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Selection of metric for indoor-outdoor source apportionment of metals in $PM_{2.5}$: mg/kg versus ng/m^3

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Abstract

Trends in the elemental composition of fine particulate matter ($PM_{2.5}$) collected from indoor, outdoor, and personal microenvironments were investigated using two metrics: ng/m^3 and mg/kg. Pearson correlations that were positive using one metric commonly disappeared or flipped to become negative when the other metric was applied to the same dataset. For example, the correlation between Mo and S in the outdoor microenvironment was positive using ng/m^3 ($p < 0.05$) but negative using mg/kg ($p < 0.05$). In general, elemental concentrations (mg/kg) within $PM_{2.5}$ decreased significantly ($p < 0.05$) as $PM_{2.5}$ concentrations (μg/m^3) increased—a dilution effect that was observed in all microenvironments and seasons. An exception was S: in the outdoor microenvironment, the correlation between wt% S and $PM_{2.5}$ flipped from negative in the winter ($p < 0.01$) to positive ($p < 0.01$) in the summer, whereas in the indoor microenvironment, this correlation was negative year-round ($p < 0.05$). Correlation analyses using mg/kg indicated that elemental associations may arise from Fe-Mn oxyhydroxide sorption processes that occur as particles age, with or without the presence of a common anthropogenic source. Application of mass-normalized concentration metrics (mg/kg or wt%), enabled by careful gravimetric analysis, revealed new evidence of the importance of indoor sources of elements in $PM_{2.5}$.

KEYWORDS
metal exposure, buoyancy correction, spurious correlation, sulfur infiltration factor, uncertainty

1 | INTRODUCTION

Recently, there has been an increased research focus on the chemical constituents of fine particulate matter ($PM_{2.5}$) to better understand potential health effects of $PM_{2.5}$ exposures, particularly oxidative stress and inflammation.[1–3] Understanding the metal composition of non-occupational indoor $PM_{2.5}$ (including speciation and sources) has gained particular attention due to the large amount of time people spend indoors, combined with the potential impacts of airborne metals on human health.[4] Although some studies have shown that metal data from central monitoring sites correlate well with personal exposures,[5,6] there is growing evidence that indoor sources may have a greater influence on personal exposures than outdoor sources.[7] Several studies have shown that certain metals of toxicological concern (eg, Ag, Ni, Cr, and Cu) in submicron, fine and coarse PM commonly occur at higher concentrations indoors

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than outdoors,[8–11] underscoring the importance of indoor sources of metals in residential environments. It is now recognized that indoor sources must be better characterized in epidemiological studies before personal exposures to metals can be fully understood.[4,7,12–15]

Detailed studies of individual particles have demonstrated differences in the composition of indoor $PM_{2.5}$ compared with outdoor $PM_{2.5}$, that reflect the presence of humans, their behaviors, their choice of consumer products, emissions from coatings, building materials, and other indoor sources.[16–18] Indoor $PM_{2.5}$ is enriched in organic carbon (OC) compared with outdoor $PM_{2.5}$ due to multiple indoor OC sources.[13,19–21] In addition to cooking emissions, key indoor sources of OC include clothing fibers, skin cells, and other organic emissions originating from the residents themselves.[16,22–24] Understanding metal speciation (ie, the chemical and physical form of the particle-bound metal), which is critical in determining the toxicity of particles,[3] also assists in identifying metal sources. Molecular-scale metal speciation studies using synchrotron X-Ray techniques have proven valuable for identifying the contribution of common building materials to indoor particles, including calcium sulfate (gypsum and bassanite) from drywall and plaster,[25,26] paint pigments containing zinc, titanium, barium, chromium and lead,[25–30] arsenic, copper and chromium from treated wood,[26] and lead solder.[30] Indoor sources of Cu include motor-generated particles released during vacuuming and emissions from electrical appliances.[9,31] Other important indoor sources of metals include resuspension of settled dust, natural and synthetic carpet fibers and other textile fibers, and cooking emissions.[17,18,32,33] The elevated OC content of indoor $PM_{2.5}$ is related to its elemental composition, as skin flakes (keratin) and other biogenic indoor particles contain elements such as S, Fe, Na, K, Cl, and Zn.[24,34–36] Textile fibers also may be colored with dyes containing metals such as Cr, Sb, and Cu.[37] Consumer spray products release indoor particles containing Ag, Zn, Li, Sr, Ba, Pb, Mn, and other metals.[38] Metallic nanomaterials such as Ag bactericides and nanosprays that emit metals and metal oxides such as Zn, ZnO, Cu, and TiO_2 are considered emerging indoor pollutants.[15] Use of scanning electron microscopy (SEM) demonstrated that cosmetics and personal hygiene products contribute Al, Bi, Ti, Mg, Si, and Fe to personal $PM_{2.5}$ exposures.[39]

The complexity of characterizing indoor sources of metals is compounded by the fact that ambient (outdoor) particles penetrate into indoor air and add to the exposure observed in indoor and personal samples.[14,17,19,40,41] Detailed characterization techniques can identify sources of individual particles, but generally cannot quantify their relative contributions. To evaluate the relative contribution of indoor and outdoor sources to personal exposures, most studies have relied on bulk measurements of indoor, outdoor and personal PM samples, using methods such as X-ray Fluorescence (XRF) and/or inductively coupled plasma (ICP) spectroscopic approaches. Bulk methods yield total element concentration data which have been used for Pearson correlation analysis, principal component analysis (PCA), and/or positive matrix factorization (PMF) approaches for hypothesizing indoor source profiles.[40–43] For example, two studies have inferred stainless steel debris as an indoor source based on a Cr-Ni- Mo association observed in settled dust (mg/kg) using PCA[36] and in indoor air (ng/m^3) using PMF.[44] A drawback is that trace elements do not uniquely identify individual sources, and therefore, an elemental signature may represent a mixture of elements arising from multiple sources operating at the same time.[41,45] This complexity presents challenges in developing indoor source profiles and has yielded inconsistencies among studies. For example, some studies used Br as a marker for brominated flame retardants in indoor particles,[46,47] in contrast to other studies that used Br as a conservative indoor tracer of external factors such as traffic and/or marine aerosols.[13,48,49] Pant and Harrison[42] found similar inconsistencies among factor analyses of trace elements in ambient air PM, noting that conflicting interpretations make it difficult to apportion sources with confidence. Their key recommendation was to improve locally derived source profiles with additional measurements[42]—a recommendation that has been echoed by others in the context of indoor-outdoor source apportionment.[7,12,14,17,18]

Recent studies have used alternate metrics to represent PM constituents (other than the traditional μg/m^3 metric) for investigating relationships between the chemical composition of PM and health effects. For example, oxidative potential measurements may be normalized per mass of PM rather than per sampled volume of air.[3,44] A study of PM_{10} across seven cities in northern China[50] applied the mg/kg metric for distinguishing combustion versus non-combustion sources, which led to the conclusion that resuspended soil and dust was the predominant source of V and Ni in the western cities, in contrast with eastern cities where the main source of V and Ni was oil combustion and industry. With respect to residential environments, converting indoor air concentrations to mg/kg revealed significant correlations between elemental concentrations in settled dust and

Practical Implications

- Selecting the appropriate metric is critical for $PM_{2.5}$ source apportionment modelling. Normalizing elemental measurements per mass of PM (eg, mg/kg) avoids spurious correlations that can cause inconsistent source interpretations.
- Mass-normalized metrics (mg/kg) revealed new evidence of indoor sources of several elements (such as S and Zn) previously assumed to be conservative tracers of outdoor particles. Use of volume-normalized element concentrations (ng/m^3) to evaluate indoor/outdoor relationships resulted in an underestimation of indoor sources.
- Mathematical models that rely on *a priori* assumptions that indoor sources are absent, despite contrary evidence, introduce the risk of underestimating indoor exposures. Future models should rely on the more realistic assumption that elements have both indoor and outdoor sources.

indoor PM_{10}, which evidenced the contribution of resuspended dust to airborne metals.[10] Thus, a potential benefit of using the mg/kg metric for source apportionment is the ability to make direct comparisons of elemental concentrations in PM and relevant source media such as building materials, settled dust, street dust, and soil, which are typically measured in mg/kg (or wt%) and which contribute to airborne PM through disintegration/resuspension. However, in the context of ambient $PM_{2.5}$ receptor models, Luo et al[51] observed that application of different metrics (mg/kg vs. ng/m^3) yielded inconsistencies in the spatial distribution pattern of $PM_{2.5}$ metals such as Pb and Ni, which influenced the interpretation of regional metal sources in China. Based on the potential benefit of the mg/kg metric for improving indoor/outdoor source profiles, it is important to investigate any such inconsistencies in interpretation that may be caused by the selection of metric.

This study explored the value of using mg/kg (or wt%) metrics for investigating trends in $PM_{2.5}$ elemental concentrations, in comparison with results obtained using traditional ng/m^3 (or μg/m^3) metrics. The data analyses were based on a large set of matched indoor, outdoor, and personal $PM_{2.5}$ filter samples that were collected concurrently from residential microenvironments in the city of Windsor, Ontario, Canada.[10] Windsor is located across the international border from Detroit, Michigan, USA, in the hub of the North American motor vehicle manufacturing industry. Other factors influencing ambient air quality in this region include vehicular traffic, steel manufacturing, and cement factories.[52] The $PM_{2.5}$ filter samples were analyzed gravimetrically followed by XRF determination for S and inductively coupled plasma mass spectrometry (ICP-MS) for all other elements. Particular care was taken to avoid all sources of filter contamination and to ensure accurate gravimetric measurements of PM loaded on the filter samples.

