

Using Sulfur as a Tracer of Outdoor Fine Particulate Matter

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Six homes in the metropolitan Boston area were sampled between 6 and 12 consecutive days for indoor and outdoor particle volume and mass concentrations, particle elemental concentrations, and air exchange rates (AERs). Indoor/outdoor (I/O) ratios of nighttime (i.e., particle nonindoor source periods) sulfur, PM_{2.5} and the specific particle size intervals were used to provide estimates of the effective penetration efficiency. Mixed models and graphical displays were used to assess the ability of the I/O ratios for sulfur to estimate corresponding I/O ratios for PM_{2.5} and the various particle sizes. Results from this analysis showed that particulate sulfur compounds were primarily of outdoor origin and behaved in a manner that was representative of total PM_{2.5} in Boston, MA. These findings support the conclusion that sulfur can be used as a suitable tracer of outdoor PM_{2.5} for the homes sampled in this study. Sulfur was more representative of particles of similar size (0.06–0.5 μm), providing evidence that the size composition of total PM_{2.5} is an important characteristic affecting the robustness of sulfur-based estimation methods.

Introduction

Numerous epidemiologic studies have reported associations between outdoor fine particle (PM_{2.5}) concentrations and adverse health effects (1, 2). Since people spend the majority (85–90%) of their time indoors (3), it is likely that a substantial fraction of exposure to outdoor PM_{2.5} occurs while indoors. Currently, however, it is not possible to measure indoor concentrations of outdoor origin directly, making it difficult to interpret risk estimates associated with outdoor PM_{2.5}.

In a recent paper examining the association between ambient PM_{2.5} concentrations and corresponding personal PM_{2.5} exposures, we used fine particle sulfate (SO₄²⁻) to estimate personal exposure to PM_{2.5} of ambient origin (4). Similarly, sulfur has been used to estimate the fraction of indoor PM_{2.5} originating outdoors (5). Since sulfur exists predominantly in the form of SO₄²⁻, it is expected that both

species will provide equivalent estimates of outdoor source contributions (6).

Sulfur compounds have been used to estimate PM_{2.5} of outdoor origin based on the assumptions that 1) sulfur compounds are primarily of outdoor origin and 2) their physical behavior is similar to that of other outdoor PM_{2.5} constituents. The first of these assumptions has been the subject of several monitoring studies, which show that few indoor or personal sources of sulfur or SO₄²⁻ exist (7, 8) and that outdoor sulfur and SO₄²⁻ concentrations are strongly associated with corresponding indoor concentrations and personal exposures (9, 10).

Fewer studies have focused on the validity of the second assumption. Results from theoretical particle deposition theory and field monitoring studies suggest that the behavior of sulfur particles, which has been shown to fall in or near the 0.2–0.7 μm size range (11–13), differs from that of smaller and larger sized particles (14, 15). Particles in the accumulation mode exhibit higher effective penetration efficiencies (i.e., higher penetration efficiencies and lower deposition rates) as compared to smaller (ultrafine) and larger (coarse) particles. These findings suggest that the effective penetration efficiencies will be higher for sulfur and similarly sized particles as compared to other sized particles. Since no studies have been conducted that directly compare the behavior of sulfur, total outdoor PM_{2.5} and size-specific PM_{2.5}, however, the magnitude of these differences and their impact on the ability of sulfur to act as tracer of outdoor PM_{2.5}, as well as of ultrafine and coarse particles, is not known.

This paper examines the ability of sulfur to serve as a tracer for PM_{2.5} of outdoor origin by examining nighttime indoor and outdoor PM_{2.5} and fine particle sulfur data from a study conducted in Boston, MA. The nighttime sampling periods were chosen to include times when no major indoor particle producing events occurred. In addition, data were used to examine the effect of air exchange rates, season, home characteristics and particle size on the associations among the effective penetration efficiencies.

Methods

(a) Study Design. Indoor and outdoor particle concentrations and composition data were collected as part of a comprehensive particle characterization study in the Boston area during 1998 (16). A complete description of the study design, sampling methods and quality assurance procedures has been discussed in ref 16. Nine homes in the metropolitan Boston area were sampled between 6 and 12 consecutive days for indoor and outdoor particle volume and mass concentrations, particle elemental analysis, and air exchange rate. Sampling was conducted during two seasons, spring-summer (March–July) and fall-winter (October–February) with 5 of the 9 homes sampled during both seasons.

The current analysis uses a subset of data (46 sampling days) from 6 homes for which sulfur and other elemental concentrations were measured. Four of the six homes were measured during both the spring-summer and fall-winter sampling periods. Daily time-activity records and household characteristics surveys were completed by household residents to provide information on indoor particle sources and particle generating activities that may have occurred during the sampling. All of the sampled homes were single-family dwellings. Homes ranged in age from 14 to 300 years old and had indoor volumes ranging between 265 and 677 m³. Three of the six homes in the current analysis used gas as their primary source of cooking and heating fuel. Only one home, House 5, used central air conditioning for cooling. With the

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exception of this air-conditioned home, residents typically opened windows and doors during the summer sampling months. Windows and doors were predominantly kept closed during the winter months as well as for most fall and spring sampling days (14).

(b) Sampling Methods. Indoor and outdoor continuous particle count concentrations of 13 discrete particle sizes were collected using a Scanning Mobility Particle Sizer (SMPS) and an Aerodynamic Particle Sizer (APS). The SMPS was used to provide data on particle volume concentrations for particle sizes ranging from 0.02 to 0.5 μm in diameter (0.02–0.03, 0.03–0.04, 0.04–0.06, 0.06–0.08, 0.08–0.1, 0.1–0.15, 0.15–0.2, 0.2–0.3, 0.3–0.4 and 0.4–0.5 μm). The APS provided data on particle volume concentrations for particle sizes ranging from 0.7 to 3.0 μm in diameter (0.7–1.0, 1.0–2.0, and 2.0–3.0 μm). Data for particles between 0.5 and 0.7 μm were not included in this analysis since previous studies have shown that neither the SMPS nor the APS accurately measures particles in this size range (16, 17). Twelve-hour nighttime concentrations for these continuous data were created using the median of the hourly size-resolved concentrations.

Indoor and outdoor 12-hour integrated $\text{PM}_{2.5}$ concentrations were measured using Harvard Impactors (HIs) and Teflon filters. The 12-hour $\text{PM}_{2.5}$ concentrations corresponded to both daytime (8AM–8PM) and nighttime (8PM–8AM) sampling periods.

Forty-nine pairs of outdoor and indoor $\text{PM}_{2.5}$ filters were analyzed for sulfur using X-ray fluorescence (XRF) analysis. The samples included nights during which no major particle producing events occurred, with 2 to 6 $\text{PM}_{2.5}$ sample pairs selected per home. Continuous air exchange rates (AERs) for the homes were calculated using a sulfur hexafluoride source with a photoacoustic monitor (16, 18). The continuous AER data were subsequently used to calculate 12-hour integrated measurements of AER.

As described in greater detail in ref 16, one set of SMPS and APS monitors located in a central room in the main living area of the study home (e.g., living room or dining room) was used to create indoor and outdoor continuous particle size measurements. A specially designed stainless steel sampling manifold was used to conduct the near-simultaneous indoor and outdoor sampling. The instruments sampled from ports in the manifold, which consisted of two identical arms, one extending into the sampling room and the other extending through a plywood board in a window to the outdoors. Electronically controlled ball valves were used to rotate between indoor and outdoor samples, with sampling occurring for three five-minute intervals indoors followed by one five-minute interval outdoors. The window was sealed around the manifold to prevent air leaks.

