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Assessment of trace elements directly from archived total suspended particulate filters by laser ablation ICP-MS: A case study of South Carolina

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Abstract

Background: Exposure to particulate air pollution is one of the greatest environmental risk factors for adverse human health outcomes. However, the constituents that may be responsible for such adverse health effects have not been fully studied.

Methods: Total suspended particulates filters collected every 6 days in 2011 from three South Carolina locations were used in this case study. An inductively coupled plasma mass spectrometer interfaced with a laser ablation system (LA-ICP-MS) was used to directly analyze 41 inorganic elemental species on air pollution filters. Then, machine learning and multivariate statistical methods was employed to identify combinatorial patterns in the data and classify sites based on their elemental composition.

Results: Forty-one elements were assessed and 33 were used in subsequent analysis. Correlations between United States Environmental Protection Agency (US EPA)'s chemical analysis dataset and data from the current study revealed significant associations between 7/15

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Declaration of Competing Interest

None.

CRediT authorship contribution statement

Sarah Commodore: Investigation, Data curation, Writing – original draft. **Steven Christopher:** Conceptualization, Methodology, Resources, Data curation, Investigation. **Bethany Wolf:** Visualization, Formal analysis, Validation, Writing – review & editing. **Erik Svendsen:** Supervision, Funding acquisition, Writing – review & editing.

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Ethics statement

N/A this was a non-human subjects or animal subjects research.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jtemin.2022.100041.

elements with enough variation for comparison (r between 0.28 to 0.66, $p < 0.05$). Subsequent multivariate analyses revealed four distinct patterns in the distribution of elements by sample location throughout the year.

Conclusion: The different airborne elements may need to be assessed to understand combinations of elements which occur together over space and/or time. Such information can be helpful in planning effective counter measures and strategies to control particulate air pollution.

Keywords

Air quality; Air filter media; Laser ablation ICP-MS; Total suspended particulates; Spatio-temporal patterns

Introduction

Evidence for the adverse health impacts of air pollution has been mounting for decades [1,2]. Exposure to ambient air pollutants is associated with both acute and chronic health effects and the impacts are felt on both global and local scales [3]. A recent review on the human health impact of airborne particulate matter highlighted the dramatic growth in studies that have shown strong associations between exposure to particulate matter (PM) and various health outcomes including premature death, cardiovascular disease, asthma, decreased lung function, and increased adverse respiratory symptoms such as breathing difficulties [4]. PM is currently regulated on its total mass concentrations in air ($\mu\text{g}/\text{m}^3$), yet these adverse health effects have been observed even at very low levels of PM [5]. It is unclear whether a threshold concentration exists below which little or no effects on health are observed [6], and knowledge on the differential toxicities of airborne particulate matter (PM) constituents remains a crucial research gap [7].

Regulatory control of PM can be improved with a better understanding of the nature of the various constituents of the PM mixture and their sources [8]. Mounting evidence from studies throughout the United States shows that there are significant associations between exposures to PM constituents and adverse health, both in the short term and, although limited, in the long term [7]. However, due to differences in study design, statistical analyses and specific PM constituents, further research is needed. Such elemental composition data are available through the United States Environmental Protection Agency (US EPA)'s PM_{2.5} National Chemical Speciation Network (CSN), as well as the Interagency Monitoring of Protected Visual Environments (IMPROVE) Network [9,10]. The choices in existing measurement and analytical tools were made based on funding, and available technology [11]. A shift towards time- and cost-effective analytical technologies will be necessary to rapidly examine a more comprehensive mix of airborne PM to improve its regulatory control [12]. In fact, as far back as 1999, Chin et al. [13] demonstrated the feasibility of a multi-element analysis of airborne particulate matter collected on PTFE-membrane filters. However, the current standard of practice is still in use for obtaining particle constituent or chemical composition data.

Historically, accepted filter-based approaches and wet-chemistry methods are used to acquire elemental composition data [14]. The US EPA measures over 50 chemical

constituents; analyzing all available constituents presents problems with multiple comparisons, and most researchers typically select the constituents that are the largest contributors to PM total mass [15]. However, different monitors are used to measure PM total mass and chemical constituents, and this creates data alignment problems. Furthermore, the CSN are more sparsely distributed compared to the mass concentrations monitoring network and this introduces measurement and prediction errors in exposure assessment. As such, understanding the local air quality at locations with no air monitoring can be challenging.