2 | MATERIALS AND METHODS

2.1 | Field Sampling

Samples of fine particulate matter ($PM_{2.5}$) were collected on 37 mm polytetrafluoroethylene (PTFE) filters (Teflo™; PALL Ltd; pore size 2 μm) using the R&P Chempass multi-pollutant personal environmental monitor (PEM) manufactured by Chempass System R&P/Thermo equipped with BGI 400 sampling pumps. Details regarding sampling methodology, selection of homes, and home locations have been described previously.[53,54] Briefly, sampling was conducted over 2 years (2005 and 2006), at 48 homes of asthmatic children and nonsmokers, in the city of Windsor, Ontario, Canada, for eight consecutive weeks in winter (January–March) and summer (July–August) of each year. In each season, the sampling campaign consisted of 24-h concurrent indoor, personal, and outdoor monitoring for five consecutive sampling days (Monday to Friday) per home.

Personal samples were collected by participants using a backpack containing the PEM equipment to collect 24-h personal air samples throughout all daily activities. Simultaneous indoor and outdoor samples were collected by locating PEM equipment 1.5 m above the ground to represent breathing height. The "indoor microenvironment" refers to samples collected using PEMs located in the family or living room. The "outdoor microenvironment" refers to samples collected using PEMs located in the backyard, several meters away from the home or any combustion sources. The field protocol included daily calibration of flow rates using a soap bubble flow meter (AP Buck) and leak tests. Samples were assessed for validity using the following acceptance criteria: sampling duration within ±20% of the standard 24-h protocol and flow rate within ±20% of the target flow rate of 4.0 L/min. Other efforts to assure quality under field conditions are described in Appendix S1. Briefly, the PEMs were assembled and disassembled in the field inside a clean laminar flow hood using powder-free gloves, and filters were shipped in their dedicated, bar-coded 50 mm Petri dishes, which were double-bagged and secured in coolers.

2.2 | Gravimetric analysis

Measurements of $PM_{2.5}$ mass were made in Health Canada's patented Archimedes M3™ facility,[55] consisting of a custom-designed Plexiglass environmental chamber that housed a microbalance with readability of 0.1 μg (Model UMX2, Mettler-Toledo GmbH). The environmental chamber sat on top of a stable 700 lb marble table, inside a certified ISO-14644-1 clean room. Environmental conditions inside the chamber were electronically monitored and digitally recorded at 1 min intervals, which permitted simultaneous measurement and recording of the three independent parameters (air pressure, air temperature, and dew point temperature) required for calculating buoyancy corrections.[56] Details of the weighing protocol were described previously.[56] Briefly, each filter sample was conditioned for 24 h inside the environmental chamber and remained there until the weighing process was completed, at which time the filter was returned to its labeled Petri dish and securely packaged. Static charge was removed with Po-210 de-ionizers. Gravimetric measurements for the present study were performed on a total of 207 days during which time the temperature and relative humidity (RH) inside the chamber were maintained at 21.7 ± 0.2°C and 39.7% ± 0.8%, respectively. Air density and air pressure (mean and standard deviation) monitored simultaneously were 1.1878 ± 0.0098 kg/m^3 and 100.9 ± 0.8 kPa, respectively. To calculate detection limits, two preconditioned blank reference filters were weighed at the beginning and end of each weighing session and after every 10 samples during the session. The average daily standard deviation (SD) of blank reference filter measurements was typically ±0.5–0.6 μg per filter (n = 10–14 measurements per day), resulting in daily laboratory detection limits of 1.5–1.6 μg based on 3 times standard deviation. Field blanks were handled in precisely the same fashion as sample filters throughout all steps, including pre-weighing, shipping, loading, and unloading from the PEMs, to post-weighing, with the exception that PEMs loaded with field blanks were not attached to the pump during monitoring. A total of 654 field blanks were collected,

TABLE 1 Summary of $PM_{2.5}$ (μg/m^3) concentrations in Windsor residential microenvironments over two sampling years (n = 2349 samples)

	2005			2006		
	Indoor	Outdoor	Personal	Indoor	Outdoor	Personal
N	378	409	413	378	377	394
Geomean	7.72	16.0	9.41	5.83	10.6	7.46
Mean ± SD	10.0 ± 9.47	19.2 ± 12.1	11.4 ± 9.19	7.55 ± 7.04	12.7 ± 7.36	8.79 ± 5.67
RSD	94%	63%	80%	93%	58%	65%
Range (min-max)	1.00–114	1.20–76.7	1.50–112	0.100–63.5	0.400–49.5	0.700–51.1
Percentiles						
50th (median)	7.45	16.3	9.00	5.65	11.4	7.40
95th	24.0	43.5	24.0	17.6	24.6	18.3

Abbreviations: RSD, relative standard deviation; SD, standard deviation.

representing 12% of samples in all microenvironments. According to protocols in place for the Windsor study,[53] sample results were to be adjusted by subtracting the median of the field blanks. However, median values for field blanks were below the method detection limit in all seasons and environments, and therefore, field blanks were not subtracted from results. Collocated duplicates were collected in each microenvironment, and duplicate gravimetric measurements were made every 10 samples; see Appendix S1 for an assessment of uncertainty based on the field duplicates, gravimetric duplicates, and field blanks.

2.3 | Elemental determinations

Details of the ICP methods (and associated recoveries and limits of detection) for multi-element analysis of the $PM_{2.5}$ samples have been described previously,[10,57,58] including quality assurance procedures during sampling, handling and analysis, analytical method comparisons, and collocated duplicates. Although the gravimetric measurements were conducted immediately after sampling (in 2005 and 2006), the elemental analyses were delayed several years until resources became available, and during that time the filter samples were stored in sealed containers in a laminar flow hood to avoid contamination. The filter samples were digested using a mixture of 4.0 ml HNO_3 and 0.1 ml HF with ultrasonication proceeding at 90°C for 1-h, followed by 10-fold dilution and ICP determination. Trace elements were determined in the digests using ICP-Mass Spectroscopy (ICP-MS; Perkin Elmer Sciex Elan DRC II or Perkin Elmer NexION300s), and elements occurring at higher concentrations (eg, Al and Fe) were determined using ICP-Optical Emission Spectroscopy (ICP-OES; Perkin Elmer Optima 5300V). Certified reference materials (CRMs), procedural reagent blanks, and filter blanks were included in all batches to evaluate the efficiency (recovery) and reproducibility of the digestion procedures. To ensure that trace element concentrations in the digests of the lightly loaded filters exceeded ICP-MS detection limits, it was necessary to combine two to three filters into one digest (collected within the same week from the same residence and microenvironment). Calculations of limits of detection (LOD) were based on the variability of procedural blanks (three times the standard deviation of eight or more procedural blanks). Sulfur (S) was determined in the remaining $PM_{2.5}$ filter samples using energy-dispersive X-Ray Fluorescence (XRF) spectrometry (PANalytical Epsilon 5 XRF analyzer) in a clean air cabinet at the UK Health and Safety Laboratory. The instrument was calibrated for S using MICROMATTER calibration standards. Raw intensities were blank corrected to account for background contamination from the filter substrate and spectral noise. All field blanks (n = 16) and filter blanks (n = 7) submitted for XRF analysis were below LOD.

2.4 | Data analysis and evaluation criteria

Nineteen elements were deemed reportable for $PM_{2.5}$ (Ag, Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Sn, Sr, Ti, U, V, and Zn) based on the following criteria: a minimum of 50% of the dataset exceeded LOD after blank subtraction, and recoveries were consistent across various matrix-matched CRMs, as detailed previously.[10,57] As the datasets were lognormally distributed, statistical summaries were reported using percentiles and/or geomeans (mean and standard deviation reported for information only). Pearson correlation coefficients (r) and significance (p) values were determined using log-transformed data. Elemental concentrations for matched indoor, outdoor, and personal 24-h samples were averaged on a weekly basis for each microenvironment in each of the four Windsor sampling seasons (n = 152 matched indoor/outdoor/personal sets for S and n = 141 matched sets for other elements; combined total for the 2005 and 2006 sampling campaigns). Data processing, storage, and quality evaluation were performed using an Oracle database management system (version 11g). Statistical analyses were performed using SPSS (version 21). Elemental datasets are summarized in the Supplementary Information (Appendix S3 for $PM_{2.5}$ and Appendix S7 for PM_{10}).

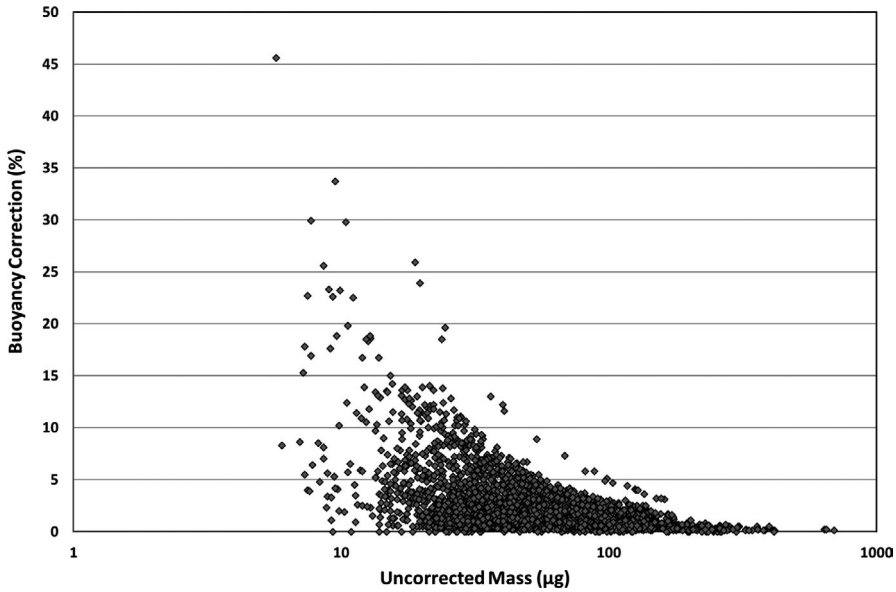

FIGURE 1 Relative magnitude of the buoyancy correction (*y*-axis) against the uncorrected mass of particulate matter loaded on each filter for the set of 2349 $PM_{2.5}$ samples summarized in Table 1. The buoyancy correction (%) equals the absolute value of [corrected mass subtracted from uncorrected mass] divided by the uncorrected mass, expressed as percent