Quality assurance results pertaining to the size distribution and calibration of the SMPS and APS instruments has been described elsewhere (16, 19, 20). Harvard Impactors were operated at a flow rate of 10 LPM according to previously reported protocols (16). XRF analysis of 37-mm Teflon filters was performed at the Desert Research Institute (DRI) according to DRI standard analysis protocols (21).

(c) Data Analysis. $\text{PM}_{2.5}$ and sulfur concentrations are reported in $\mu\text{g}/\text{m}^3$. Size-resolved particle volume concentrations are reported in $\mu\text{m}^3/\text{cm}^3$. Data for the various particle species and sizes were characterized using descriptive statistics and mixed model regression analysis.

Data analyses were conducted using nighttime sampling periods exclusively when indoor particle generating activities (i.e., cooking and cleaning) were limited. Mixed model regression analysis was used to determine the strength of the nighttime association between indoor and outdoor concentrations and examine potential indoor source contributions. Indoor concentrations were modeled as dependent variables; outdoor concentrations were modeled as

independent, fixed variables; and home was modeled as an independent, random effect. Regression intercepts (i.e., indoor concentrations when outdoor concentrations equal zero) from these models provide information about the presence of indoor source contributions. Significance is reported at the 0.05 level. All analyses were conducted using the SAS system, version 8 (SAS Institute, Cary, NC)

Indoor/outdoor (I/O) ratios of nighttime sulfur, $\text{PM}_{2.5}$ and the specific particle size intervals were used to provide estimates of the effective penetration efficiency (P_{eff}). The steady-state solution to the indoor air mass balance equation shows that effective penetration efficiency is a function of AER, penetration efficiency and deposition rate

$$P_{\text{eff}} = \frac{C_{\text{in}}}{C_{\text{out}}} = \frac{Pa}{a + k} \quad (1)$$

where C_{in} and C_{out} are indoor and outdoor concentrations of sulfur or the specific particle measures ($\mu\text{g}/\text{m}^3$ or $\mu\text{m}^3/\text{cm}^3$); P is the penetration efficiency (dimensionless); a is the air exchange rate (h^{-1}); and k is the deposition rate (h^{-1}).

Since previous studies have used I/O sulfur ratios to predict indoor $\text{PM}_{2.5}$ concentrations of outdoor origin (5), much of the current analysis examines the associations between I/O ratios for sulfur and the specific particle measures. It should be noted that the concentrations for $\text{PM}_{2.5}$ and sulfur concentrations, expressed as mass concentrations, are not directly comparable with the particle size concentrations, which are expressed as particle volume concentrations.

Mixed models and graphical displays were used to assess the ability of the I/O ratios for sulfur to estimate corresponding I/O ratios for $\text{PM}_{2.5}$ and the various particle sizes. Model predictive ability was evaluated by examining the slope of the regression of the I/O sulfur ratios through the origin on those for either $\text{PM}_{2.5}$ or the specific particle size intervals. A slope of one indicated an unbiased (i.e., accurate) relationship between the I/O ratios, whereas a slope of 0.5 indicated that on average the sulfur I/O ratios were 50% greater than those for the other particle measures.

In addition, the predictive ability of sulfur was examined using the mean deviation between the I/O ratio for sulfur and that for the other particle measures. Mean deviations, which were used to provide a measure of relative agreement, were calculated as the mean of the absolute relative deviation

$$\left| \frac{(I/O)_{\text{sulfur},ij} - (I/O)_{\text{particle},ij}}{(I/O)_{\text{sulfur},ij}} \right| * 100 \quad (2)$$

where $(I/O)_{\text{sulfur},ij}$ is the I/O ratio of sulfur for home i on day j ; and $(I/O)_{\text{particle},ij}$ is the I/O ratio of a corresponding particle measure for home i on day j .

Mixed models were used to examine the effect of season on the strength of the I/O sulfur associations as

$$(I/O)_{\text{particle},ij} = \beta_0 + \beta_1(I/O)_{\text{sulfur},ij} + \beta_2(\text{season}_{ij}) + \beta_3(I/O)_{\text{sulfur},ij} * \text{season}_{ij} + b_i + \epsilon_{ij} \quad (3)$$

where $(I/O)_{\text{sulfur},ij} * \text{season}_{ij}$ is the interaction term characterizing the effect of season; b_i is the home-specific random effect; and ϵ_{ij} is the random error term. Similar models were also used to assess the effects of AER and home on the predictive ability of sulfur. Season, home and AER have been shown in previous studies to be highly collinear (23), thereby, precluding the use of regression models including more than one of these factors in the same model.

Sampling sessions were classified as having high AERs when 24-hour mean AERs exceeded 0.86 h^{-1} (i.e., the overall median AER for all of the homes), while homes with mean

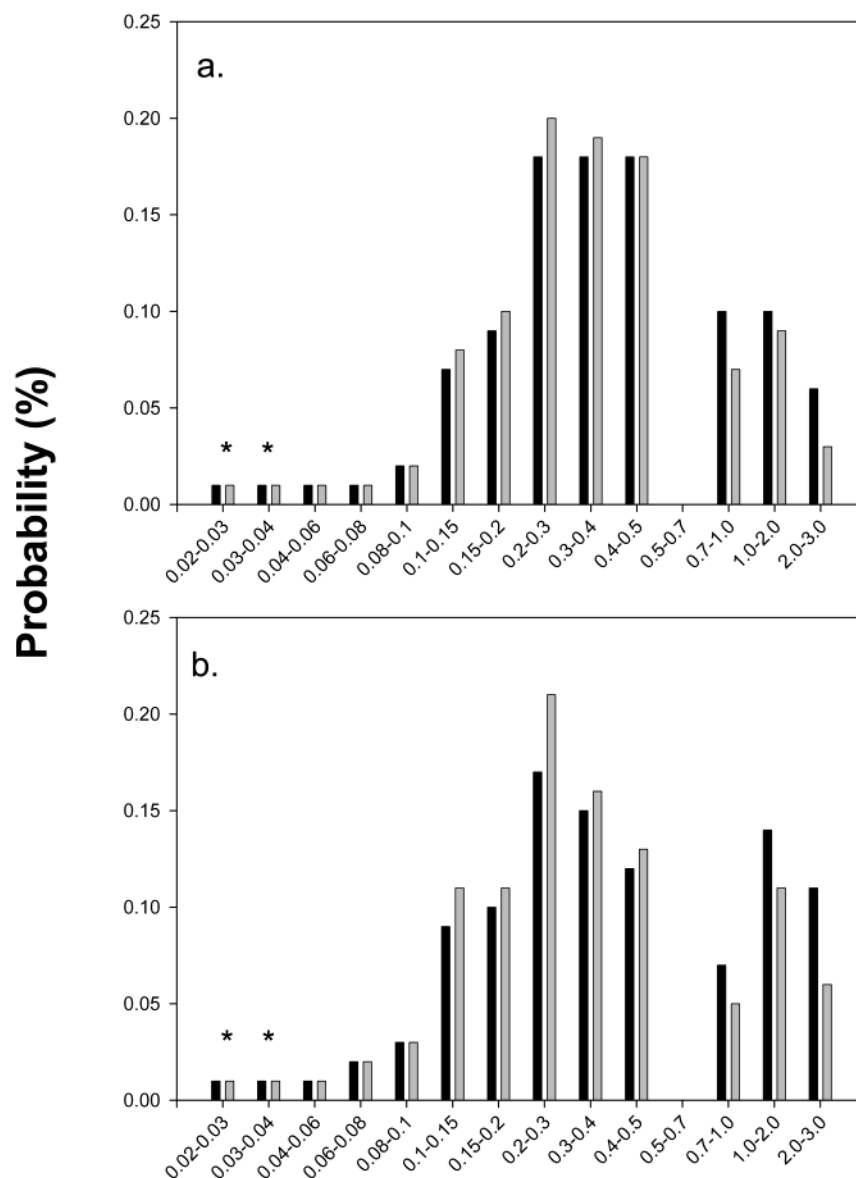


FIGURE 1. Probability distributions of indoor and outdoor particle volume size concentration by size interval during the a. spring-summer and b. fall-winter sampling periods. Black bars represent outdoor distributions. Grey bars represent indoor distributions. * indicates less than 1%.

