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.\textsuperscript{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.\textsuperscript{4} Although some studies have shown that metal data from central monitoring sites correlate well with personal exposures,\textsuperscript{5,6} there is growing evidence that indoor sources may have a greater influence on personal exposures than outdoor sources.\textsuperscript{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.
than outdoors, 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.

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. Indoor PM$_{2.5}$ is enriched in organic carbon (OC) compared with outdoor PM$_{2.5}$ due to multiple indoor OC sources. In addition to cooking emissions, key indoor sources of OC include clothing fibers, skin cells, and other organic emissions originating from the residents themselves. Understanding metal speciation (ie, the chemical and physical form of the particle-bound metal), which is critical in determining the toxicity of particles, 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, paint pigments containing zinc, titanium, barium, chromium and lead, arsenic, copper and chromium from treated wood, and lead solder.

Indoor sources of Cu include motor-generated particles released during vacuuming and emissions from electrical appliances. Other important indoor sources of metals include re-suspension of settled dust, natural and synthetic carpet fibers and other textile fibers, and cooking emissions. 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. Textile fibers also may be colored with dyes containing metals such as Cr, Sb, and Cu.

Consumer spray products release indoor particles containing Ag, Zn, Li, Sr, Ba, Pb, Mn, and other metals. 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. 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.

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. 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. 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 and in indoor air (ng/m$^3$) using PMF. 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. 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, in contrast to other studies that used Br as a conservative indoor tracer of external factors such as traffic and/or marine aerosols. Pant and Harrison 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—a recommendation that has been echoed by others in the context of indoor-outdoor source apportionment.

Recent studies have used alternate metrics to represent PM constituents (other than the traditional $\mu g/m^3$ 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. A study of PM$_{10}$ across seven cities in northern China 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...
outdoor PM$_{30}$, which evidenced the contribution of resuspended dust to airborne metals.\textsuperscript{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\textsuperscript{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.\textsuperscript{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.\textsuperscript{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\textsuperscript{®}; 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.\textsuperscript{53,54} Briefly, sampling was conducted over 2 years (2005 and 2006), at 48 homes of asthmatic children and non-smokers, 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\textsuperscript{®} facility,\textsuperscript{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.\textsuperscript{56} Details of the weighing protocol were described previously.\textsuperscript{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 pre-conditioned 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)

| Element | 2005 Indoor | 2005 Outdoor | 2005 Personal | 2006 Indoor | 2006 Outdoor | 2006 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, 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, 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 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. 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$_{10}$).
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, 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
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. 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/m³) on elemental correlations with PM₂.₅

The relationship between PM₂.₅ and the elemental content of PM₂.₅ is strongly influenced by the metric chosen for the elemental concentration, as demonstrated by Figure 2. Correlations with PM₂.₅ were positive when elemental concentrations were calculated using air volume in the denominator, that is, ng/m³ (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 PM₂.₅ concentration in µg/m³ 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 PM₂.₅ and the PM₂.₅ concentration in air (Figure 3), which aligns with the purported use of S as a surrogate for PM₂.₅. 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 PM₂.₅ and PM₂.₅ (Figures 2B and 3).
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, 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/m³ 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/m³ (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 PM₂.₅ 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 PM₂.₅ 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/m³. 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 PM₂.₅ 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. The significant Cr-S outdoor relationship observed for the whole dataset (Figure 4A,B) was lost when ng/m³ 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/m³. The strong Ni-Cr correlation is evident in both indoor PM₂.₅ and outdoor PM₂.₅ 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$_{2.5}$ ($\mu$g/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$_{2.5}$ ($\mu$g/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, airborne fibers impregnated with metallic dyes, and Ag bactericides; consumer spray products (including nanosprays), paper particles generated from home offices (printing and shredding), and cooking emissions. The influence of metric was even greater when 95th percentile values were used to calculate I/O ratios; 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. 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 ($\mu$g/m$^3$) decreased.