3 | RESULTS

Table 1 summarizes all gravimetric measurements of $PM_{2.5}$ collected from indoor, outdoor, and personal microenvironments for both sampling years of the Windsor study. There was a marked improvement in $PM_{2.5}$ in all three microenvironments in 2006 compared with 2005 ($p < 0.001$), most notably in the outdoor microenvironment where median $PM_{2.5}$ levels decreased from 16.3 μg/m^3 in 2005 to 11.4 μg/m^3 in 2006 (Table 1). This improvement in outdoor $PM_{2.5}$ observed in residential monitoring (Table 1) was consistent with central location $PM_{2.5}$ ambient monitoring results reported for Windsor by the province of Ontario,[59] which showed that 2005 represented the worst air quality for the decade from 2003 to 2012, while 2006 was more typical of Windsor air quality during that decade.[10,59]

3.1 | Sources of variability in $PM_{2.5}$ measurements

The summary of $PM_{2.5}$ values for the participating Windsor homes (Table 1) shows that the lowest values occurred indoors (median 5.7–7.5 μg/m^3), consistent with the residents being non-smokers. The highest $PM_{2.5}$ exposures occurred outdoors (median 11.4–16.3 μg/m^3), with personal exposures falling in-between (median 7.4–9.0 μg/m^3). The total number of $PM_{2.5}$ samples ($n = 2349$; Table 1) includes five consecutive sampling days (Monday to Friday) per home in each microenvironment for two sampling seasons per year (winter and summer) over two years. For the remainder of this paper, weekly averages for all $PM_{2.5}$ and elemental measurements (ie, one averaged value per home per season) are used for statistical interpretations. Table 1 is the exception in that the statistical summaries are calculated on the basis of individual samples, to assist in examining variability using relative standard deviation (%RSD = SD/mean expressed as percent).

With respect to variability, Table 1 indicates that the outdoor microenvironment (O) in Windsor exhibited smaller %RSD values than either indoor (I) or personal (P) microenvironments, in the order I > P > O for both 2005 and 2006 (Table 1), consistent with previous reports of low spatial variability in $PM_{2.5}$ across the city of Windsor.[54] The standard deviation (SD) values in Table 1 reflect temporal variability of $PM_{2.5}$ in addition to spatial variability, plus measurement uncertainty. The overall measurement uncertainty for this study was calculated to be 3.87 μg/m^3, based on the SD of 144 collocated field duplicates as detailed in the Supplementary Information (Appendix S1). This assessment demonstrated that the measurement uncertainty associated with air volume measurements (ie, sampling pump flow rate) accounted for 93% of the variance associated with the $PM_{2.5}$ measurements, and the remainder was associated with field blanks and laboratory blanks (Appendix S1).

3.2 | Influence of buoyancy corrections on gravimetric measurements

Figure 1 shows the relative magnitude of buoyancy corrections that were applied to the $PM_{2.5}$ samples in the present study. The general fan shape of the data points in Figure 1 demonstrates that the relative magnitude of the buoyancy correction increases as the sample mass decreases. The graph shows that the application of buoyancy corrections was especially relevant for sample masses <50 μg, for which the magnitude of the correction exceeded 10% of the uncorrected sample mass (Figure 1). A total of 133 samples in the Windsor study contained <50 μg sample mass, and out of these lightly loaded samples, 57% were collected indoors, 31% were personal samples, and only 12% were collected outdoors. This breakdown underscores the greater challenges associated with obtaining accurate gravimetric measurements of indoor and personal $PM_{2.5}$ samples.

The isolated row of high values above the dense portion of the fan in Figure 1 indicates gravimetric measurements that required buoyancy corrections of greater magnitude than usual. This row of outliers was associated with incidents of elevated air density in the

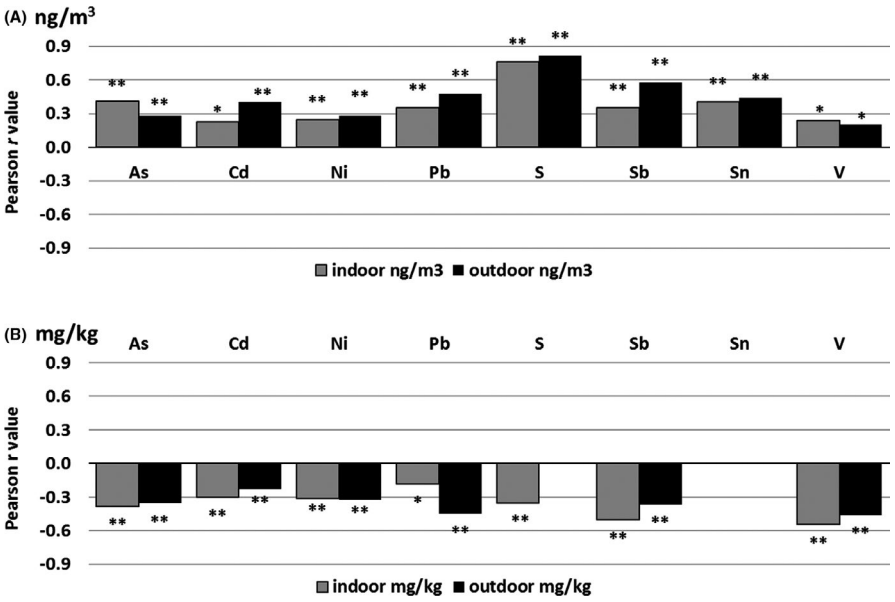

FIGURE 2 Pearson correlations (r values) between $PM_{2.5}$ ($\mu g/m^3$) and elemental content of $PM_{2.5}$ expressed (A) using ng/m^3, and (B) using mg/kg. **Significant at $p < 0.01$; *significant at $p < 0.05$. Out of the 19 studied elements, only those which displayed a significant correlation using ng/m^3 in both indoor and outdoor microenvironments are included

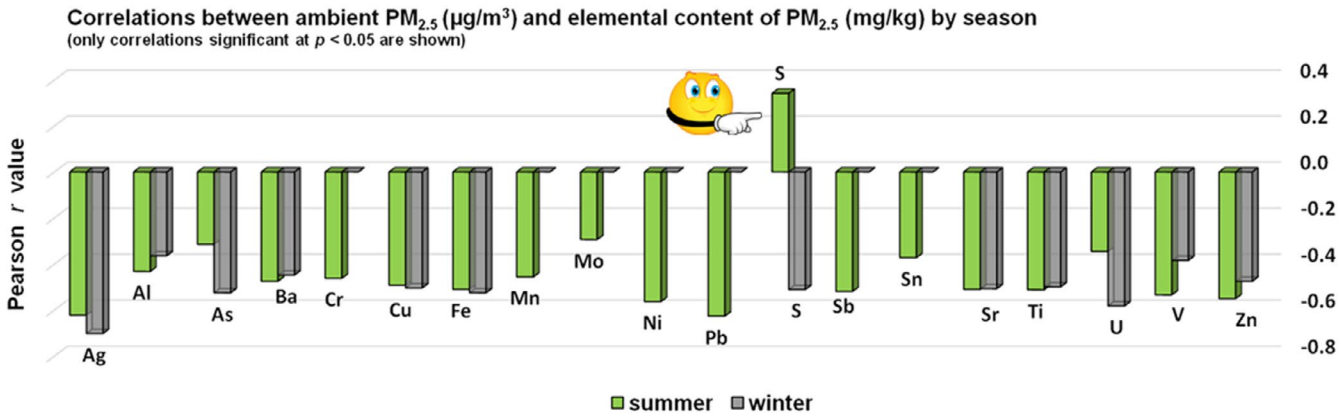

FIGURE 3 Correlations between outdoor $PM_{2.5}$ concentrations in air ($\mu g/m^3$) and mass-normalized elemental concentrations in outdoor $PM_{2.5}$ (mg/kg) are negative, with the exception of sulfur (S) in the summer season. Bars display Pearson r values for the outdoor (ambient) environment in summer (green) and winter (grey) seasons; only correlations that are significant ($p < 0.05$) are included

gravimetric facility which occurred when the air pressure was higher than usual (>1 SD above the mean). While temperature and relative humidity were tightly controlled in the chamber, air pressure was monitored but not controlled.[56] Buoyancy calculations successfully corrected for the influence of such large changes in air density between initial filter weighing and the final weighing of the loaded filter, which shows the value of monitoring air pressure inside the lab itself (rather than relying on regional airport data).

3.3 | Influence of metric (mg/kg vs. ng/m^3) on elemental correlations with $PM_{2.5}$

The relationship between $PM_{2.5}$ and the elemental content of $PM_{2.5}$ is strongly influenced by the metric chosen for the elemental concentration, as demonstrated by Figure 2. Correlations with $PM_{2.5}$ were positive when elemental concentrations were calculated using air volume in the denominator, that is, ng/m^3 (Figure 2A). In contrast, correlations using the same dataset were negative or disappeared when elemental concentrations were calculated using mass in the denominator, that is, mg/kg (Figure 2B). The negative trends in Figure 2B indicate a dilution effect: that is, an increase in the airborne $PM_{2.5}$ concentration in $\mu g/m^3$ is accompanied by a decrease in its metal content in mg/kg.