AERs less than 0.86 h^{-1} were classified as having low AERs. Since AERs naturally vary by housing characteristics, geographic location and season, the “high” and “low” AER categories are study-specific and may not be representative of AERs in studies conducted elsewhere. A previous survey of 2844 U.S. homes from various geographic locations reported a mean AER of 0.76 h^{-1} (SD: 0.88) (22).

Results

Summary Statistics and Indoor–Outdoor Associations.

Mean AERs differed by home and by season and tended to be higher and more variable for homes sampled during the spring and summer as compared to homes sampled during the fall and winter (Table 1a,b). Mean nighttime AERs were 2.0 h^{-1} (CV = 1.1) and 0.8 h^{-1} (CV = 0.6) for the spring-summer and fall-winter sampling periods, respectively, reflecting the effect of open windows and increased ventilation during the warmer months and a tighter sealing of the homes during the colder months, as reported in Long et al. (16). During both seasons, mean nighttime AERs were lowest in House 5 (spring-summer: 0.18 h^{-1} ; fall-winter: 0.31 h^{-1}),

which may be due to its relative newness and its use of central air conditioning. For all of the homes, time-activity records indicated that indoor particle generating activities, such as cooking and cleaning, were infrequent (<3% of the time) during the nighttime sampling periods.

Nighttime outdoor concentrations of sulfur, $\text{PM}_{2.5}$ and the various particle sizes were generally higher than corresponding indoor concentrations, with outdoor sulfur and $\text{PM}_{2.5}$ concentrations exceeding indoor concentrations 89 and 93% of the sampling periods, respectively (Tables 1a,b and 2a,b). During both sampling seasons, sulfur compounds (expressed as $(\text{NH}_4)_2\text{SO}_4$) comprised approximately 45% of $\text{PM}_{2.5}$ in the spring-summer and 35% during the fall-winter. Both outdoor and indoor $\text{PM}_{2.5}$ fell primarily within the 0.01 to $0.5 \mu\text{m}$ range on a particle volume basis, accounting for approximately 70 and 65% of the measured particles during the spring-summer and fall-winter sampling seasons, respectively (Figure 1). I/O sulfur ratios ranged between 0.33 and 1.07 during the nighttime sampling periods, with a mean of 0.72 (Table 3). Mean I/O ratios for the specific particle size intervals were comparable to $\text{PM}_{2.5}$, ranging from 0.42 to

TABLE 1. Summary of Nighttime Outdoor (a) and Indoor (b) Sulfur and PM_{2.5} Concentrations^a

	house	N	AER		sulfur				PM _{2.5}			
			mean	SD	mean	SD	median	max	mean	SD	median	max
a. Outdoors												
spring-summer	1	5	0.88	0.26	1.8	0.5	1.8	2.6	15.8	5.3	13.4	23.8
	2	5	4.35	2.59	1.5	1.4	1.0	3.9	13.2	9.8	8.7	30.6
	3	6	0.93	0.23	1.5	1.0	1.0	3.0	12.7	5.6	10.7	21.8
	4	4	4.69	0.63	3.9	1.9	3.6	6.4	26.0	12.3	24.4	41.4
	5	6	0.18	0.02	1.2	0.6	1.2	2.0	13.6	5.4	11.1	22.1
total spring-summer		26	1.98	2.17	1.9	1.4	1.4	6.4	15.6	8.5	12.9	41.4
fall-winter	1	5	0.82	0.21	1.1	0.7	0.8	2.3	11.6	6.7	8.0	22.3
	3	2	1.66	0.52	1.0	0.0	1.0	1.0	10.3	2.7	10.3	12.2
	4	5	0.73	0.38	0.9	0.4	1.0	1.3	10.2	5.5	10.9	13.8
	5	6	0.31	0.04	0.7	0.2	0.7	1.0	10.6	3.8	9.9	15.4
	6	2	1.48	0.23	1.0	0.3	0.9	1.3	10.9	2.4	10.5	14.8
total fall-winter		20	0.80	0.50	0.9	0.4	0.9	2.3	10.8	4.1	9.4	22.3
total		46	1.47	1.76	1.4	1.2	1.0	6.4	13.5	7.3	11.6	41.4
b. Indoors												
spring-summer	1	5	0.88	0.26	1.5	0.5	1.6	2.0	13.9	5.1	10.9	19.6
	2	5	4.35	2.59	1.3	1.1	0.8	3.3	12.3	7.8	9.7	26.1
	3	6	0.93	0.23	1.2	0.7	0.9	2.1	9.5	2.9	8.7	12.9
	4	4	4.69	0.63	3.6	1.5	3.7	4.8	22.2	9.4	23.2	31.0
	5	6	0.18	0.02	0.6	0.3	0.6	1.0	7.9	2.7	7.9	12.1
total spring-summer		26	1.98	2.17	1.5	1.2	0.9	4.8	12.5	7.1	9.9	31.0
fall-winter	1	5	0.82	0.21	0.8	0.6	0.6	1.7	8.3	3.6	6.1	14.1
	3	2	1.66	0.52	0.7	0.1	0.7	0.7	7.1	0.2	7.1	7.3
	4	5	0.73	0.38	0.7	0.3	0.7	1.3	7.7	3.7	8.4	10.1
	5	6	0.31	0.04	0.3	0.1	0.3	0.5	5.4	1.4	5.9	6.6
	6	2	1.48	0.23	0.7	0.4	0.5	1.0	8.4	2.2	7.5	11.0
total fall-winter		20	0.80	0.50	0.6	0.4	0.5	1.7	7.2	2.5	6.4	14.1
total		46	1.47	1.76	1.1	1.1	0.7	4.8	10.2	6.2	8.5	31.0
a Units for all concentration data are in µg/m³. Units for AERs are in exchanges/hour.												

^a Units for all concentration data are in $\mu\text{g}/\text{m}^3$. Units for AERs are in exchanges/hour.

0.76 for 2.0–3.0 and 0.1–0.3 μm particles, respectively, as compared to a mean I/O ratio of 0.76 for PM_{2.5}. Generally, mean I/O ratios were lowest for the smallest ($<0.06\mu\text{m}$) and largest ($>0.7\mu\text{m}$) sized particles and did not exceed 0.63.

Nighttime indoor concentrations of PM_{2.5}, sulfur and all of the particle size intervals were strongly associated with their corresponding outdoor concentrations, with nonsignificant intercepts when indoor concentrations were regressed on outdoor levels (Table 4). These nonsignificant intercepts suggest that indoor source contributions to indoor particle concentrations were minimal during the nighttime periods.