Challenges with filter sample analysis also exist, and include approaches such as thermal optical analysis (for carbon), ion chromatography (for nitrates and sulfates) and X-ray fluorescence (for metals) [16]. Additionally, three different filter media are required: Teflon, nylon, and quartz-fiber filters [14]. While this supports the EPA's goal in understanding the spatial and temporal composition of fine particles in ambient air, several issues remain. First, ambient monitors dedicated for PM constituent analysis are sparsely located across the US and are not measured on a daily basis. Secondly, for trace elements, the energy-dispersive X-ray fluorescence method is not sufficiently sensitive to detect a majority of the elements; precision results are usually 20% to 40% for ion/carbon/trace elements, and poorer for lighter elements [14]. While several approaches have been taken to compare CSN analytical protocols [17,18], we would like to focus on a case study from one state to highlight how data can be obtained at locations that may have need of but are currently without elemental composition data.

The motivating hypothesis for this work is that the patternicity of elements on the PM filters will exhibit variability in terms of location and/or time in South Carolina and that one site would not adequately represent all sites. To address this hypothesis, we sought to answer the following *questions*. *First what types of different elements occur on the PM filter media and what are their mass fractions? Secondly how do these elements compare with those measured in the Chemical Speciation Network? Thirdly, are there combinations (or mixtures) of elements that occur together over space and/or time?* Such information will be extremely helpful to plan effective counter measures and strategies to control particulate air pollution.

Materials and methods

Sample collection and information

Archived high volume sampler filters collected by the South Carolina Department of Health and Environmental Control were available for the research team's use. We used filters from three sites for the initial method development of this constituent analysis. These archived filters represent total suspended particulates (TSP) samples collected every 6 days in 2011. We used the lab blanks and loaded filters from the same batches, and we do not expect much impact on our results after blank subtractions. They were from three locations in the state of South Carolina representing the northern ($n = 56$), middle ($n = 56$) and southern regions ($n = 53$) [Fig. 1].

Sample preparation

Minimal sample preparation steps included cutting and mounting the TSP filter samples and fixing them onto 3 mm thick by 38 mm diameter glass discs with double sided tape. The glass substrate supported the thin TSP filter samples and prevented the samples from sticking to the laser cell o-ring or falling away during sample interchange. National Institute of Standards and Technology (NIST) calibration and control materials were pressed into 13 mm diameter pellets using a sample press, with application of approximately 36 MN of force. The pelletized samples were centered in the carousel sample slots using custom nylon mounts that allowed for sealing against the 18 mm laser cell o-ring. A triple quadrupole inductively coupled plasma mass spectrometer (Agilent Technologies 8800, Palo Alto, CA) interfaced with a laser ablation system (LA-ICP-MS) was used to analyze samples.

Calibration and quality assurance/quality control (QA/QC)

First, storage blank filters were used to establish background levels of elements present within the filter substrate – these filters that came from the same or a similar batch as the loaded air sample filters used in the study. Second, pressed pellets of NIST SRM 2584 Trace Elements in Indoor Dust (Nominal Mass Fraction of 1% Lead) served as the calibration material (single calibrant). NIST SRM 1649a Urban Dust served as the control (Supplementary Fig. 1). Filter blank samples were placed between five loaded air sample filters from each site during ablation, with the calibrant run at the beginning of the sequence and the control at the end. Signals from the ICP-MS were converted to elemental mass fractions using SRM 2584.

LA-ICP-MS procedures

The specifications and operating conditions used for LA-ICP-MS are provided in Supplementary Table 1. For each filter, an area representing approximate 0.002% of the total filter area was ablated via raster scanning to measure the elements present in the filter. Each sample was independently sealed against the laser cell, and the cell was purged with helium gas in between each sample analysis. Additionally, a pre-ablation cleaning run was performed before the main run was executed. Together, these procedures eliminated sample cross contamination. The signals were detected with the triple quadrupole ICP-MS. LabVIEW software was used for data reduction and quantification.

This LA-ICP-MS analytical technique was used to assess TSP filter samples from January 3rd 2011, through December 29th 2011 from three different air monitoring sites in South Carolina. Data from January 2011 are omitted from the final data analysis because the He gas setting was too low to push the samples to the ICP-MS. As such, data are summarized from February 2011 to December 2011. There were 165 TSP filter samples and 33 filter blanks. Each analytical batch of 20 samples, (consisting of calibrants, blanks, unknowns and controls) was completed in approximately 60 min. This translates to a total filter analysis time of approximately three minutes, including sample interchange, laser cell washout, and acquisition time. A single laser acquisition is performed in approximately 30 s to complete a 900 μm sample transect. The laser system has the flexibility to perform multiple transects over a finite area, if desired.

