differences.\textsuperscript{98} Simulated OM remains underestimated at most SPARTAN sites, reiterating that development is needed to aerosol processes (e.g., SOA formation) and emission inventories that control this primary component (e.g., residential energy use and open fires). SPARTAN provides specified PM$_{2.5}$ measurements in many traditionally under-sampled regions, which could be used to constrain assimilations and inform developments to global chemical transport models. Additional ground-based, global measurements of PM$_{2.5}$ mass and composition will also be important to evaluate and improve these source attribution estimates.

We welcome expressions of interest to join this grass-roots network. Data collected by SPARTAN are publicly available at www.spartan-network.org.

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b01658.

Detailed description of SPARTAN chemical composition measurements and uncertainty estimates based on collocated measurements, GEOS-Chem simulation, and extent of sulfate neutralization; supporting figures for the site characteristics section (PDF)

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## REFERENCES