Seasonal differences in indoor-outdoor associations for PM_{2.5}, the smaller particles (0.03–0.04 μm , $p < 0.03$; 0.04–0.06 μm , $p < 0.0005$) and the larger particles (1.0–2.0 μm , $p < 0.0004$; 2.0–3.0 μm , $p < 0.01$) were found, with typically stronger associations found during the spring-summer period. Consistent with previous studies (10, 16), associations between indoor and outdoor particle concentrations were influenced by AERs (Figure 2). AERs were shown to have a significant effect on the association between indoor and outdoor levels of PM_{2.5}, sulfur and many of the particle size intervals ($p < 0.005$). Stronger indoor-outdoor associations were generally observed when AERs were classified as “high” as compared to “low”. AERs were not found to significantly influence indoor-outdoor associations for particles in the 0.02–0.03, 0.04–0.06 and 2.0–3.0 μm size ranges. Likewise, no significant differences by home in indoor-outdoor associations for PM_{2.5}, sulfur and the size-resolved particle concentrations were found.

Sulfur as a Tracer of PM_{2.5}. Results from regression analysis showed that I/O sulfur ratios were strongly associated with corresponding I/O PM_{2.5} ratios, with a regression slope of 1.02 (CL: 0.96–1.08, $p < 0.0001$) (Figure 3). These results suggest that I/O sulfur ratios provided accurate predictions of I/O PM_{2.5} ratios. The use of I/O ratios for sulfur-to-predict

ratios for PM_{2.5} resulted in a mean deviation of $\pm 14.2\%$ (SD: 12.2) (Figure 4).

Season was not shown to have a significant influence explaining the correlation between I/O ratios for sulfur and PM_{2.5} ($p = 0.31$). Slopes from season-specific regression models were significant, comparable, and had confidence intervals that included one, indicating that I/O sulfur ratios were accurate predictors of I/O PM_{2.5} ratios during both seasons (Figure 3). The mean deviation in the association between I/O sulfur and I/O PM_{2.5} ratios also did not differ statistically across seasons, as shown by pooled t -tests (p -value = 0.53), with mean deviations of 13.2 and 15.4% in the spring-summer and fall-winter, respectively.

Similarly, the accuracy of using sulfur to estimate I/O ratios for PM_{2.5} was not affected by AER ($p = 0.46$). Based on regression results, I/O sulfur ratios were accurate predictors of I/O PM_{2.5} ratios for both high and low AER values (Figure 5). Although the mean deviation between I/O sulfur and I/O PM_{2.5} did vary significantly by AER, with greater mean deviations shown for the low AER group (mean deviation: high AER = 10.1%, low AER = 18.3%, t -test p -value = 0.02), these differences did not affect the general ability of sulfur ratios to predict I/O PM_{2.5} for homes in the low AER group.

The relatively few measurements per home resulted in limited statistical power for models assessing differences in the ability of sulfur to accurately predict I/O ratios for PM_{2.5} among homes. Home-specific regression slopes and mean deviations between I/O sulfur and I/O PM_{2.5} were, however, comparable among the homes, with the exception of House 5 (Figure 7). House 5 had a regression slope that differed significantly from one (slope = 1.13, 95% CI: 1.00–1.26) as well as a spring-summer mean deviation (28.0%) that was considerably higher to that for the other homes sampled (mean: 8.6%), which may be again reflective of the low AERs in this home.

TABLE 2. Summary of Nighttime Outdoor and Indoor Size-Resolved Particle Concentrations for the Spring-Summer (a) and Fall-Winter (b) Sampling Seasons^a

size (μm)	outdoor				indoor			
	mean	SD ^b	median	max	mean	SD ^b	median	max
a. Spring-Summer								
0.02–0.03	0.006	0.003	0.005	0.012	0.003	0.003	0.002	0.010
0.03–0.04	0.013	0.008	0.014	0.036	0.008	0.006	0.007	0.027
0.04–0.06	0.076	0.042	0.075	0.189	0.051	0.034	0.048	0.136
0.06–0.08	0.154	0.083	0.147	0.303	0.107	0.070	0.094	0.294
0.08–0.1	0.223	0.125	0.215	0.479	0.157	0.099	0.154	0.455
0.1–0.15	0.927	0.505	0.889	1.898	0.675	0.367	0.595	1.282
0.15–0.2	1.182	0.790	0.974	3.706	0.872	0.536	0.740	2.356
0.2–0.3	2.369	1.574	1.746	7.247	1.776	1.180	1.381	5.162
0.3–0.4	2.418	1.357	1.958	5.920	1.932	1.418	1.347	6.468
0.4–0.5	2.300	1.448	1.753	6.082	1.823	1.375	1.299	5.448
0.5–0.7								
0.7–1.0	1.353	1.634	0.830	7.157	0.857	1.134	0.508	5.247
1.0–2.0	1.338	1.125	1.044	5.803	0.831	0.774	0.648	3.828
2.0–3.0	0.735	0.382	0.636	1.746	0.344	0.260	0.247	0.913
b. Fall-Winter								
0.02–0.03	0.002	0.001	0.002	0.006	0.001	0.001	0.001	0.002
0.03–0.04	0.011	0.008	0.009	0.039	0.005	0.003	0.004	0.015
0.04–0.06	0.079	0.059	0.067	0.289	0.043	0.030	0.035	0.144
0.06–0.08	0.140	0.094	0.124	0.488	0.087	0.061	0.076	0.315
0.08–0.1	0.173	0.093	0.166	0.506	0.114	0.075	0.105	0.393
0.1–0.15	0.584	0.233	0.584	1.077	0.398	0.184	0.336	0.808
0.15–0.2	0.634	0.234	0.696	1.141	0.449	0.219	0.352	0.914
0.2–0.3	1.128	0.492	1.032	2.330	0.813	0.466	0.652	1.792
0.3–0.4	0.963	0.507	0.843	1.945	0.709	0.514	0.518	2.133
0.4–0.5	0.772	0.482	0.669	2.227	0.547	0.393	0.410	1.545
0.5–0.7								
0.7–1.0	0.438	0.494	0.336	2.463	0.236	0.223	0.158	1.094
1.0–2.0	0.904	0.819	0.674	3.447	0.464	0.364	0.335	1.541
2.0–3.0	0.694	0.595	0.560	2.840	0.242	0.197	0.191	0.938

^a N = 46 for all intervals. Units for all data are in $\mu\text{m}^3/\text{cm}^3$. ^b SD refers to pooled standard deviation.

TABLE 3. Comparison of Nighttime Indoor-Outdoor Ratios for Sulfur, PM_{2.5} and the Size-Resolved Particle Data

	mean	median	minimum	maximum	CV ^a
sulfur	0.72	0.72	0.33	1.07	0.27
PM _{2.5}	0.76	0.76	0.41	1.11	0.23
Particle Size Interval					
0.02–0.03	0.57	0.48	0.16	2.55	0.70
0.03–0.04	0.57	0.51	0.19	1.33	0.46
0.04–0.06	0.63	0.62	0.22	1.17	0.34
0.06–0.08	0.69	0.68	0.25	1.07	0.33
0.08–0.1	0.71	0.74	0.27	1.31	0.33
0.1–0.15	0.74	0.76	0.29	1.08	0.30
0.15–0.2	0.76	0.79	0.27	1.32	0.29
0.2–0.3	0.76	0.79	0.25	1.30	0.29
0.3–0.4	0.75	0.77	0.29	1.37	0.30
0.4–0.5	0.74	0.74	0.37	1.42	0.30
0.7–1.0	0.60	0.61	0.19	0.96	0.30
1.0–2.0	0.58	0.54	0.12	1.04	0.37
2.0–3.0	0.42	0.40	0.08	0.83	0.45

^a CV refers to coefficient of variation.

Sulfur as a Tracer of Discrete Particle Sizes. I/O ratios for sulfur were plotted against I/O ratios for the 13 particle size intervals to examine whether the effective penetration efficiency of sulfur was similar to that for all particle sizes (Figure 6). Although I/O sulfur ratios were significant predictors of corresponding I/O ratios for all particle sizes, the accuracy and agreement among the predictions varied by particle size (Figure 4).