Out of all the study elements, S was the only element that displayed a significant positive correlation between its wt% concentration in $PM_{2.5}$ and the $PM_{2.5}$ concentration in air (Figure 3), which aligns with the purported use of S as a surrogate for $PM_{2.5}$.[60] However, this positive relationship was observed only in the summer season and only in the outdoor environment; otherwise, there was a negative relationship between the wt% S concentration in $PM_{2.5}$ and $PM_{2.5}$ (Figures 2B and 3).

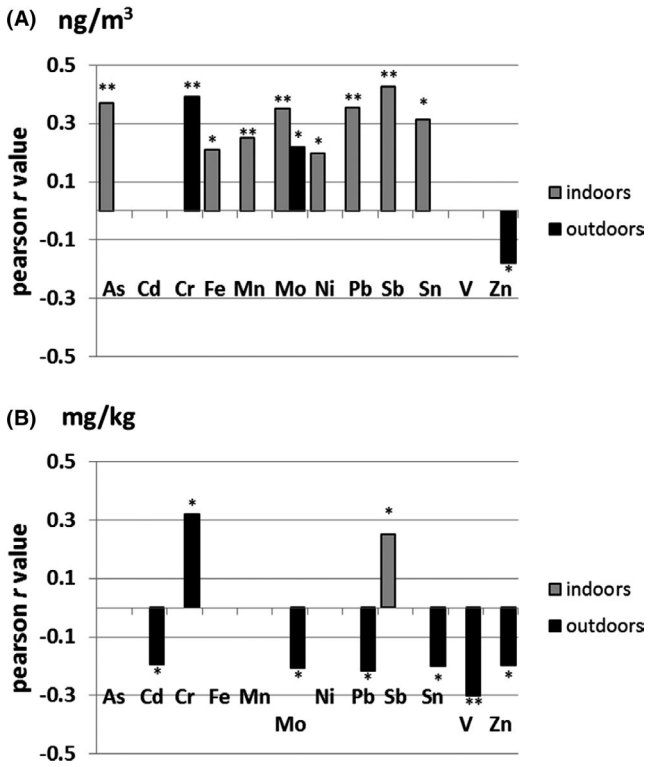

FIGURE 4 Elemental correlations with S in indoor $PM_{2.5}$ and outdoor $PM_{2.5}$ based on (A) ng/m^3 metric and (B) mg/kg metric. The same log-transformed dataset was used for both (A) and (B) and includes all samples from both years; only elemental correlations with significant Pearson *r* values were included. **Significant at $p < 0.01$; *significant at $p < 0.05$. Refer to Appendix S2 for all inter-elemental correlations in all environments

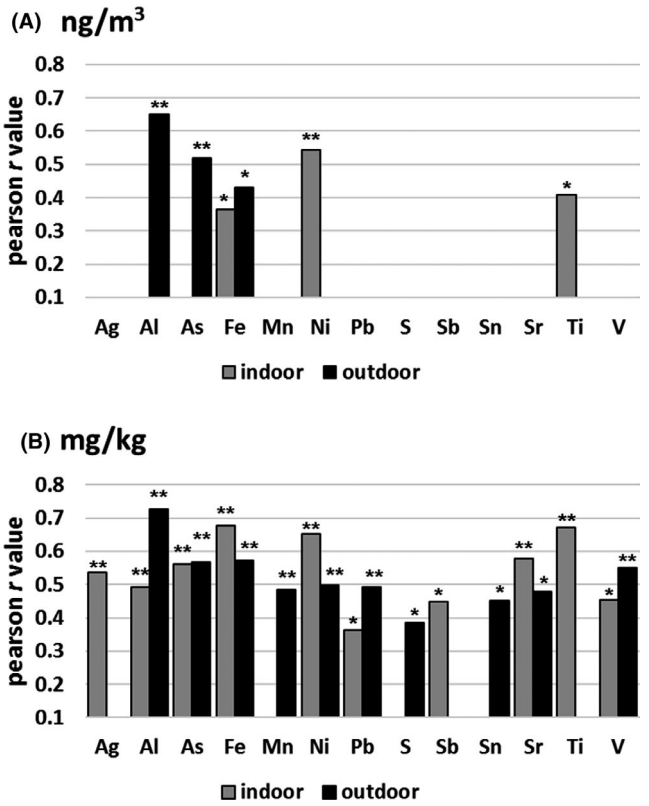

FIGURE 5 Elemental correlations with Cr in indoor and outdoor $PM_{2.5}$ based on (A) ng/m^3 metric and (B) mg/kg metric. Dataset for the summer of 2006; data were log-transformed; only correlations with significant Pearson *r* values were included; **significant at $p < 0.01$; *significant at $p < 0.05$

3.4 | Influence of metric on inter-elemental correlations

Figure 4 shows how the two metrics compare when used for examining elemental relationships with S (based on the combined dataset for both years), and Figure 5 shows how the two metrics compare for elemental relationships with Cr (2006 summer subset). While elemental correlations with S and Cr have particular relevance to source apportionment in the Windsor-Detroit region,[52] all inter-elemental correlations (mg/kg) are summarized for indoor, personal, and outdoor microenvironments in the Supplementary Information (Appendix S2). Figure 4 indicates that, in the outdoor environment, correlations between Zn and S were consistently negative, and correlations between Cr and S were consistently positive, regardless of whether the ng/m^3 metric or the mg/kg metric was used. Otherwise, Figure 4 reveals many discrepancies between correlation results generated by the two metrics. The most obvious discrepancy was the correlation between Mo and S in the outdoor microenvironment which was positive using ng/m^3 ($p < 0.05$) but negative using mg/kg ($p < 0.05$). Apart from Cr-S (outdoor) and Sb-S (indoor) correlations, other elemental correlations with S that mapped as significantly positive in Figure 4A were non-existent in Figure 4B (as in the case of indoor Mo, As, Fe, Mn, Pb, Ni, and Sn). It follows that, when air volume is used in the denominator (Figure 4A), any increase in $PM_{2.5}$ mass per volume of air is accompanied by an increase in its elemental components; thus, some correlations between elements may be driven purely by their co-occurrence in the $PM_{2.5}$ matrix. However, when the air volume term is omitted, as in Figure 4B, those positive relationships in Figure 4A either disappear or flip to become negative. These observations demonstrate the value of normalizing elemental concentrations against mass, to avoid spurious correlations that may occur using ng/m^3. Inconsistencies in results generated by the two metrics are further explored in Appendix S8 using principal component analysis (PCA) of the indoor and outdoor datasets.

The value of using mg/kg to check the validity of inter-elemental correlations is further illustrated by examining relationships between Cr and other elements in $PM_{2.5}$ samples collected in the summer of 2006 (Figure 5). Refining tools for residential source apportionment of Cr is important as this metal has been identified as an environmental carcinogen having significant indoor sources.[61] The significant Cr-S outdoor relationship observed for the whole dataset (Figure 4A,B) was lost when ng/m^3 units were used for this smaller dataset (Figure 5A), but remained significantly positive when mg/kg units were used (Figure 5B). Several other significant positive elemental relationships with Cr were identified using mg/kg but not using ng/m^3. The strong Ni-Cr correlation is evident in both indoor $PM_{2.5}$ and outdoor $PM_{2.5}$ using mg/kg (Figure 5B). However,

the Ni-Cr relationship disappears in outdoor $PM_{2.5}$ using ng/m^3 (Figure 5A), which has notable consequences for source apportionment efforts in a region characterized by steel manufacturing.

Overall, when the correlation analyses were conducted using ng/m^3 (Figure 5A), only three elements correlated with Cr in outdoor $PM_{2.5}$ (Al, As, and Fe) and only three correlated with Cr in indoor $PM_{2.5}$ (Fe, Ni, and Ti). In contrast, when the analyses were repeated using mg/kg units (Figure 5B), seven elements showed significant positive correlations with Cr both indoors and outdoors (Al, As, Fe, Ni, Pb, Sr, and V); an additional three elements correlated with Cr in outdoor $PM_{2.5}$ (Mn, S, and Sn); and an additional three elements correlated with Cr in indoor $PM_{2.5}$ (Ag, Sb, and Ti), all of which were characterized by moderate to strong *r* values (0.4 to 0.7; Figure 5B).

3.5 | Transitory nature of indoor/outdoor relationships

Figure 6 summarizes median elemental concentrations (mg/kg) in indoor and outdoor $PM_{2.5}$, grouped by year (2005 and 2006) and by season (winter and summer). A visual comparison of indoor and outdoor concentrations (bar heights) in Figure 6 reveals the transitory nature of I/O ratios for certain elements. In the case of Ni for example, I/O ratios switched back and forth from <1 to >1 from one season to the next (Figure 6). Median values of Al and Zn displayed I/O ratios below unity (<1) in 2005, but I/O ratios for both elements were above unity (>1) in 2006 (Figure 6). Titanium (Ti) and strontium (Sr) displayed a similar trend: I/O ratios were below unity for Ti and Sr in the winter of 2005, but switched to exceed unity in the remaining three seasons (Figure 6). Based on the observed transitory nature of I/O ratios, it follows that inter-elemental correlations are likely to be transitory as well, underscoring the value of collecting and assessing indoor-outdoor data used for source apportionment on a seasonal basis.