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

The negative relationship between airborne PM$_{2.5}$ ($\mu$g/m$^3$) and its elemental content (mg/kg), shown in the Figures 2 and 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. Redox cycling of Fe...
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. Recent solid-phase speciation studies have shown that metals are sorbed by Fe-Mn oxohydroxides in outdoor particles and indoor particles. 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 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 positive 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 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 found that variability in personal sulfate exposure was predicted better by indoor sulfate than outdoor sulfate. Sulfate exposures in the Pennsylvania homes displayed the same trend as the present study (outdoor > personal > indoor), and personal exposures were 125% of indoor concentrations (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. 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.

### TABLE 2 Indoor/outdoor concentration ratios for elements in PM$_{2.5}$; both years combined.

| Elements | 50th (mg/kg) | 95th (mg/kg) | 50th (µg/m$^3$) | 95th (µg/m$^3$) |
|----------|-------------|-------------|----------------|----------------|
| 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.

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 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. In the present study, particular attention was paid to obtaining accurate gravimetric measurements, as well as rigorous quality control
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. 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 µg/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
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

![Figure 9](image-url) 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.
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; drywall and plaster particles; food wastes and cooking emissions; humidifiers; and other synthetic organosulphur compounds found indoors including plasticizers, insecticides for pets, PFAS (FTS 6:2), and bactericides. The fact that S can accumulate to percentage level concentrations in settled dust (eg, 4.52 ± 0.16% in NIST 2583 Indoor Dust) implicates resuspended dust as an important indoor source of S. Additionally, consumer products containing Sb$_2$S$_3$ were suggested by S correlations unique to the indoor environment (Figures 4 and 5), for example safety matches. 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, as sulfates are commonly used as Cr(VI) reducers in cement manufacturing.

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 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, and subsequent models have used indoor/outdoor S ratios to predict indoor PM$_{2.5}$. 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. 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.