Results from regression analyses provide evidence that I/O sulfur ratios over-predicted I/O ratios for particles less than 0.06 μm and greater than 0.7 μm in size (Figure 6).

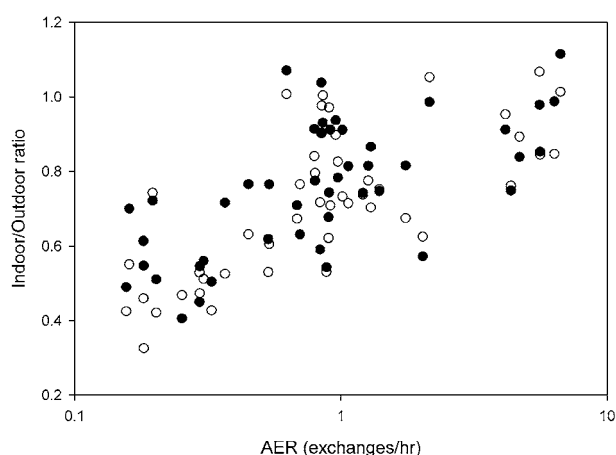
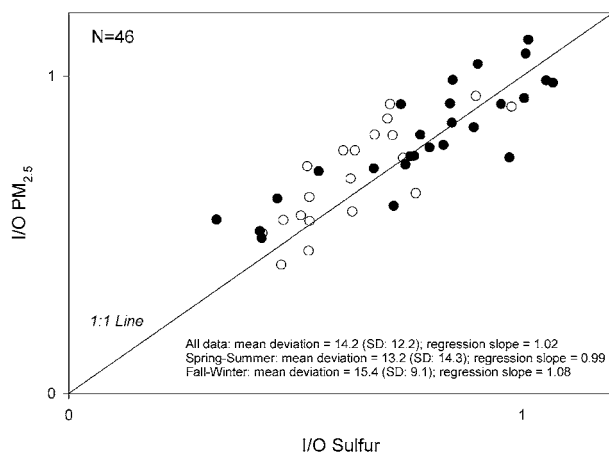
Slopes from the regression models comparing I/O ratios for these size intervals were significantly lower than one, suggesting greater effective penetration efficiencies for sulfur as compared to smaller and larger particles. Similarly, the agreement between I/O ratios for sulfur and I/O ratios for particles less than 0.06 μm and greater than 0.7 μm in size was weaker than those for other sized particles (Figure 4). Mean deviations between I/O sulfur and I/O ratios for these particle sizes were greater and more variable than for particles in the intermediate size ranges (0.06–0.5 μm). For the six particle size intervals less than 0.06 μm and greater than 0.7 μm in size, mean deviations were on average equal to 28% (SD: 9.1%), whereas for the seven particle size intervals between 0.06 and 0.5 μm in size mean deviations were on average 16.3% (SD: 1.0%).

As with PM_{2.5}, the accuracy of sulfur as a tracer of discrete outdoor particle sizes did not vary by home as suggested by the comparable regression slopes obtained for the different particle sizes. There was evidence that mean deviations differed among the homes for the specific particle size intervals, with greater variability in the mean deviations across homes for particles in the smallest and largest size intervals (Figure 7).

Results also indicated that there was little seasonal difference in the associations between I/O sulfur ratios and the I/O ratios for the specific particle sizes (Figure 8a). I/O sulfur ratios were significantly associated with corresponding I/O ratios for the various particle sizes during both sampling seasons. Seasonal differences in the slope between I/O sulfur and the particle sizes were significant for only 4 of the 13 particle size intervals ($p = 0.03, 0.01, 0.01$ and 0.01 for 0.03–0.04, 0.3–0.4, 0.4–0.5 and 2.0–3.0 μm intervals, respectively). Additionally, t -tests comparing mean deviations between seasons showed that there were no significant seasonal

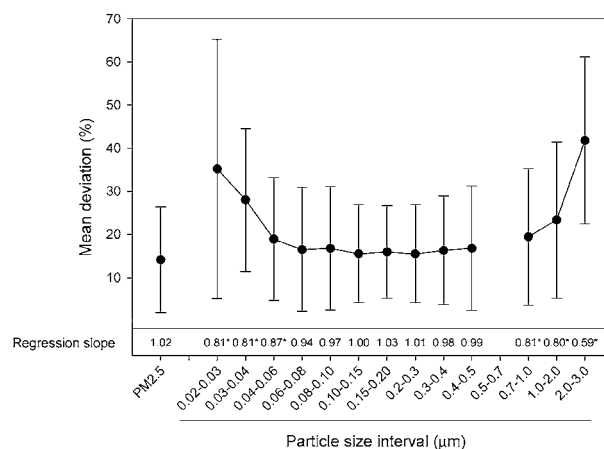
TABLE 4. Results from Indoor on Outdoor Mixed Model Regression Analysis by Season

	N	all data		spring-summer			fall-winter		
		slope	intercept	N	slope	intercept	N	slope	intercept
sulfur	46	0.84 ^a	-0.09	26	0.77 ^a	1.09	20	0.83 ^a	-0.16
PM _{2.5}	46	0.74 ^a	0.36	26	0.72 ^a	1.48	20	0.47 ^a	2.22
Size-Resolved Data									
0.02–0.03	46	0.32 ^a	0.001	26	0.35 ^a	0.001	20	0.32 ^a	0.0003
0.03–0.04	46	0.39 ^a	0.003	26	0.48 ^a	0.002	20	0.38 ^a	0.001
0.04–0.06	46	0.52 ^a	0.01	26	0.68 ^a	0.0004	20	0.48 ^a	0.005
0.06–0.08	46	0.64 ^a	0.008	26	0.73 ^a	-0.002	20	0.60 ^a	0.004
0.08–0.1	46	0.67 ^a	0.01	26	0.73 ^a	-0.001	20	0.70 ^a	-0.006
0.1–0.15	46	0.62 ^a	0.09	26	0.68 ^a	0.06	20	0.59 ^a	0.06
0.15–0.2	46	0.57 ^a	0.17	26	0.57 ^a	0.23	20	0.63 ^a	0.05
0.2–0.3	46	0.61 ^a	0.3	26	0.58 ^a	0.46	20	0.72 ^a	0.01
0.3–0.4	46	0.83 ^a	-0.06	26	0.83 ^a	-0.03	20	0.82 ^a	-0.1
0.4–0.5	46	0.80 ^a	-0.03	26	0.75 ^a	0.14	20	0.65 ^a	0.05
0.7–1.0	46	0.64 ^a	-0.06	26	0.61 ^a	0.05	20	0.43 ^a	0.06
1.0–2.0	46	0.57 ^a	0.02	26	0.60 ^a	0.06	20	0.42 ^a	0.1
2.0–3.0	46	0.33 ^a	0.09	26	0.42 ^a	0.04	20	0.29 ^a	0.05

^a Indicates significance at the 0.0001 level.FIGURE 2. Relationships between I/O ratios and AERs. Filled circles represent relationships for PM_{2.5}. Open circles represent relationships for sulfur. N = 46 for both plots.FIGURE 3. Indoor-outdoor ratio of PM_{2.5} vs sulfur by season. Filled circles represent samples collected during the spring or summer. Open circles represent samples collected during the fall or winter.

differences between I/O ratios for sulfur and I/O ratios for any of the particle size intervals.