The trend of increasing concentrations of certain elements (notably Al, Cr, and Zn) in 2006 compared to 2005 (Figure 6) was the opposite of the $PM_{2.5}$ concentration trend shown in Table 1: that is, airborne concentrations of $PM_{2.5}$ (μg/m^3) were elevated in 2005 (the highest annual average $PM_{2.5}$ of the decade) compared to 2006. Concentrations of other elements (Mn, Pb, Sr, and S) increased in summer 2006 compared to summer 2005, and Sb increased in winter 2006 compared to winter 2005 (Figure 6). These opposing temporal trends displayed by elemental concentrations versus $PM_{2.5}$ are explained by the dilution effect illustrated in Figure 2B: that is, as $PM_{2.5}$ (μg/m^3) increased, the mg/kg concentrations of most elements in $PM_{2.5}$ decreased.

Table 2 lists indoor/outdoor (I/O) ratios of median and 95th percentile concentrations calculated using both metrics. Note that I/O ratios calculated using ng/m^3 are consistently lower than I/O ratios calculated using mg/kg, with the result that fewer elements display I/O ratios exceeding unity when the ng/m^3 metric is used in the calculation (Table 2). When median I/O ratios were calculated using ng/m^3 (Table 2), three elements (Ag, Cr, and Cu) displayed ratios exceeding unity. When median ratios were calculated using mg/kg in the present study, a total of five elements (Ag, Cr, Cu, Sn, and Sr) displayed I/O ratios exceeding unity (Table 2). These results are consistent with international studies reporting indoor sources of metal aerosols such as motor-generated particles released during vacuuming and emissions from electrical appliances and humidifiers[9,31,62]; airborne fibers impregnated with metallic dyes[32,37] and Ag bactericides[63]; consumer spray products (including nanosprays)[15,38]; paper particles generated from home offices (printing and shredding)[64]; and cooking emissions.[33,62] The influence of metric was even greater when 95th percentile values were used to calculate I/O ratios (instead of median values): in this case, most of the study elements displayed I/O ratios >1 when mg/kg units were used (Table 2).

There are large sources of spatial and temporal variability in I/O ratios, which are not apparent in the summarized data in Table 2. Generally, variability in $PM_{2.5}$ elements was greater indoors than outdoors using both metrics (illustrated in Appendix S4); such indoor variability can reflect important differences in building characteristics, consumer products, and occupant behavior.[17,18] While temporal variability in I/O ratios can be discerned from Figure 6, annual changes are displayed more clearly in Appendix S5 which compares I/O ratios for 2005 with I/O ratios for 2006, calculated using both metrics. The graphs in Appendix S5 show that more elements displayed median I/O ratios >1 in 2006 (Ag, Al, Cr, Cu, Sn, Sr, Ti, U, and Zn using mg/kg), than in 2005, reflecting the greater impact of indoor sources of these elements relative to outdoor sources, as ambient $PM_{2.5}$ concentrations (μg/m^3) decreased.

3.6 | Elemental associations in indoor, personal, and outdoor microenvironments

The negative relationship between airborne $PM_{2.5}$ (μg/m^3) and its elemental content (mg/kg), shown in the Figures 2and 3, is a trend that holds in both winter and summer seasons for most elements. In this regard, the negative trend displayed by Fe represents the behavior of many other elements, as Fe displays a significant positive correlation with most metals in all three microenvironments (Figure 7A). The correlations in Figure 7B show that Mn also behaves similarly to most other elements, although elemental correlations with Fe tend to be stronger than those with Mn. These elemental associations may be influenced by redox reactions that occur during weathering (aging) of the aerosol particle. The role of Fe and Mn oxyhydroxides, as principal controls on metal sorption in environmental media, was established more than 50 years ago.[65,66] Redox cycling of Fe

FIGURE 6 Seasonal and annual variations of median elemental concentrations in indoor $PM_{2.5}$ (light gray) and outdoor $PM_{2.5}$ (black); wt% for S and Fe; mg/kg for all other elements. Asterisks indicate values transformed to fit graphs: *Cr, *Cu, and *Zn were divided by five, and **Al was divided by 100. Medians based on 30–40 homes per season; error bars show 95% confidence interval

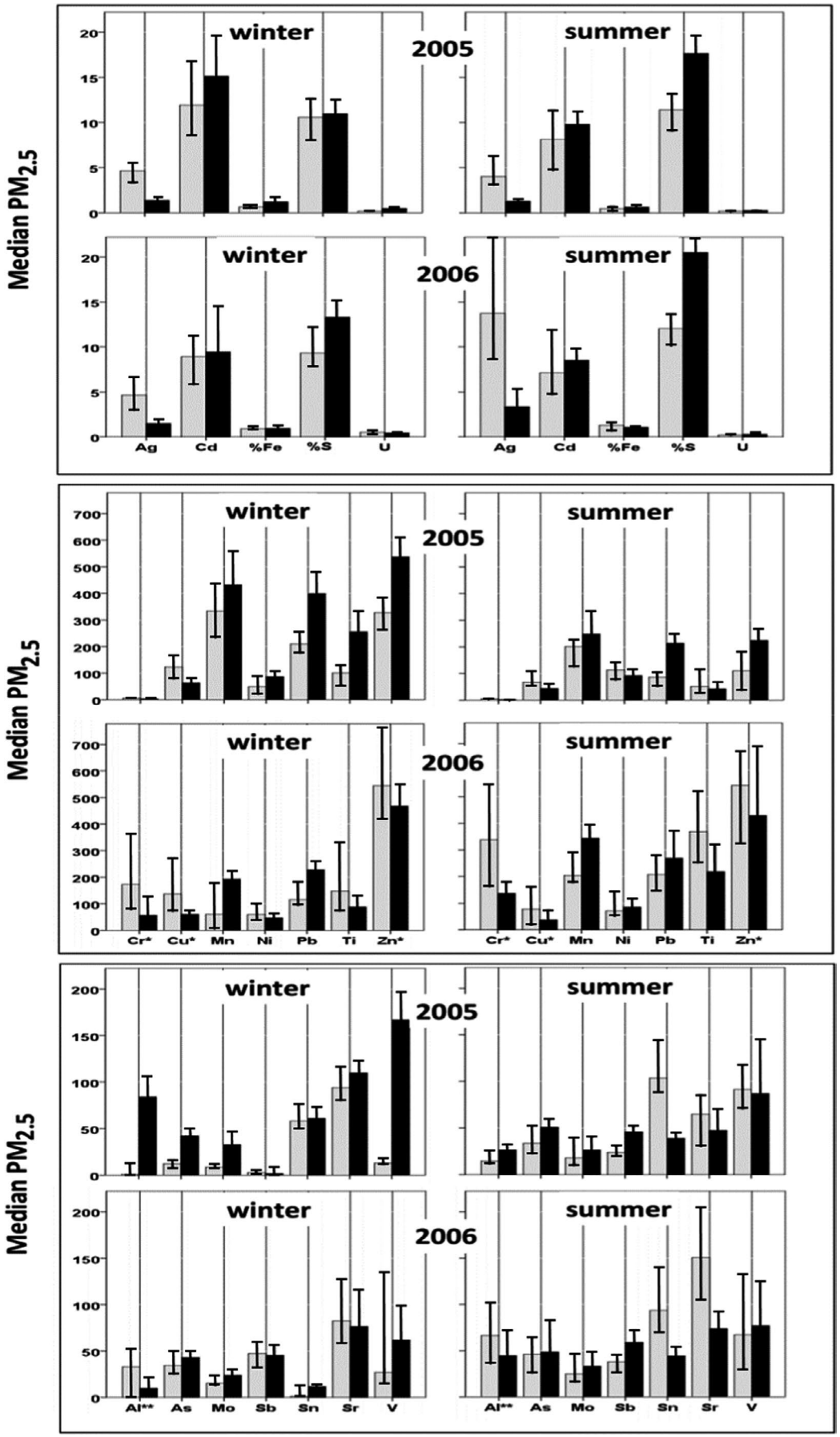
Median PM2.5
winter
2005
summer
winter
2006
summer
Ag
Cd
%Fe
%S
U
Cr*
Cu*
Mn
Ni
Pb
Ti
Zn*
Al**
As
Mo
Sb
Sn
Sr
V

TABLE 2 Indoor/outdoor concentration ratios for elements in $PM_{2.5}$; both years combined. Ratios were calculated using both mg/kg and ng/m^3 metrics for 50th percentile (median) and 95th percentile concentrations from Appendix S3 ($50th_{indoor}/50th_{outdoor}$ and $95th_{indoor}/95th_{outdoor}$); n = 141 weekly averages unless indicated otherwise. Ratios exceeding unity are shaded

	mg/kg		ng/m^3	
Elements	50th	95th	50th	95th
Ag	3.7	3.6	2.2	2.0
Al	0.6	1.3	0.3	0.7
As	0.6	1.1	0.3	0.5
Cd	0.8	1.4	0.4	0.9
Cr[a]	2.5	3.7	1.3	1.0
Cu	1.9	2.7	1.0	1.7
Fe	0.8	1.1	0.4	0.6
Mn	0.7	1.4	0.4	0.5
Mo	0.5	1.1	0.3	0.7
Ni	0.9	1.7	0.5	0.8
Pb	0.6	0.8	0.3	0.5
S[b]	0.8	0.8	0.3	0.4
Sb	0.6	0.8	0.3	0.4
Sn	1.7	3.5	0.8	1.8
Sr	1.2	1.4	0.7	1.1
Ti	0.9	1.5	0.6	0.8
U	0.7	2.3	0.2	2.3
V	0.5	0.8	0.3	0.5
Zn	0.9	1.4	0.4	0.6

[a]Cr ratios are for 2006 only (n = 61); values for 2005 were predominately below LOD.