US EPA chemical speciation network (CSN) data

CSN data for January through December 2011 were measured from a stationary air monitor in Columbia, South Carolina, from EPA's only National Core (NCORE) Monitoring Network site in the state and operated by the South Carolina Department of Health and Environmental Control. The speciation monitor at this NCORE site is a SuperSass sampler which uses two different filter types (Teflon and Nylon), with each filter analyzed for different PM species (organic and elemental carbon, major ions and trace metals). Data were retrieved online from the US EPA's portal for air quality data collected from outdoor monitors across the US (<https://www.epa.gov/outdoor-air-quality-data>). For the purposes of the current study, only trace metal data obtained from Teflon filters were used for comparison.

Statistical analyses

Filter data were blank subtracted using the average filter blank in each run before employing descriptive statistics. Nonparametric univariate analyses were conducted with the Kruskal Wallis test to compare differences for each element between sites, since the raw data did not meet the assumptions of normal distribution. Pairwise correlations using Spearman's rank correlation coefficients between elements obtained from this LA-ICP-MS method were also examined. Furthermore, Spearman's rank correlation coefficients were assessed between the US EPA CSN data and data from the current study. Correlations between mass fraction (mg/kg) and mass concentrations ($\mu\text{g}/\text{m}^3$) were conducted. Then, with the assumption there was a pressure of 1 atmosphere and a temperature of 25 °Celsius, we converted CSN mass concentrations to mass fractions with the following equation:

$$\begin{aligned} CNS \text{ (mg/kg)} \\ = (24.45 \times \text{concentration } [\mu\text{g}/\text{m}^3] \div \text{molecular weight}) \times 1000 \end{aligned}$$

After preliminary analysis, all data were centered around the mean and dividing by the standard deviation so that their relative magnitudes would be similar. Heat maps were used to identify possible patterns by location. Finally, three multivariate approaches were employed to identify possible patterns of elemental mass fractions by location and/or time. The first approach, hierarchical cluster analysis, was used to assess the similarities and differences between elements. The second approach was self-organizing maps (SOMs). The SOM algorithm is an efficient means of interpreting and visualizing complex data sets; the 'map' facilitates understanding of between-class relationships [19]. Thirdly, partial least-squares discriminant analysis (PLS-DA) was used to identify potential patterns in element composition between the sites. Statistical analyses were conducted with R [20] and MetaboAnalyst 4.0 [21].

Results

Proof-of-concept

In answer to the initial question: *Which elements are detectable on the PM filter media and what are their mass fractions?* A total of 44 element isotopes were assessed. These include: ${}^7\text{Li}$, ${}^9\text{Be}$, ${}^{11}\text{B}$, ${}^{24}\text{Mg}$, ${}^{27}\text{Al}$, ${}^{29}\text{Si}$, ${}^{31}\text{P}$, ${}^{34}\text{S}$, ${}^{43}\text{Ca}$, ${}^{44}\text{Ca}$, ${}^{47}\text{Ti}$, ${}^{51}\text{V}$, ${}^{52}\text{Cr}$, ${}^{55}\text{Mn}$, ${}^{56}\text{Fe}$, ${}^{59}\text{Co}$, ${}^{60}\text{Ni}$, ${}^{63}\text{Cu}$, ${}^{64}\text{Zn}$, ${}^{66}\text{Zn}$, ${}^{75}\text{As}$, ${}^{78}\text{Se}$, ${}^{79}\text{Br}$, ${}^{85}\text{Rb}$, ${}^{88}\text{Sr}$, ${}^{90}\text{Zr}$, ${}^{95}\text{Mo}$, ${}^{101}\text{Ru}$, ${}^{103}\text{Rh}$, ${}^{105}\text{Pd}$, ${}^{111}\text{Cd}$,

^{118}Sn , ^{121}Sb , ^{127}I , ^{133}Cs , ^{137}Ba , ^{138}Ba , ^{195}Pt , ^{202}Hg , ^{205}Tl , ^{208}Pb , ^{209}Bi , ^{232}Th , and ^{238}U . However, ^{11}B , ^{90}Zr , ^{101}Ru , ^{103}Rh , ^{105}Pd , ^{127}I , ^{195}Pt , and ^{205}Tl were excluded from the final data analyses; those elements were not quantified in the NIST calibrant SRM 2584. Data are presented as mass fractions with units in mg/kg (Supplementary Table 2).