I/O sulfur ratios were significantly associated with corresponding I/O ratios for the various particle sizes both for low and high AERs (Figure 8b). Regression analyses using

FIGURE 4. Regression slopes and mean deviation between I/O ratios for sulfur and I/O ratios for PM_{2.5} and the various particle sizes. Error bars represent standard errors of mean deviation values. * Indicates regression slope significantly different from one.

I/O sulfur ratios to predict I/O ratios for the particle sizes showed that AER did not significantly affect the strength of this association for any of the particle sizes examined. (For two particle size intervals, 0.02–0.03 and 0.03–0.04 μm, slopes were significantly lower than one for low AERs but not for high AERs, suggesting that I/O ratios for sulfur over-predicted I/O ratios for these particles sizes in low AERs). There were significant differences in the mean deviation between I/O ratios for sulfur and particles in the smallest size intervals (0.02–0.03 and 0.03–0.04 μm) as well as two of the largest size interval (0.7–1.0 and 2.0–3.0 μm). For these particle sizes, mean deviations for homes with low AERs were significantly higher than that for homes with high AERs ($p = 0.02, 0.04, 0.04$ and 0.01 for the 0.02–0.03, 0.03–0.04, 0.7–1.0 and 2.0–3.0 μm size intervals, respectively).

Discussion

Results from the current analysis provide evidence of the lack of indoor sulfur sources. Consistent with earlier studies (24–26), indoor sulfur concentrations were strongly associated with outdoor levels. The nonsignificant regression intercepts also suggest that sulfur was largely outdoor in origin. Although these results were shown for nighttime periods, when few indoor particle sources were present, other studies have found similar strong indoor and outdoor sulfur

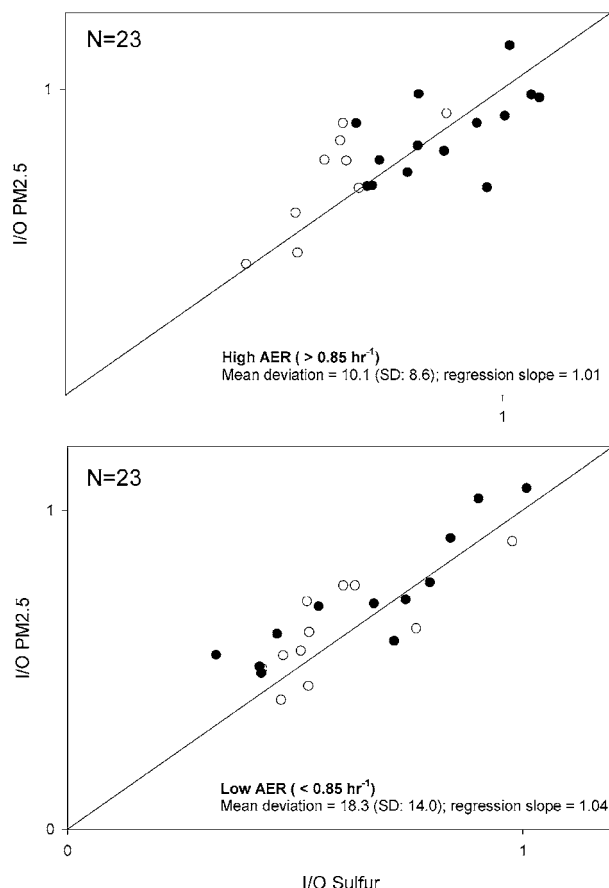


FIGURE 5. Indoor-outdoor ratio of PM_{2.5} vs sulfur by AER. Filled circles represent samples collected during the spring or summer. Open circles represent samples collected during the fall or winter.

correlations for daytime periods as well. Results from a study conducted in State College, PA, for example, show that the relationship between indoor and outdoor SO_4^{2-} concentrations did not differ substantially between day and night (10). Both daytime and nighttime outdoor SO_4^{2-} concentrations were strongly associated with corresponding indoor SO_4^{2-} concentrations ($p < 0.0001$) with nonsignificant regression intercepts. Moreover, there was little difference in the daytime and nighttime slopes for SO_4^{2-} from State College, suggesting that indoor particle generating activities that occurred during the daytime had little effect on the strong indoor-outdoor SO_4^{2-} associations. Studies from personal exposure studies have also shown home outdoor sulfur (27) and central site outdoor sulfate (4, 28) to be strongly correlated with corresponding personal exposures, providing further evidence of limited personal and indoor sulfur sources.

I/O sulfur ratios were strongly associated with corresponding I/O PM_{2.5} ratios, suggesting that sulfur behaved in a manner that was representative of total PM_{2.5} across the range of observed effective penetration efficiencies. Based on these findings, we can expect that applying the observed mean I/O sulfur ratio of 0.72 to outdoor PM_{2.5} concentrations would generate suitable estimates of indoor PM_{2.5} concentrations of outdoor origin for this study conducted in Boston.

There were indications, however, that sulfur may not be as strong a tracer of outdoor PM_{2.5} for studies conducted in different locations or under different sampling conditions. The results showed that sulfur-based predictions of PM_{2.5} of outdoor origin were less accurate for locations or indoor environments with lower mean AERs, as the difference in the mean deviation between homes with high and low mean AERs (~8%) was significant. It should be emphasized,

however, that the association between I/O sulfur and PM_{2.5} was still strongly significant. Similarly, sulfur's ability to act as a tracer of outdoor fine particles was not uniform across the sampled homes, as evidenced by House 5, for which the mean deviation between I/O sulfur and PM_{2.5} ratios was considerably higher as compared to that for other homes.

The independent effects of home, AER and season (which was not shown to significantly influence either the accuracy or agreement of the sulfur-based predictions) were difficult to separate, however, since it is likely that correlations between home, season and AERs existed (23). House 5, for example, was the newest home, had the lowest mean AERs, and was also the only home that used central air conditioning. Likewise, AERs were significantly higher during the spring-summer sampling period as compared to the fall-winter sampling period. It is reasonable to assume that, in the current study, the variables of season and home are both serving as rough surrogates of AER, which may explain why associations attributable to AERs were stronger as compared to season and home. A larger sample size and more heterogeneous sampling conditions both between and within homes may clarify the independent effects and relative strengths of these factors on the observed associations in this Boston study.

A key finding from the current analysis is that strong associations exist between I/O ratios for sulfur and particles in the 0.06 and 0.5 μm size range, indicating that sulfur is a better tracer of particles within this size range. These results were consistent with findings from recent studies showing strong associations between particle size and effective penetration efficiency and the fact that sulfur typically falls in or near the 0.2–0.7 μm size range (11–14). In contrast, regression results showed that the use of I/O sulfur ratios as a tracer for particles less than 0.06 or greater than 0.7 μm in size would over predict the amount of those sized particles of outdoor origin. As a result, sulfur-based estimates of ambient origin particles in these smallest and largest size intervals were less accurate, with the mean deviation between I/O ratios for sulfur and 0.02–0.03 μm size particles, for example, over two times greater than the mean deviation between sulfur and 0.2–0.3 μm sized particles.

AERs significantly influenced the accuracy of the sulfur-based tracer method, but only for particles in the smallest and largest size interval. For particles in the 0.10–0.15 μm size interval, for example, AER-associated differences in mean deviation were only 2%, as compared to over 20% for particles in the 0.02–0.03 μm size interval. For particles between 0.06 and 0.5 μm in size, the robustness of sulfur as an outdoor particle tracer method across AERs (as well as across seasons and homes) was important, since it indicates that sulfur-based estimates are not sensitive to site-specific parameters, such as AERs and other household and building characteristics.