[b]S based on 152 weekly averages for 2005 and 2006 combined.

and Mn in the presence of organic ligands is a key factor controlling complexation/precipitation reactions of soluble trace elements in the atmospheric aqueous phase.[67] Recent solid-phase speciation studies have shown that metals are sorbed by Fe-Mn oxyhydroxides in outdoor particles[68] and indoor particles.[26,30] Thus, while some elemental correlations in Figure 7 may reflect common sources, it is important to consider the potential influence of commonplace sorption reactions involving Fe and Mn oxides and hydroxides during particle aging. Resuspension of settled house dust was previously identified[10] as an indoor source of airborne Fe, Mn, Al, and associated trace elements (Ag, As, B, Cu, B, Pb, U, V, and Zn) in the Windsor study homes.

The scatter plots in Figure 8 illustrate seasonal influences on the relationship between outdoor $PM_{2.5}$ and the elemental composition of $PM_{2.5}$, which expands on information presented in the Figure 3. The negative correlation between airborne concentrations of $PM_{2.5}$ (μg/m^3) and mg/kg concentrations of Fe in $PM_{2.5}$ was observed in both winter and summer (Figure 8). The negative relationship displayed by Fe in Figure 8 also represents the behavior of most of the trace elements by proxy (supported by Figures 3 and 7A). The key exception was the relationship between the wt% concentration of S within $PM_{2.5}$ and the aerosol concentration of $PM_{2.5}$ (μg/m^3) in the outdoor environment, which flipped from positive in the summer to negative in the winter (Figure 8). The outdoor "seasonal flip" displayed by S in $PM_{2.5}$ was observed in both years: from negative in winter 2005 ($r = -0.37$; $p = 0.02$) to positive in summer of 2005 ($r = +0.54$; $p < 0.01$) and from negative in winter 2006 ($r = -0.53$; $p < 0.01$) to positive in summer of 2006 ($r = +0.34$; $p = 0.02$). Thus, the positive correlation between the wt% S content in $PM_{2.5}$ and $PM_{2.5}$ concentration in μg/m^3 was solely an outdoor phenomenon, occurring only in the summertime. Although indoor data are not included in Figure 8, it is noteworthy that this "seasonal flip" did not occur in the indoor microenvironment, where the relationship between wt% concentrations of indoor S within $PM_{2.5}$ and the aerosol concentration of indoor $PM_{2.5}$ in μg/m^3 was negative ($r = -0.35$; $p < 0.01$) over the two year monitoring period. A study of schools in Spain[69] also found that sulfate displayed different patterns indoors compared to outdoors as a function of season, and identified the influence of an indoor-specific source of sulfate.

Further examination of indoor S and outdoor S using mass-normalized metrics (Figure 9) showed that their relationships with personal S exposures were different in summer compared to winter. During the summer season, both outdoor S and indoor S displayed similar correlations with personal S ($r = 0.55, 0.57$; $p < 0.01$; Figure 9). In contrast, during winter the personal-outdoor S correlation was lost ($p > 0.8$), while personal exposure to S continued to display a significant correlation with indoor S ($r = 0.56$; $p < 0.01$; Figure 9). Similarly, a residential study in Pennsylvania, USA[70] found that variability in personal sulfate exposure was predicted better by indoor sulfate than outdoor sulfate. Sulfate exposures in the Pennylvania homes[70] displayed the same trend as the present study (outdoor > personal > indoor), and personal exposures were 125% of indoor concentrations[62,70] (comparable to 117% in the present study; Appendix S3). The observation of a persistent year-long correlation between indoor and personal S exposures in the present study (Figure 9) is consistent with the PCA interpretation of an indoor biogenic S factor by Yoshinaga et al.[36] Inter-environmental correlation results (personal:outdoor, personal:indoor, and indoor:outdoor) for all the study elements in $PM_{2.5}$ are summarized in the Supporting Information (Appendix S6) using both metrics.

4 | DISCUSSION

The current information gap on indoor metal sources is related to a number of challenges, one being the problem that indoor air sampling is labor-intensive and costly[4,71] and another being the technical difficulty of characterizing the small sample mass (often less than 100 μg PM/filter) that tends to result from the low flow rate samplers used to monitor non-occupational indoor and personal exposures.[57,72–74] In the present study, particular attention was paid to obtaining accurate gravimetric measurements, as well as rigorous quality control

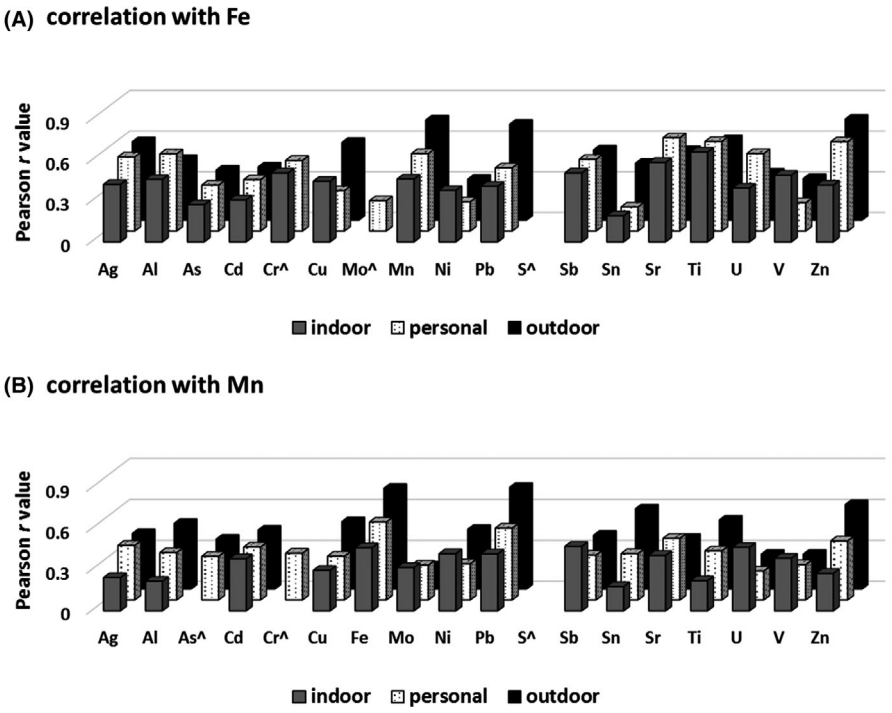

FIGURE 7 Pearson correlations in indoor, personal, and outdoor $PM_{2.5}$ between (A) Fe and other elements, and (B) Mn and other elements. Bar graphs include all elements for which there was a significant correlation (based on mg/kg metric); ^indicates the correlation was not significant in one or more environment for that element

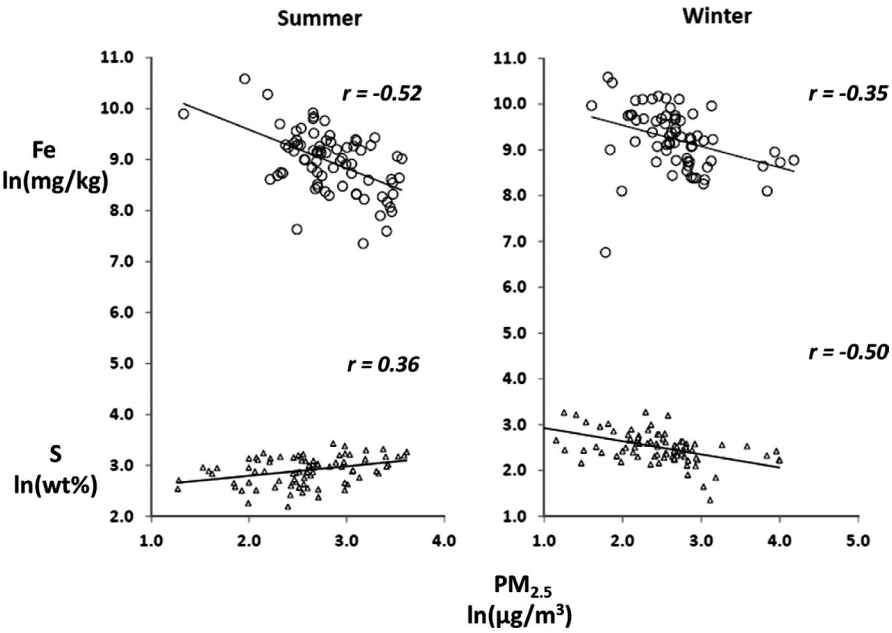

FIGURE 8 Relationship in outdoor environment between Fe (mg/kg) and $PM_{2.5}$ ($\mu g/m^3$) is negative in both summer and winter, whereas relationship between S (wt%) and $PM_{2.5}$ ($\mu g/m^3$) is positive in the summer and negative in the winter. (*r* values significant at $p < 0.01$; all data from 2005 and 2006 combined)

of the elemental analyses. Contamination was minimized by loading and unloading filter samples in a particle-free enclosure in the field, as well as in the laboratory (Appendix S1). Weighing errors associated with water sorbed onto the filter substrate vary with the filter material chosen, the best choice being PTFE.[75] Maintaining tight controls on air temperature and relative humidity during conditioning and weighing of PTFE filters greatly reduced this source of error, and the application of buoyancy corrections further improved measurement accuracy. Overall, indoor and personal samples benefitted the most from the buoyancy corrections, as these were typically the most lightly loaded filters (Figure 1).