Filter homogeneity

One important aspect of this LA-ICP-MS technique is the fact that the laser line (sampled from the center of the filter) represents approximately 0.002% of the filter area (Supplementary Fig. 2). Hence it is important to assess heterogeneity across the large (2 cm \times 2 cm) filter samples used. Subtle differences in the particle loading across specific areas of the filters or hotspots of unique particles might influence sample homogeneity, thus eight other locations on loaded and blank filters were assessed (total $n = 9$ for each type of filter sample). We then assessed the signal-to-background (S/B) ratios and mass fraction variability (Supplementary Fig. 3). Ideal elements with high S/B and low spatial mass fraction variation (under 30% relative at 95% confidence level) were Cu, P, Mo, Th, Ti, Sb, Mn, I, Tl, S, Co, Br, Be and Bi. Some elements were more challenging to measure due to low S/B and also due to the nature/composition of the blank filters. Such elements included Ca, Ba, B, Mg, Se, Si, As, and Zn. Nevertheless, this assessment ensured that the sampling area was standardized close to the center of the filters.

Summary statistics

Daily air pollution summaries generated by federal reference method (FRM) air monitoring techniques suggest that regional air quality was generally good at the three sites during the study year. Over the course of 2011, the average \pm standard deviation (sd) reported for $\text{PM}_{2.5}$ were $11.2 \mu\text{g}/\text{m}^3 \pm 5.7 \mu\text{g}/\text{m}^3$ and $11.7 \mu\text{g}/\text{m}^3 \pm 5.5 \mu\text{g}/\text{m}^3$ for the North and Middle regions, respectively. $\text{PM}_{2.5}$ mass concentrations are not measured at the Southern site. PM_{10} mass concentrations were $15.9 \mu\text{g}/\text{m}^3 \pm 6.5 \mu\text{g}/\text{m}^3$, $17.1 \mu\text{g}/\text{m}^3 \pm 7.7 \mu\text{g}/\text{m}^3$, and $18.2 \mu\text{g}/\text{m}^3 \pm 7.6 \mu\text{g}/\text{m}^3$ for the North, Middle and Southern regions respectively. High levels of calcium were consistent across all three sites. Mean \pm sd ^{44}Ca mass fractions were $304.7 \text{ mg}/\text{kg} \pm 244.7 \text{ mg}/\text{kg}$, $242.2 \text{ mg}/\text{kg} \pm 365.7 \text{ mg}/\text{kg}$ and $251.8 \text{ mg}/\text{kg} \pm 244.5 \text{ mg}/\text{kg}$ at the Northern, Middle and Southern sites respectively (Supplementary Table 2). Beryllium had the lowest mass fractions at all three sites, and the 99th percentile was $0.01 \text{ mg}/\text{kg}$. ^{202}Hg , ^{232}Th and ^{121}Sb were detected in 100% of all samples.

Comparison with CSN data

The middle site is the only location with CSN data for the whole of South Carolina. As such, to answer the second question of interest (*how do these elements compare with those measured in the Chemical Speciation Network?*), data from the middle site only are compared with the CSN data for 2011. While there are about 50 inorganic elements assessed in the CSN, the current study had 28 elements in common. As this was a case study, the elements characterized were selected *a priori* to show proof of concept in identifying inorganic element mixtures on TSP filters (Supplementary Table 3, 5 elements were novel, while 21 elements routinely measured for the CSN were not assessed in this study). A total of 15 elements had enough variation for subsequent comparisons (Supplementary Table 3) and seven correlation analysis were statistically significant ($p < 0.05$, Fig. 2). Silicon was

marginally significant ($p = 0.24$, $p = 0.085$, Fig. 2G), as were calcium (both isotopes) and strontium ($p < 0.1$, data not shown). Additionally, results for Spearman ranked correlation coefficients between CSN data (mg/kg) and LA-ICP MS data (mg/kg) and their statistical significance remained unchanged.

Preliminary data analysis and correlations

Non-parametric (Kruskal–Wallis) analysis was employed to test for differences in median elemental mass fractions at the three sampling sites. Results (chi square statistic and p value) reveal that 20/36 elements were significantly different between sites. Specifically, ^{63}Cu ($X^2 = 43.8$ $p < 0.0001$), ^{95}Mo ($X^2 = 16.1$ $p = 0.0003$), ^{79}Br ($X^2 = 38.2$ $p < 0.0001$), ^{202}Hg ($X^2 = 13.3$ $p = 0.001$), ^{47}Ti ($X^2 = 21.3$ $p < 0.0001$), ^{137}Ba ($X^2 = 20.8$ $p < 0.0001$), ^{138}Ba ($X^2 = 19.9$ $p < 0.0001$), ^{85}Rb ($X^2 = 17.5$ $p = 0.0002$), ^{121}Sb ($X^2 = 16.3$ $p = 0.0002$), ^{118}Sn ($X^2 = 12.6$ $p = 0.002$), ^{111}Cd ($X^2 = 11.7$ $p = 0.003$), ^{29}Si ($X^2 = 9.4$ $p = 0.009$), ^{59}Co ($X^2 = 7.6$ $p = 0.02$), ^7Li ($X^2 = 10.9$ $p = 0.004$), ^{51}V ($X^2 = 24.1$ $p < 0.0001$), ^{60}Ni ($X^2 = 10.9$ $p = 0.004$) did not have identically shaped distributions when the ranked scores were examined per site. The median mass fractions of the aforementioned elements differed significantly at the three locations.