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, 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, 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, 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 ($r > 0.6$) 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...
infiltration 17,18,99 and provides further evidence of the influence of variability in itself limits the usefulness of I/O ratios for quantifying more variable indoors than outdoors (Appendix S4). Such large guarded as conservative tracers (including Fe, Ni, S, and Zn) were considered 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 Portuguese 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. 201 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 (e.g., 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 (e.g., 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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REFERENCES
1. Lippmann M. Toxicological and epidemiological studies of cardiovascular effects of ambient fine particulate matter (PM$_{2.5}$) and its chemical components: coherence and public health implications. Crit Rev Toxicol. 2014;44(4):299-347.
2. Van Donkelaar A, Martin RV, Li C, Burnett RT. Regional estimates of chemical composition of fine particulate matter using a combined geoscientific statistical method with information from satellites, models, and monitors. Environ Sci Technol. 2019;53(5):2595-2611.
3. Gao D, Ripley S, Weichenthal S, Pollitt KJ. Ambient particulate matter oxidative potential: chemical determinants, associated health effects, and strategies for risk management. Free Radic Biol Med. 2020;151:7-25.
4. National Academies of Sciences, Engineering, and Medicine; Health and Medicine Division; Board on Population Health and Public Health Practice. Health Risks of Indoor Exposure to Particulate Matter: Workshop Summary. National Academies Press (US); 2016:158.
5. Long CM, Sarnat JA. Indoor-outdoor relationships and infiltration behavior of elemental components of outdoor PM$_{2.5}$ for Boston Area Homes. Aerosol Sci Technol. 2004;38(S2):91-104.
6. Montagne D, Hoe G, Nieuwenhuijsen M, et al. Temporal associations of ambient PM$_{2.5}$ elemental concentrations with indoor and personal concentrations. Atmos Environ. 2014;86:203-211.
7. Brokamp C, Rao MB, Fan ZT, Ryan PH. Does the elemental composition of indoor and outdoor PM$_{2.5}$ accurately represent the elemental composition of personal PM$_{2.5}$? Atmos Environ. 2015;101:226-234.
8. Lim JM, Jeong JH, Lee JH, Moon JH, Chung YS, Kim KH. The analysis of PM$_{2.5}$ and associated elements and their indoor/outdoor pollution status in an urban area. Indoor Air. 2011;21(2):145-155.
9. Bari MA, Kindzierski WB, Wallace LA, Wheeler AJ, Macneill M, Héroux M-E. Indoor and outdoor levels and sources of submicron particles (PM$_{2.5}$) at homes in Edmonton, Canada. Environ Sci Technol. 2015;49(11):6419-6429.
10. Rasmussen PE, Levesque C, Chénier M, Gardner HD. Contribution of metals in resuspended dust to indoor and personal inhalation exposures: relationships between PM$_{10}$ and settled dust. Build Environ. 2018;143:513-522.
11. Martins V, Faria T, Diapouli E, et al. Relationship between indoor and outdoor size-fractionated particulate matter in urban microenvironments: levels, chemical composition and sources. Environ Res. 2020;183:109203.
12. Viana M, Kuhlbusch TAJ, Querol X, et al. Source apportionment of particulate matter in Europe: a review of methods and results. J Aerosol Sci. 2008;39(10):827-849.
13. Habre R, Coulb B, Moshier E, et al. Sources of indoor air pollution in New York City residences of asthmatic children. J Expo Sci Environ Epidemiol. 2014;24(3):269-278.
14. Morawska L, Afshari A, Bae GN, et al. Indoor aerosols: from personal exposure to risk assessment. Indoor Air. 2013;23(6):462-487.
15. Salthammer T. Emerging indoor pollutants. Int J Hyg Environ Health. 2020;224:113423.
16. Weschler CJ. Roles of the human occupant in indoor chemistry. Indoor Air. 2016;26(1):6-24.
17. Hodas N, Loh M, Shih H-M, et al. Indoor inhalation intake fractions of fine particulate matter: review of influencing factors. Indoor Air. 2016;26(6):836-856.
18. Rivas I, Fussell JC, Kelly FJ, Querol X. Indoor sources of air pollutants. In: Harrison RM, Hester RE, eds. Indoor Air Pollution. Royal Society of Chemistry; 2019:1-34.
19. Mohammed MQA, Song WW, Ma WL, et al. Trends in indoor-outdoor PM$_{2.5}$ research: a systematic review of studies conducted during the last decade (2003-2013). Atmos Pollut Res. 2015;6(5):893-903.
20. Polidori A, Cheung KL, Arhami M, Delfino RJ, Schauer JJ, Sioutas C. Relationships between size-fractionated indoor and outdoor trace elements at four retirement communities in southern California. Atmos Chem Phys. 2009;9(14):4521-4536.

21. Balasubramanian R, Lee SS. Characteristics of indoor aerosols in residential homes in urban locations: a case study in Singapore. J Air Waste Manag Assoc. 2007;57(8):981-990.

22. Fox K, Castanha E, Fox A, Feigley C, Salzberg D. Human K10 epithelial keratin is the most abundant protein in airborne dust of both occupied and unoccupied school rooms. J Environ Monit. 2008;10(1):55-59.

23. Schneider T. Dust and fibers as a cause of indoor environment problems. Scand J Work Environ Health Suppl. 2008;10:10-17.

24. Oeder S, Dietrich S, Weichenmeier I, et al. Toxicity and elemental composition of particulate matter from outdoor and indoor air of elementary schools in Munich, Germany. Indoor Air. 2012;22(2):148-158.

25. Beauchemin S, MacLean LCW, Rasmussen PE. Lead speciation in indoor dust: a case study to assess old paint contribution in a Canadian urban house. Environ Geochim Health. 2011;33(4):343-352.

26. Walker SR, Jamieson HE, Rasmussen PE. Application of synchrotron microprobe methods to solid-phase speciation of metals and metalloids in house dust. Environ Sci Technol. 2011;45(19):8233-8240.

27. Rasmussen PE, Beauchemin S, Nugent M, Dugandzic R, Lanouette M, Chénier M. Influence of matrix composition on the bioaccessibility of copper, zinc, and nickel in urban residential dust and soil. Hum Ecol Risk Assess. 2008;14(2):351-371.