Results showed that the mass-normalized metal composition of $PM_{2.5}$ (mg/kg) and the volume-normalized concentration of $PM_{2.5}$-bound metals (ng/m^3) are two different parameters that need to be considered separately. The ng/m^3 metric is appropriate for the purpose of assessing inhalation exposures to metals. The observed positive correlations between $\mu g/m^3$ concentrations of $PM_{2.5}$ and ng/m^3 concentrations of $PM_{2.5}$-bound metals (Figure 2A) aligned with this purpose intuitively: The more $PM_{2.5}$ inhaled per volume of air, the greater the exposure to the metal constituents hosted by those inhaled particles. However, the mg/kg metric proved advantageous for different purposes. Calculating the elemental content

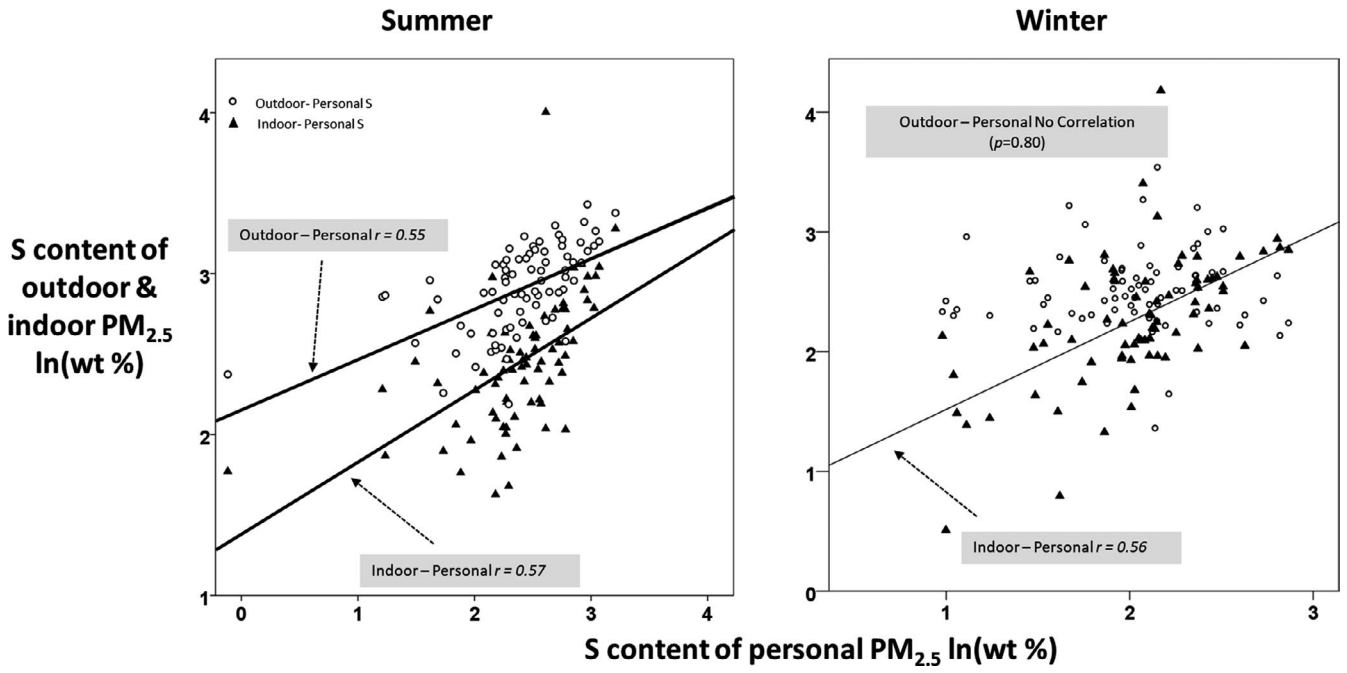

FIGURE 9 Seasonal variations in personal-outdoor and personal-indoor S correlations (note log scale). Personal-outdoor correlation is insignificant in winter season; *r* values significant at $p < 0.01$; all data from 2005 and 2006 combined

of $PM_{2.5}$ using mg/kg brought greater clarity to the study of particle composition and interpretations of elemental associations that help to identify sources. When the above correlation analyses were repeated using mg/kg for $PM_{2.5}$-bound metals (instead of ng/m^3), most relationships flipped from positive to negative (Figure 2B), revealing an important dilution effect. That is, as $PM_{2.5}$ (μg/m^3) increased, mass-normalized concentrations of most elements within $PM_{2.5}$ (mg/kg) decreased (Figures 2B and 8). Selection of metric had a profound impact on inter-elemental correlations in $PM_{2.5}$ (Figures 4 and 5) and on the PCA results in Appendix S8. The flip in the outdoor Mo-S correlation in Figure 4 (from positive using ng/m^3 to negative using mg/kg) provided the most obvious example of a spurious positive correlation caused by normalizing against air volume. These results demonstrated that while ng/m^3 is a useful exposure metric, mg/kg is the more useful metric for understanding particle composition. Selecting the correct metric is therefore critical for residential source apportionment modeling.

4.1 | Causes for discrepancies between metrics

This study showed that the selection of metric can significantly affect interpretations of elemental associations, and relationships between indoor and outdoor microenvironments. To select the appropriate metric, it is helpful to understand whether discrepancies between metrics are caused by measurement uncertainty, spurious correlations, and/or other artifacts. Certain discrepancies may be partly attributable to the uncertainty associated with air volume measurements (eg, differences in inter-environment correlations using mg/kg vs. ng/m^3; Appendix S6). Use of the mg/kg metric, where applicable, omits uncertainty associated with air volume (related to pump performance), which was shown to be the dominant source of uncertainty in the gravimetric measurement of $PM_{2.5}$ in the present study (Appendix S1). Uncertainty in air volume can be caused by periodic pulsations that disrupt air flow during sampling, despite pulsation dampers that are built into pump designs.[76]

It is notable that discrepancies caused by air volume measurement uncertainty (eg, Appendix S6) were not as prominent as those caused by spurious correlations (Figures 2,4, and 5). The complete reversal of the relationships illustrated in Figure 2 occurred because correlations using the ng/m^3 metric were influenced by the co-occurrence of the PM mass and the metal content of the PM matrix in a given volume of air, not because of any source of measurement uncertainty. When the metal content on the filter substrate is normalized against sampled air volume, it is the mass of PM on the filter that is the hidden driver for air concentrations of metals expressed using ng/m^3. Thus, it was PM mass that drove the erroneous ng/m^3 correlations in Figures 4A and 5A, which disappeared using the mg/kg metric in Figures 4B and 5B, respectively. Seven elemental correlations with S in the indoor environment (Figure 4A) were spurious correlations caused by normalizing against air volume.

The use of mg/kg (instead of ng/m^3) resulted in more I/O elemental ratios exceeding unity, especially in 2006 (Table 2; Appendix S5). This discrepancy occurred because sampled air volumes were nominally equal in both microenvironments, and therefore, calculating elemental I/O ratios using ng/m^3 was roughly equivalent to calculating I/O ratios simply using ng/filter (ie, the air volume terms in the numerator (I) and in the denominator (O) canceled out). Thus, elemental I/O ratios calculated using ng/m^3 reflected the difference in $PM_{2.5}$ exposures indoors versus outdoors (Table 1), but did not

accurately reflect the difference in composition between indoor particles and outdoor particles. To examine the impact of indoor and outdoor sources on particle composition, it was necessary to calculate I/O ratios using mg/kg, which involved normalizing the mass of metal on the filter against the mass of $PM_{2.5}$ in both numerator (I) and denominator (O). The discrepancies in Table 2 and Appendix S5 underscore the point that while ng/m^3 is an appropriate metric to assess exposure, mg/kg is a composition metric that brings greater clarity to source apportionment.

4.2 | Seasonal variations revealed by the mg/kg metric

Application of the mg/kg metric for correlation analyses yielded several novel findings, particularly with respect to S behavior. The correlation between the S content (wt%) of personal and indoor $PM_{2.5}$ ($p < 0.01$) persisted throughout both summer and winter seasons (Figure 9), in contrast to the personal-outdoor S correlation which was present in the summer but disappeared in the winter season ($p > 0.8$). The consistent year-round indoor-personal S correlation points to the influence of indoor S sources such as keratin in skin flakes and animal fibers[16,18,22,24,35,77]; drywall and plaster particles[25,26]; food wastes and cooking emissions[78,79]; humidifiers[18,80]; personal care products[81]; and other synthetic organosulphur compounds found indoors including plasticizers, insecticides for pets, PFAS (FTS 6:2), and bactericides.[82] The fact that S can accumulate to percentage level concentrations in settled dust (eg, 4.52 ± 0.16% in NIST 2583 Indoor Dust)[36] implicates resuspended dust as an important indoor source of S. Additionally, consumer products containing Sb_2S_3 were suggested by S correlations unique to the indoor environment (Figures 4 and 5), for example safety matches.[83] Other examples of elemental signatures that were unique to indoor $PM_{2.5}$ are provided in Appendix S2. In contrast, the Cr-S correlation was unique to the outdoor environment (Figure 4), which was consistent with previous identification of local cement plants as a source of airborne Cr in the Windsor area,[52] as sulfates are commonly used as Cr(VI) reducers in cement manufacturing.[84]

Another important seasonal trend revealed by using mg/kg was the negative correlation between the S content of $PM_{2.5}$ (wt%) and $PM_{2.5}$ concentration in air which occurred both indoors and outdoors in the winter season (Figure 8). A positive relationship between S content and $PM_{2.5}$ concentration occurred only in the summer and only outdoors (Figures 3 and 8). These observations provide new evidence in support of previous studies[20,80] which concluded that S is not an acceptable tracer for indoor-infiltrated $PM_{2.5}$. Sulfate was first proposed as a surrogate for ambient $PM_{2.5}$ in epidemiological studies over 25 years ago,[60] and subsequent models have used indoor/outdoor S ratios to predict indoor $PM_{2.5}$.[71] However, the observed dissimilarity in S-$PM_{2.5}$ behavior between indoor and outdoor microenvironments in the summer, and negative S-$PM_{2.5}$ relationships in both microenvironments in the winter, run counter to these models. Summertime increases in ambient S concentrations have been reported widely: in eastern United States for example, filter samples of ambient S almost doubled in summer (12.8 μg/m^3) compared to winter (6.7 μg/m^3), which was attributed to higher rates of photo-oxidation of SO_2 to SO_4^{2-} in summer.[45] Nevertheless, this atmospheric reaction does not in itself explain the seasonal reversal shown in Figure 8; nor does it account for the observed differences in indoor/outdoor S trends. Research is needed to understand why the seasonal reversal occurs outdoors but not indoors; one explanation may be the decrease in volatile S emissions from soil and water surfaces during ice and snow cover in the winter season. Biogenic emissions of volatile S compounds from soils, marshes, and fresh water surfaces are a significant but poorly constrained component of the atmospheric S budget for eastern North America.[85]