Correlation analysis revealed strong relationships between some pairs of elements in terms of their mass fractions. Strong correlations emerged between Ni–V ($r = 0.82$), Mn–Fe ($r = 0.80$), Fe–V ($r = 0.82$), Fe–Cr ($r = 0.82$), V–P ($r = 0.92$), V–Cr ($r = 0.94$), P–Cr ($r = 0.96$), Zn–Rb ($r = 0.85$) and Rb–Sr ($r = 0.94$). These were all significant at $p < 0.0001$. Other notable correlations occurred between Co–Ti, Cd–Br, Ca–Cs, Zn–Mn, K–Zn, Al–V, Si–Cr, Pb–Bi, U–Li, and Bi–Ca. These were also significant at $p < 0.05$.

Machine learning approaches

To address the third question of interest (*Are there combinations (or mixtures) of elements that occur together over space and/or time?*), three approaches were employed. The first was hierarchical clustering, and the result of this approach is seen in Fig. 3. This first approach points to four distinct clusters of elements by sample location throughout the year. Cluster 1 contains ^{29}Si , ^{24}Mg , ^{43}Ca , ^{44}Ca , ^{209}Bi , ^{238}U , ^{232}Th , ^{34}S , ^9Be , and ^{133}Cs which are significantly lower at the middle site. Cluster 2 contains ^{55}Mn , ^{59}Co , ^{75}As , ^{27}Al , ^{85}Rb , ^{78}Se , and ^{111}Cd which had relatively similar mass fractions across all three sites. Cluster 2 also contains ^{60}Ni which was highest at the Southern site, as well as ^{52}Cr , ^{208}Pb , ^{31}P , ^{56}Fe , ^{66}Zn , ^{88}Sr , ^{51}V and ^{64}Zn which were lowest at the Northern sites compared to the two other sites. Cluster 3 contains ^{63}Cu , ^{202}Hg and ^{79}Br which were highest at the Middle site. Cluster 4 contains ^{138}Ba , ^7Li , ^{47}Ti , ^{95}Mo , ^{118}Sn , ^{121}Sb and ^{137}Ba which were lowest at the Southern site and higher at the Northern site. This first approach takes all measured elements into consideration.

In the second approach to addressing Q3 (*Are there combinations (or mixtures) of isotopes that occur together over space and/or time?*), a 2×2 self-organizing map (SOM) was applied to identify categories that capture the primary temporal ‘patterns’ observed in the data (Fig. 4A). For each SOM category, patterns are presented as profiles depicted with line graphs

that reflect the median element mass fraction on a scaled y-axis. The SOM coordinates are on the top and right panels, shaded gray [x,y].

Profile [0,0; orange] in the upper left of the map included 27% of observations. This profile identifies ambient PM conditions during this study when all element levels were relatively low (close to their median mass fractions). This mostly occurred at the Southern site (45% of the time, compared to 16% and 21% at the Northern and Middle sites respectively (data not shown)). Profile [1,0; blue] in the upper right of the map, with a relatively low frequency of occurrence (23% of the time), identifies ambient PM conditions with relatively high measurements for most of the elements. Profile [1,0] was more prevalent at the Middle site (54%) compared to the Northern (30%) or the Southern (26%) sites. The bottom right profile [1,1; purple] occurred about 37% of the time and was the most common profile. It represents ambient PM conditions where less than half of the elements had relatively high measurements compared to median values. The final profile [0,1; green], in the bottom left corner, captures the lowest (12.1%) occurrence of ambient PM conditions where only some element levels were slightly higher than their median mass fractions. Both profile [0,1] and [1,1] were more common at the Northern site. Collectively, these profiles characterize the range of ambient PM element conditions experienced at the three sites within the same state.