The variable impact of AER on the different particle sizes suggests that these differences were responsible for the observed AER-associated differences in I/O ratios for sulfur and total PM_{2.5}. These findings are consistent with particle behavior, where particle removal mechanisms, which have the greatest influence on ultrafine and coarse particles, have been shown to be less important for homes with higher AERs (14). Long et al. (14), for example, also showed that mean I/O ratios varied by particle size (0.02 to 10 μm) but that mean I/O ratios for all particle sizes approached one as AERs reached approximately 2 h^{-1} .

Together, these findings suggest that sulfur is a good tracer of outdoor PM_{2.5} for areas, such as Boston, where outdoor PM_{2.5} tends to fall within a size range typical of that for sulfur and is comprised of a large fraction of sulfur compounds. Sulfur may be a less robust tracer of outdoor PM_{2.5} for areas such as the western U.S., where smaller, ultrafine particles or larger, coarse particles comprise a greater fraction of PM_{2.5}.

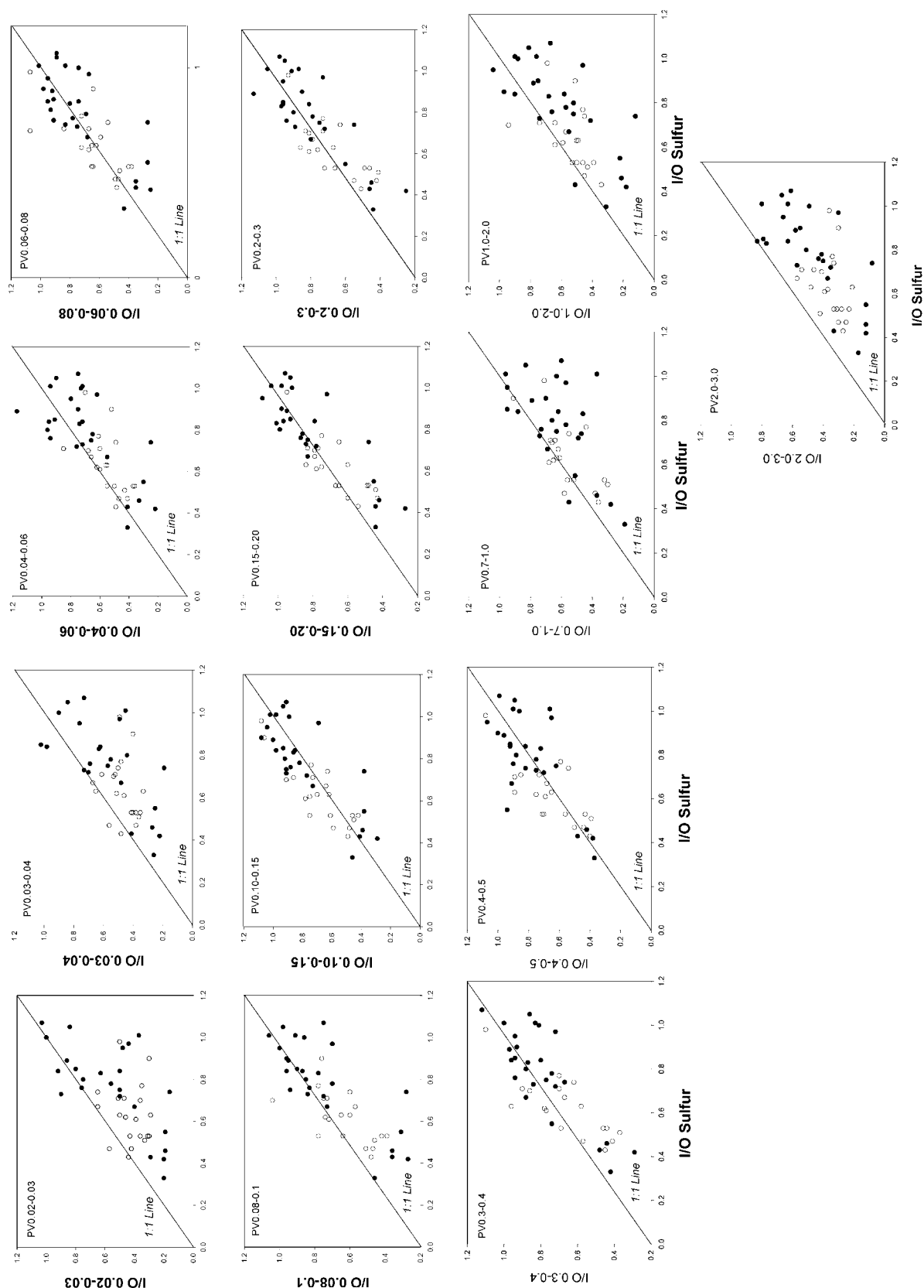


FIGURE 6. I/O size-resolved data vs I/O sulfur. Filled circles represent samples collected during the spring or summer. Open circles represent samples collected during the fall or winter. $N = 46$ for all plots. One outlier (1.4, 1.0) not shown in plot of I/O 0.02–0.03 vs I/O sulfur.

and where sulfur compounds comprise a smaller fraction of total $PM_{2.5}$. Previous particulate matter monitoring studies, for example, have shown that the relative mass contribution of ammonium sulfate to total outdoor $PM_{2.5}$ can be as much

as three times higher in eastern U.S. locations as compared to locations in the western U.S. (29). In addition, the results indicate that using sulfur-based methods in locations where residences typically have lower mean AERs, such as those

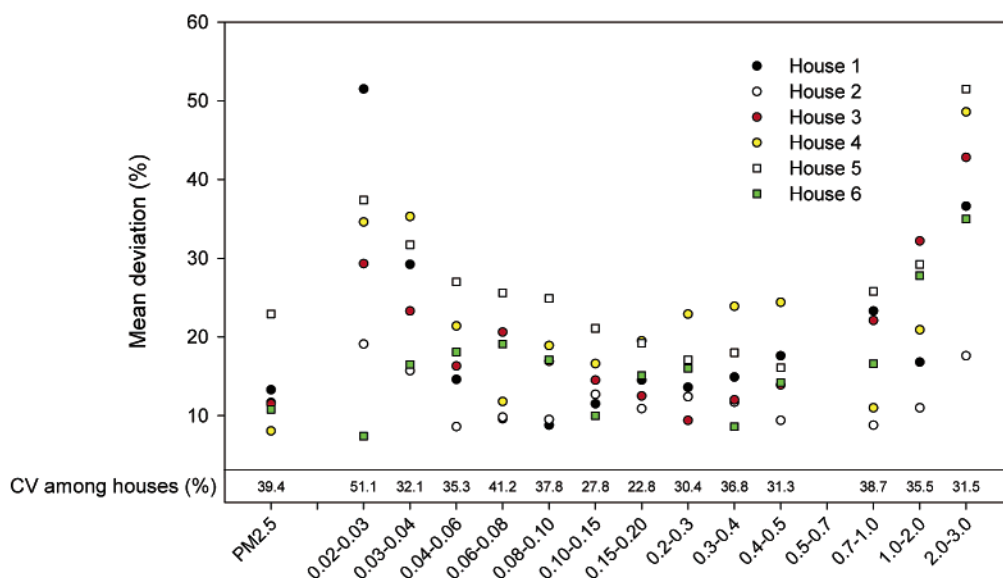


FIGURE 7. Mean deviation by home and particle size.