Seasonal changes in $PM_{2.5}$ elemental concentrations in both indoor and outdoor environments caused some I/O ratios to flip from <1 to >1 over time (Figure 6, Appendix S5). Elements such as Zn, Al, and Ti, which some source apportionment models have attributed solely to outdoor sources,[5,19,21,86] displayed I/O ratios >1 in both seasons of 2006 (Figure 6, Appendix S5), indicating that indoor sources can occasionally dominate elements that typically have higher outdoor concentrations. Resuspended house dust was an indoor source of these elements in the Windsor homes as discussed previously,[10] which likely contributed to the high variability of indoor $PM_{2.5}$ elemental concentrations (eg, Zn RSD was 133% indoors and 59% outdoors; Appendix S4). A second key observation from Figure 6 and Appendix S5 was that many more elements displayed median I/O ratios >1 in 2006 than in 2005 (Ag, Al, Cr, Cu, Sn, Sr, Ti, U, and Zn using mg/kg). The occurrence of elevated I/O elemental ratios in the year characterized by improved ambient air quality (2006) supports concerns raised previously by others,[7] that indoor sources of metals can exert a greater influence on personal exposures than outdoor sources.

4.3 | Impact on Source Apportionment Models

There are two key benefits of using the mg/kg metric for indoor-outdoor $PM_{2.5}$ source apportionment. First, the validity of correlations observed using ng/m^3 should be checked using mg/kg as described earlier. The second benefit of using the mg/kg metric is the ability to directly compare elemental signatures of $PM_{2.5}$ with elemental signatures of local environmental media (eg, house dust, soil, road dust, building materials, consumer products, and fossil fuels). Metals in source media, which are typically measured in mg/kg, contribute to airborne PM through a variety of release, dissipation, resuspension, and combustion processes. Settled house dust has proven to be a sensitive indicator of indoor sources[15,87,88] and a useful medium for estimating indoor inhalation exposures where sample collection is limited by inadequate resources.[89,90]

Strong indoor-outdoor correlations ($r > 0.6$) for many $PM_{2.5}$ elements in the Windsor study homes (Appendix S6) provide evidence of particle infiltration from outdoor sources, but this observation does not necessarily mean an absence of indoor sources (discussed

further in Appendix S5). Settled house dust is a ubiquitous indoor source of elements, and the contribution of resuspended dust to personal and indoor inhalation exposures in these homes was demonstrated previously.[10] Multiple studies from around the world report that house dust accumulates metals such as Zn, Ni, Cu, and Pb to elevated concentrations (100s to 1000s mg/kg), whether the metal originates from indoor, outdoor, anthropogenic, and/or natural sources.[29,36,90–97] Nevertheless, many residential source apportionment models have employed S, Ni, Zn, Cu, Fe, and other elements as "conservative tracers" of infiltrated outdoor sources, without considering their concentrations in house dust, on the premise that strong indoor-outdoor correlations and I/O ratios <1 signify the absence of indoor sources.[5,9,19,21,86,98] Results of the present study showed that many $PM_{2.5}$ elements previously regarded as conservative tracers (including Fe, Ni, S, and Zn) were more variable indoors than outdoors (Appendix S4). Such large variability in itself limits the usefulness of I/O ratios for quantifying infiltration[17,18,99] and provides further evidence of the influence of indoor sources.

Mathematical models that rely on *a priori* assumptions that indoor sources are absent, despite contrary evidence, introduce the risk of underestimating indoor exposures. It is recognized that predicting inhalation exposures to elements becomes more complicated when both indoor and outdoor sources are considered.[19] Nevertheless, a number of mathematical models have successfully incorporated indoor sources of elements such as Zn in Portugese house dust[93] and biogenic S in Japanese homes.[36] As settled dust is both a repository and a source for a diverse range of contaminants,[15,100] future PM source apportionment efforts would benefit from exploiting the elemental composition of house dust as a valuable indicator of indoor sources. Size fractionation of house dust indicates that an abundance of fine material is available for resuspension and potential inhalation exposures, with fine particles (<1.8 μm aerodynamic diameter) constituting about 25% of settled dust by weight.[101] Future studies would benefit from solid-phase speciation techniques to identify sources of PM-bound metals: for example, Huggins et al[102] were able to distinguish Cr-spinel in urban PM (NIST 1648) from Cr(III) sulfate in diesel PM (NIST 1650) using synchrotron X-ray techniques. Such speciation techniques could elucidate differences in the elemental composition of indoor and outdoor particles, such as those observed in the present study (Figures 4 and 5; Appendix S2). Also, speciation analysis could clarify the degree to which elemental correlations with Fe and Mn (as observed in Figure 7) result from sorption of metals onto Fe-Mn oxyhydroxides during particle aging (weathering) processes.[26,30,68]

5 | CONCLUSIONS

1. This study demonstrated the importance of selecting the appropriate metric for PM source apportionment models. Mass-normalized metal concentrations (eg, mg/kg) reflect the true elemental composition of particulate matter, whereas volume-normalized metal concentrations (eg, ng/m^3) do not. Mass-normalized measurements are appropriate for characterizing elemental signatures, correlation trends, and I/O ratios; investigating seasonal variations in $PM_{2.5}$ composition; and comparing cytotoxicity of indoor versus ambient particles. This study showed that when elemental measurements are volume-normalized, the mass of PM becomes the underlying driver for correlations between airborne elements and $PM_{2.5}$, which may lead to spurious inter-elemental correlations and erroneous interpretations of sources.
2. Using mg/kg in correlation analyses revealed important differences in the composition of indoor particles compared to outdoor particles that were collected simultaneously.
   a. Mass-normalized I/O elemental ratios exceeded unity more frequently than volume-normalized I/O ratios. Volume-normalized I/O ratios were unduly influenced by PM mass, resulting in an underestimation of the influence of indoor sources of metals.
   b. Indoor particles showed unique elemental signatures that indicated indoor sources.
   c. Elemental concentrations in $PM_{2.5}$ (mg/kg) generally decreased as $PM_{2.5}$ (μg/m^3) increased; this dilution effect was observed in all microenvironments and seasons. A key exception was outdoor S in summer, which displayed the opposite trend to indoor S.
3. Examination of airborne S concentrations, using mass-normalized metrics, revealed important new indoor/personal/outdoor relationships and seasonal trends:
   a. The S content of indoor $PM_{2.5}$ decreased as indoor $PM_{2.5}$ increased. This negative relationship calls into question the validity of using S as an index of $PM_{2.5}$.
   b. Outdoors, the correlation between $PM_{2.5}$ and the S content of $PM_{2.5}$ was negative in the winter, but positive in the summer. Research is needed to understand this seasonal flip; one explanation may be the decrease in volatile S emissions from soil and water surfaces during ice and snow cover.
   c. The influence of indoor S sources (eg, keratin in skin flakes and natural fibers) was evidenced by the consistent year-round correlation between indoor S and personal S, and by unique elemental signatures of indoor $PM_{2.5}$. In contrast, outdoor S did not correlate with personal S in the winter season.
4. Collection of settled house dust alongside indoor PM monitoring, to investigate indoor elemental signatures (using mg/kg), would assist in the development of indoor source profiles and improvement of residential source apportionment models. Some models have attributed certain elements in indoor $PM_{2.5}$ to resuspension of settled house dust (eg, Ni and Sb), but arbitrarily assumed an absence of indoor sources for other elements (eg, S and Zn). Such *a priori* assumptions are contradicted by the international literature describing the multi-element composition of house dust: S occurs in the wt% range in house dust (eg, 4.5% S in NIST 2583), and Zn and many other metals also tend to accumulate to elevated concentrations in indoor dust (100s-1000s mg/kg).

5. Detailed particle characterization (eg, synchrotron X-ray speciation and/or SEM imagery) will assist in identifying indoor sources of elements and their compounds, and evaluating whether observed elemental correlations are caused by a common source or by chemical transformations that occur during particle aging (eg, scavenging of metals by Fe-Mn oxyhydroxides).
6. Results of the present study supported infiltration processes as an important source of $PM_{2.5}$-bound elements, but this did not preclude indoor sources. That is, observed correlations between indoor and outdoor concentrations of many elements did not support an assumption that infiltration was the sole source of these elements, as there was co-existing evidence that indoor sources were also important. Future mathematical models should accommodate the more realistic assumption that metals in the indoor environment are derived from both indoor and outdoor sources in varying proportions.

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CONFLICT OF INTEREST

None of the authors have a conflict of interest.

AUTHOR CONTRIBUTIONS

PER involved in conceptualization, formal analysis, funding acquisition, investigation, methodology, project administration, resources, supervision, validation, visualization, writing-original draft, and writing-review and editing. CL involved in data curation, investigation, validation, visualization, and writing-review and editing. OB involved in data curation, investigation, resources, validation, and writing-review and editing. MC involved in data curation, investigation, and validation. HDG involved in conceptualization, data curation, formal analysis, methodology, software, validation, visualization, and writing-review and editing.

DATA AVAILABILITY STATEMENT

Research data are not shared.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

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