To assess how these identified SOM profiles occurred across the year 2011 in the state of South Carolina, we examined the frequency of each SOM profile by time (Fig. 4B–D). Here we used histograms to illustrate how often a particular profile persisted in time at the three locations. All four profile types were seen at each site, however, there was pronounced seasonal dependence. During certain months we see greater distinctions among locations. For example, we see that profile [0,1] most often occurred at the Middle site throughout the year, but this was not the case at the other two sites. Profile [0,0], however, occurred more at the Southern site throughout the year. In fact, the Southern site was the only site with profile [0,0] between the months of October [10] and December [12], compared to the Northern or Middle sites. These findings suggest variability in PM may be more complex than what is traditionally presented using measured $PM_{2.5}$ mass concentrations only.

The final approach uses partial least-squares discriminant analysis (PLS-DA) to create ‘fingerprints’ for each site. The PLS-DA uses the information from all elements to discriminate between the three sites, reducing the high-dimensional data across elements into a selection of composite scores to be used as elemental “fingerprints” (Fig. 5). The variable importance in projection (VIP) scores generated by PLS-DA provide information about which elements contribute most to discriminating between sites as well as site differences. This approach identifies elements that are relatively high at one site compared to the other two sites for easy pattern recognition.

One potential avenue through which these elemental fingerprint data can inform the public is through the US EPA’s Air Quality Index (AQI). In Fig. 6, we compare our LA-ICP-MS derived data with the EPA AQI values for year 2011 in South Carolina. Data from this study had 3 categories/colors ranging from good (green), moderate (yellow) and unhealthy for sensitive groups (orange). A tri-element model, termed LA-ICP-MS AQI (green) with strontium (Sr), barium (Ba) and thorium (Th), had a similar trend as the federally reported

EPA AQI (purple) for the Northern site in SC. These three elements were used to display the potential usability of the LA-ICP-MS technique for understanding local air quality since CSN data are available for only one site (middle site) and not for all other air quality monitoring sites in South Carolina. The equation at the top of the graph depicts the model used to calculate the 'LA-ICP-MS AQI'. This suggests that local ambient air quality could potentially be predicted using element mass fraction data obtained with the LA-ICP-MS technique.

Discussion

In this study, we aimed to improve understanding of how an automated LA-ICP-MS technique can be used to assess elements on airborne TSP filters from three sites in South Carolina. To achieve our objective, we sought to answer three questions: (Q1) *What types of different elements occur on the PM media and what are their mass fractions?* (Q2) *how do these elements compare with those measured in the Chemical Speciation Network* (Q3) *Are there combinations (or mixtures) of isotopes that occur together over space and/or time?*

In answer to Q1, we identified a total of 44 isotopes, and 36 were used in subsequent statistical analysis. A few elements, (e.g. Beryllium) had low mass fractions at all three sites, while, most had median mass fractions as low as 0.01 mg/kg and as high as 652 mg/kg. This suggests the ability to assess multiple elements over a wide range of limits of detection (LOD) is a potential capability of this LA-ICP-MS tool that can prove useful when trying to identify differences in particle compositions beyond PM mass concentrations. Compared to other techniques such as X-Ray Fluorescence (XRF), far lower limits of detection in the range of 0.01 $\mu\text{g/g}$ – 1 $\mu\text{g/g}$ can be reached with the LA-ICP-MS, and a broader range of elements can be quantified for elemental signature identification purposes [22].

In answer to Q2, seven of the elements assessed with LA-ICP-MS technique correlated with CSN data available at one of the sites. Lack of variation in data prevented comparisons of other elements and future studies will focus only on elements currently measured in the CSN. Nonetheless, these results are consistent with others who have assessed a variety of elements on airborne PM filter media [23,24]. Our approach with the automated laser ablation ensured that there was minimal sample preparation and simultaneous multi-element analyses that was achieved within minutes. As demonstrated in this case study, this strategy can significantly enhance researchers' ability to rapidly quantify elements, particularly metals, that may be bound to particulate matter.

To answer Q3, we employed three machine learning approaches – namely hierarchical clustering, self-organizing maps (SOMs) and Partial Least-Squares Discriminant Analysis (PLS-DA). We found out that these approaches are useful for discovering the types of profiles within our data, their frequency of occurrence, and their duration – all of which are features of interest when characterizing exposures. Overall, the results are consistent with knowledge of particulate matter behavior in urban environments [25–28] and support the opportunity to distinguish air quality differences beyond traditional PM mass measurements [29,30]. These results may prove useful in future assessments of potential air quality trends within the state of South Carolina, as well as at other national and international sites [31].