28. Rasmussen PE, Beauchemin S, MacLean LCW, Chénier M, Levesque C, Gardner HD. Impact of humidity on speciation and bioaccessibility of Pb, Zn, Co and Se in house dust. J Anal At Spectrom. 2014;29(7):1206-1217.

29. Beauchemin S, Rasmussen PE, Mackinnon T, Chénier M, Boros K. Zinc in house dust: speciation, bioaccessibility, and impact of humidity. Environ Sci Technol. 2014;48(16):9022-9029.

30. MacLean LCW, Beauchemin S, Rasmussen PE. Lead speciation in house dust from Canadian urban homes using EXAFS, micro-XRF, and micro-XRD. Environ Sci Technol. 2011;45(13):5491-5497.

31. Knibbs LD, He C, Duchaine C, Morawska L. Vacuum cleaner emissions as a source of indoor exposure to airborne particles and bacteria. Environ Sci Technol. 2012;46(1):534-542.

32. Dris R, Gasperi J, Mirande C, et al. A first overview of textile fibres including microplastics, in indoor and outdoor environments. Environ Pollut. 2017;221:453-458.

33. Gorjinezhad S, Kerimov A, Amouei Torkmahalleh M, Meleş M, Ozturk F, Hopke PK. Quantifying trace elements in the emitted particulate matter during cooking and health risk assessment. Environ Sci Pollut Res. 2017;24(10):9515-9529.

34. Tan CCL, Finney KN, Chen Q, Russell NV, Sharifi VN, Swhitchenbank J. Experimental investigation of indoor air pollutants in residential buildings. Indoor Built Environ. 2013;22(3):471-489.

35. Voloshina OV, Shirshin EA, Lademann J, Fadeev VV, Darvin ME. Fluorescence detection of protein content in house dust: the possible role of keratin. Indoor Air. 2017;27(2):377-385.

36. Yoshinaga J, Yamasaki K, Yonemura A, et al. Indoor source apportionment in urban communities near industrial sites. Atmos Environ. 2016;139:30-36.

37. Pant P, Harrison RM. Critical review of receptor modelling for particulate matter: a case study of India. Atmos Environ. 2012;49:1-12.

38. Wang F, Wang J, Han M, Jia C, Zhou Y. Heavy metal characteristics and health risk assessment of PM_{2.5} in students' dormitories in a university in Nanjing, China. Build Environ. 2019;160:106206.

39. Conner TL, Williams RW. Identification of possible sources of particulate matter in the personal cloud using SEM/EDX. Atmos Environ. 2004;38(31):5305-5310.

40. Hopke PK. Review of receptor modeling methods for source apportionment. J Air Waste Manag Assoc. 2016;66(3):237-259.

41. Tunno BJ, Dalton R, Cambal L, Holguin F, Lioy P, Clougherty JE. Indoor source apportionment in urban communities near industrial sites. Atmos Environ. 2016;139:30-36.

42. Pant P, Harrison RM. Critical review of receptor modelling for particulate matter: a case study of India. Atmos Environ. 2012;49:1-12.

43. Wang F, Wang J, Han M, Jia C, Zhou Y. Heavy metal characteristics and health risk assessment of PM_{2.5} in students' dormitories in a university in Nanjing, China. Build Environ. 2019;160:106206.

44. Brehmer C, Norris C, Barkjohn KK, et al. The impact of household air cleaners on the chemical composition and children's exposure to PM_{2.5} metal source in suburban Shanghai. Environ Pollut. 2019;253:190-198.

45. Zhao W, Hopke PK, Norris G, Williams R, Paatero P. Source apportionment and analysis on ambient and personal exposure samples with a combined receptor model and an adaptive blank estimation strategy. Atmos Environ. 2006;40(20):3788-3801.