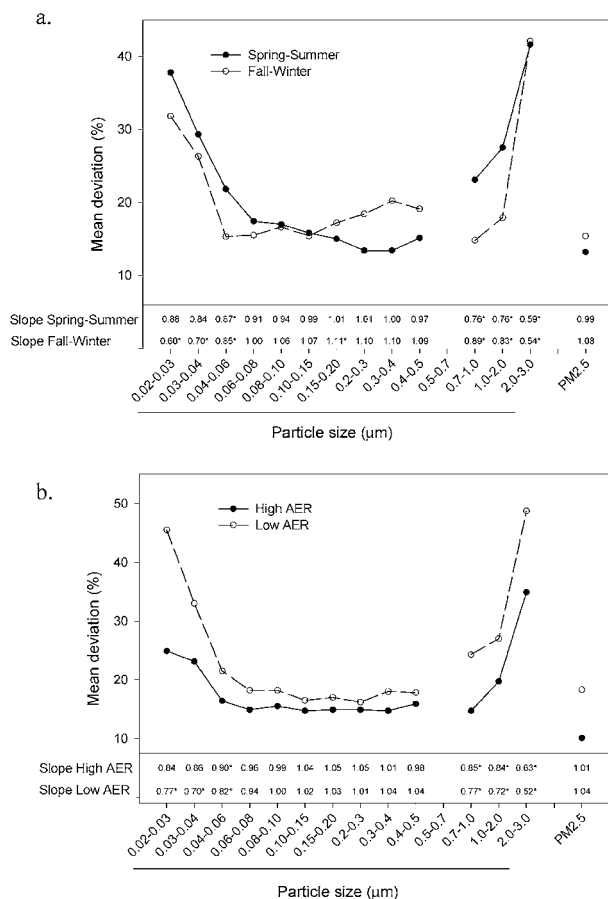


FIGURE 8. Mean deviation and regression slopes by particle size and (a) season and (b) AERs. * indicates regression slope significantly different from one.

with colder winters where homes are tightly insulated or those with hotter summers where air conditioning is used (10,30), will likely result in less suitable sulfur-based estimates of indoor particles of outdoor origin.

The results provide several logical extensions for future research including conducting similar analyses in locations where the size and species composition may differ from that found in the eastern U.S. Likewise, questions remain

concerning the suitability of this method to predict personal exposures to outdoor $PM_{2.5}$. Future work may also look to compare the relative performance of several potential tracers of outdoor $PM_{2.5}$, such as vanadium or elemental carbon with the sulfur-based method assessed in the current analysis. Finally, identifying suitable tracers for ultrafine and coarse particles will contribute toward characterizing outdoor PM source contributions for a greater range of particle sizes.

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Literature Cited

- (1) Pope, C. A. *Aerosol Sci. Technol.* **2000**, 32, 4–14.
- (2) Samet, J. M.; Dominici, F.; Currier, I.; Coursac, I.; Zeger, S. L. *N. Engl. J. Med.* **2000**, 343(24), 1742–1749.
- (3) United States Environmental Protection Agency. *Air Quality Criteria for Particulate Matter, Volumes I, II, and III*; EPA/600/P-95/001; Office of Research and Development: Washington, DC, 1996.
- (4) Sarnat, J. A.; Koutrakis, P.; Suh, H. H. *J. Air Waste Manage. Assoc.* **2000**, 50, 1184–1198.
- (5) Leaderer, B. P.; Naeher, L.; Jankun, T.; Balenger, K.; Holford, T. R.; Toth, C.; Sullivan, J.; Wolfson, J. M.; Koutrakis, P. *Environ. Health Perspect.* **1999**, 107(3), 223–231.
- (6) Tolocka, M. P.; Solomon, P. A.; Mitchell, W.; Norris, G. A.; Gemmill, D. B.; Wiener, R. W.; Vanderpool, R. W.; Homolya, J. B.; Rice, J. *Aerosol Sci. Technol.* **2001**, 34(1), 88–96.
- (7) Koutrakis, P.; Briggs, S. L. K.; Leaderer, B. P. *Environ. Sci. Technol.* **1992**, 26, 521–527.
- (8) Özkaynak, H.; Xue, J.; Spengler, J.; Wallace, L.; Pellizzari, E.; Jenkins, P. J. *Exposure Anal. Environ. Epidemiol.* **1996**, 6(1), 57–78.
- (9) Clayton, C. A.; Perritt, R. L.; Pellizzari, E. D.; Thomas, K. W.; Whitmore, R. W. *J. Exposure Anal. Environ. Epidemiol.* **1993**, 3(2), 227–250.
- (10) Suh, H. H.; Koutrakis, P.; Spengler, J. D. *J. Exposure Anal. Environ. Epidemiol.* **1994**, 4(1), 1–23.
- (11) Conner, W. D.; Bennett, R. L.; Weathers, W. S.; Wilson, W. E. *J. Air Waste Manage. Assoc.* **1991**, 41(2), 154–160.
- (12) Horvath, H.; Kasahara, M.; Pesava, P. *J. Aerosol Sci.* **1996**, 27(30), 417–435.
- (13) Milford, J. B.; Davidson, C. I. *JAPCA* **1985**, 35(12), 1249–1260.
- (14) Long, C. M.; Suh, H. H.; Catalano, P. J.; Koutrakis, P. *Environ. Sci. Technol.* **2001**, 35, 2089–2099.
- (15) Hinds, W. C. *Aerosol Technology: Properties, Behavior and Measurement of Airborne Particles*; John Wiley & Sons: New York, 1982.

- (16) Long, C. M.; Suh, H. H.; Koutrakis, P. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1236–1250.
- (17) Peters, T. M.; Chein, H.; Lundgren, D. A.; Keady, P. B. *Aerosol Sci. Technol.* **1993**, *19*, 396–405.
- (18) Brüel & Kjær. Instruction Manual for the Multi-gas Monitor Type 1302, 1990.
- (19) Abt, E.; Suh, H. H.; Allen, G.; Koutrakis, P. *Environ. Health Perspect.* **2000**, *108*(1), 35–44.
- (20) Sioutas, C.; Abt, E.; Wolfson, J. M.; Koutrakis, P. *Aerosol Sci. Technol.* **1999**, *30*(1), 84–92.
- (21) DRI, X-Ray Fluorescence Air Filter Analysis Interference-Free Minimum Detectable Limits Using DRI Standard Analysis Protocols, Protocol A. 1999.
- (22) Murray, D. M.; Burmaster, D. E. *Risk Anal.* **1995**, *15*(4), 459–465.
- (23) Rojas-Bracho, L.; Suh, H. H.; Koutrakis, P. *J. Exposure Anal. Environ. Epidemiol.* **2000**, *10*(3), 294–306.
- (24) Oglesby, L.; Kunzli, N.; Roosli, M.; Braun-Fahrlander, C.; Mathys, P.; Stern, W.; Jantunen, M.; Kousa, A. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1251–1261.
- (25) Janssen, N. A.; Hoek, G.; Brunekreef, B.; Harssema H. *Occup. Environ. Med.* **1999**, *56*, 482–487.
- (26) Suh, H. H.; Spengler, J. D.; Koutrakis, P. *Environ. Sci. Technol.* **1992**, *26*(12), 2507–2517.
- (27) Dockery, D. W.; Spengler, J. D. *JAPCA* **1981**, *31*(2), 153–158.
- (28) Ebelt, S. T.; Petkau, A. J.; Vedal, S.; Fisher, T. V.; Brauer, M. *J. Air Waste Manage. Assoc.* **2000**, *50*, 1081–1094.
- (29) Spengler, J. D.; Wilson, R. *Emissions, Dispersion, and Concentration of Particles. Particles in Our Air—Concentrations and Health Effects*; Harvard University Press: 1996; pp 41–62.
- (30) Liu, L. S.; Leech, J.; Broder, I. *J. Air Waste Manage. Assoc.* **1995**, *45*, 223–234.

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