The multi-element approach taken in this study has great potential to add to the debate on shifting from single source (“stressor”) studies to multiple source identification studies [32]. This is because, methodologies that assign specific constituents to sources often face the challenge that any individual PM constituent could originate from a variety of sources. A look in the scientific literature points to a variety of sources for the elements detected in our study. Hierarchical clustering across the sites in our study found that ^{29}Si , ^{24}Mg , ^{43}Ca , ^{44}Ca and ^{209}Bi , ^{238}U , ^{232}Th , ^{34}S , ^9Be , ^{133}Cs clustered together and these represent sources such as the earth’s crust and the industrial processes, such as cement and marble industries [23]. For instance Cs has been linked with the erosion and weathering of rocks and minerals and as well as the fly ash from waste incinerators and coal burning power plants [33].

Secondly, ^{55}Mn , ^{59}Co , ^{75}As , ^{27}Al , ^{85}Rb , ^{78}Se , ^{111}Cd , ^{60}Ni , ^{52}Cr , ^{208}Pb , ^{31}P , ^{56}Fe , ^{66}Zn , ^{88}Sr , ^{51}V and ^{64}Zn were clustered together and are mostly attributed to excavation activities, biomass burning, re-suspended soil dust, and automobile emissions. Ni and Cr, have also been specifically associated with crude oil combustion and metal processing activities [23]. Arsenic is associated with fossil fuel combustion (could be from traffic, power stations, refineries and chemical industries) [34]. Nickel was highest at the Southern site. Sources of nickel include industry, the use of liquid and solid fuels, as well as municipal and industrial waste [35].

^{63}Cu , ^{202}Hg and ^{79}Br also clustered together and point to sources such as coal combustion and to some extent cement processing. Cu has been reported in emissions from cement plants [33]. Hg is associated with coal combustion [36]. Br has been linked to coal burning in rural households as well as the photolysis of Br_2 and BrCl with ultra-violet light [37]. In our study, ^{63}Cu was relatively high in the middle of South Carolina (Middle site; Cluster 3 on left, white in heatmap, Fig. 3), and this could be mostly due to copper smelting activities near the sampling site. However, further studies are needed to assess whether this trend holds from year to year and how this may impact health.

Lastly, ^{138}Ba , ^7Li , ^{47}Ti , ^{95}Mo , ^{118}Sn , ^{121}Sb and ^{137}Ba , which are mostly from traffic-related sources grouped together. Specifically, antimony and barium are considered to be tracer elements for traffic emissions sources [38]. Molybdenum is associated with the combustion of fossil fuels and the use of Mo compounds as lubricants for vehicle maintenance [39]. Titanium originates from a variety of industrial processes, manufacturing and even the production and use of titanium nanoparticles [40]. Potential sources of Li include automobile emissions and road dust [23].

Qualifying the potential contribution of various sources (among and within the 4 identified clusters) adds to the novelty of our work. Multi-elemental air pollution exposures from a variety of sources are still poorly understood [41]. Recent evidence shows that associations between $\text{PM}_{2.5}$ exposures and respiratory hospitalizations in children can be differentially modified by the metal content (along with sulfur content and particle oxidative potential) in airborne particulates. Specifically, data from a case-crossover study of 10,500 children across Canada reported an odds ratio of 1.084 (95% confidence interval: 1.007–1.167) per $10\ \mu\text{g}/\text{m}^3$ increase in fine PM when copper was above the median mass concentration [42]. Rule and Koehler [41] have called for the prioritization and incorporation additional

constituents in studies to better understand the health effects of PM given the common sources, correlations among the constituents and variations in time and space. Indeed, the current study adds to the growing body of evidence that there is a need to shift from single-stressor studies to a “real-world” approach of assessing different sources and types of particulate air pollution collectively.

Lastly, we used our data to evaluate the EPA’s air quality index and found that the LA-ICP-MS technique can potentially inform local air quality. Living in “unmonitored” areas, and a general quest for improved air quality knowledge are noted as two of the major goals for conducting air quality studies in communities [43]. Yet even when such goals are achieved, interpreting and communicating the data remain challenging [44]. Presumably, the best elements predicting the AQI will be different at each location and/or season and that could provide useful information on which elements may be driving air quality in a locale, as opposed to the mass of the particulates.