46. Allen JG, McLean MD, Stapleton HM, Webster TF. Linking PBDEs in house dust to consumer products using X-ray fluorescence. Environ Sci Technol. 2008;42(11):4222-4228.

47. Suzuki G, Kida A, Sakai SI, Takigami H. Existence state of bromine as an indicator of the source of brominated flame retardants in indoor dust. Environ Sci Technol. 2009;43(5):1437-1442.

48. Hopke PK, Ramadan Z, Paatero P, et al. Receptor modeling of ambient and personal exposure samples: 1998 Baltimore Particulate Matter Epidemiology-Exposure Study. Atmos Environ. 2003;37(23):3289-3302.

49. Yakovleva E, Hopke PK, Wallace L. Receptor modeling assessment of particle total exposure assessment methodology data. Environ Sci Technol. 1999;33(20):3645-3652.

50. Luo X-S, Ip CC, Liu W, Li S, Li XD. Spatial–temporal variations, sources, and transport of airborne inhalable metals (PM_{10}) in urban and rural areas of northern China. Atmos Chem Phys Discuss. 2014;14:13133-13165.

51. Luo X-S, Zhao Z, Xie J, et al. Pulmonary bioaccessibility of trace metals in PM_{2.5} from different megacities simulated by lung fluid extraction and DGT method. Chemosphere. 2019;218:915-921.

52. International Joint Commission. Air Quality in Selected Binational Great Lakes Urban Regions (Detroit-Windsor, Port Huron-Sarnia, and Sault Ste. Maries) A Report from the International Air Quality Advisory Board to the International Joint Commission. February 2004 ISBN 1-894280-44-X; ijc.org/sites/default/files/ID1544.pdf. Accessed February 5, 2021.

53. Wheeler AJ, Xu X, Kulka R, et al. Windsor, Ontario exposure assessment study: design and methods validation of personal, indoor, and outdoor air pollution monitoring. J Air Waste Manag Assoc. 2011;61(2):142-156.

54. Johnson M, Macneill M, Grigcik-Mannion A, et al. Development of temporally refined land use regression models predicting daily household-level air pollution in a panel study of lung function among asthmatic children. J Expo Sci Environ Epidemiol. 2013;23(3):259-267.

55. Rasmussen PE, MacIntyre DJ, Guenette J. Buoyancy-corrected gravimetric analysis system. United States Patent and Trademark Office. 2008. Patent. No. US 7,357,045 B2. Date: 15 April, 2008. 8 Claims, 3 Drawing Sheets.

56. Rasmussen PE, Gardner HD, Niu J. Buoyancy-corrected gravimetric analysis of lightly loaded filters. J Air Waste Manage Assoc. 2010;60(9):1065-1077.

57. Rasmussen PE, Wheeler AJ, Hassan NM, Filatreault A, Lanouette M. Monitoring personal, indoor, and outdoor exposures to metals in
98. Hasheminassab S, Daher N, Shafer MM, Schauer JJ, Delfino RJ, Sioutas C. Chemical characterization and source apportionment of indoor and outdoor fine particulate matter (PM$_{2.5}$) in retirement communities of the Los Angeles Basin. *Sci Total Environ.* 2014;490:528-537.

99. Chen C, Zhao B. Review of relationship between indoor and outdoor particles: I/O ratio, infiltration factor and penetration factor. *Atmos Environ.* 2011;45(2):275-288.

100. Schultz IR, Cade S, Kuo LJ. The dust exposome. In: Dagnino S, Macherone A, eds. *Unraveling the Exposome.* Springer; 2019:247-254.

101. Levesque C, Wiseman CLS, Beauchemin S, Rasmussen PE. Thoracic fraction (PM$_{10}$) of resuspended urban dust: geochemistry, particle size distribution and lung bioaccessibility. *Geosciences.* 2021;11(2):87.

102. Huggins FE, Huffman GP, Robertson JD. Speciation of elements in NIST particulate matter SRMs 1648 and 1650. *J Hazard Mater.* 2000;74(1-2):1-23.

**SUPPORTING INFORMATION**

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

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