Our study, like all others, is subject to limitations. One limitation is the relatively short duration of our filter data (one year [2011] only), as longer periods are suggested to better understand differences between monitoring sites. As such, the differences presented here cannot be used to infer that longer term differences exist at the monitoring sites studied. A common challenge for these types of studies is the validity of the data as our data were collected using total suspended particulates rather than PM_{2.5} or PM₁₀ filters. Our reported data are generally consistent with PM_{2.5} and PM₁₀ mass concentrations reported by EPA during this time frame. Another limitation of our study was the lack of calibration and reference materials. Certainly, new calibration and reference materials are needed to better match the matrix of the filter material. Additionally, there is a need for suitable elements that may be useful as internal standards for the filters. For example, an element like Ca could be used (e.g. for a bone or tooth sample, where the composition is relatively constant, But for the filter types studied here, there seems to be significant variability for some of the elements that could potentially be investigated for use as internal standards. Finally, the representativeness of the laser micro sampling could be a shortcoming, but the analyses are relatively fast and so across filter averaging could be performed. A suitable comparison to solution-digested filters using traditional methods needs to be evaluated to fully assess the applicability of the technique. Future directions of this work will aim will include extended time periods and using enhanced filter samples that include other sites and other pollutants; and development of air pollution epidemiologic studies that can be used to explore associations between high-resolution air pollution data and health outcomes.

Conclusion

With only one air quality site with elemental composition data in South Carolina, there is currently an incomplete picture of ambient PM constituents across both space and time for the state. To assist, we sought to acquire PM mixtures data by adopting an automated laser ablation technology to analyze total suspended particulate matter filters collected at three different sites in South Carolina. The study assessed trace element mass fractions, and trends over time and space after adjustments with blank filters and NIST SRMs. We found out that assessing different trace elements may provide useful information on which combinations

(or mixtures) occur together over space and/or time. Such information can be helpful in planning effective counter measures and strategies to control particulate air pollution.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data availability statement

Data are available at <https://github.com/exposurelabiu/Laser-Ablation-Data.git>. Please contact S. Commodore or S. Christopher for further information.

Abbreviations:

US EPA	United States Environmental Protection Agency
LA-ICP-MS	Laser ablation Inductively coupled plasma mass spectrometry
TSP	total suspended particulates
CSN	Chemical Speciation Network

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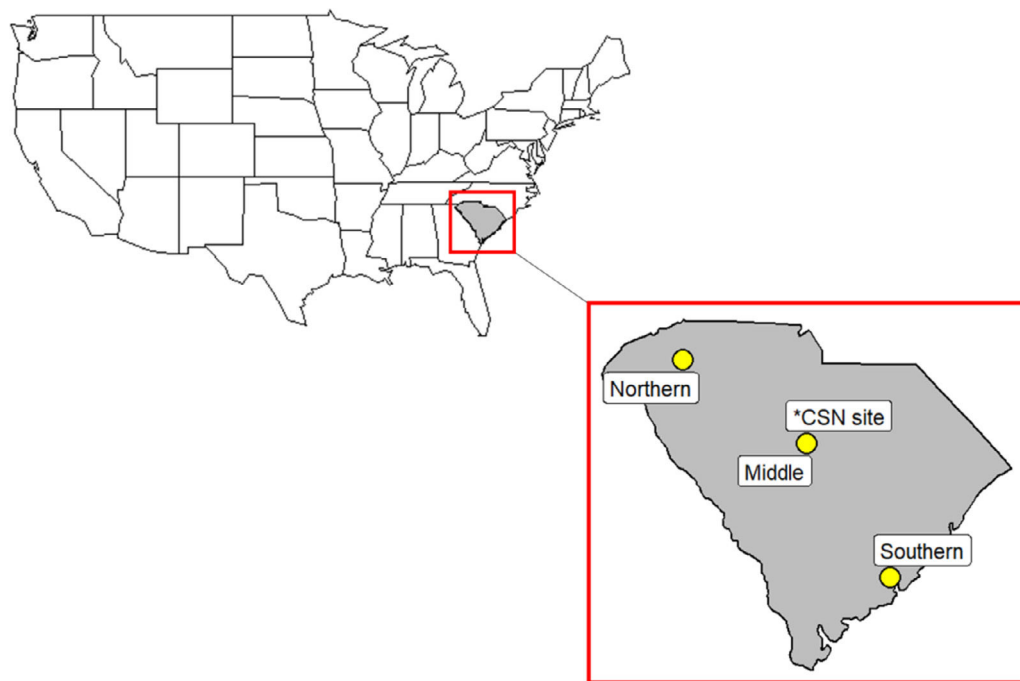


Fig. 1. Map of the state of South Carolina, USA showing the three air sampling locations, from which filter media were used for this case study. The only United States Environmental Protection Agency Chemical Speciation Network (CSN) site in the state is also shown with the asterisk, and is at the middle site.

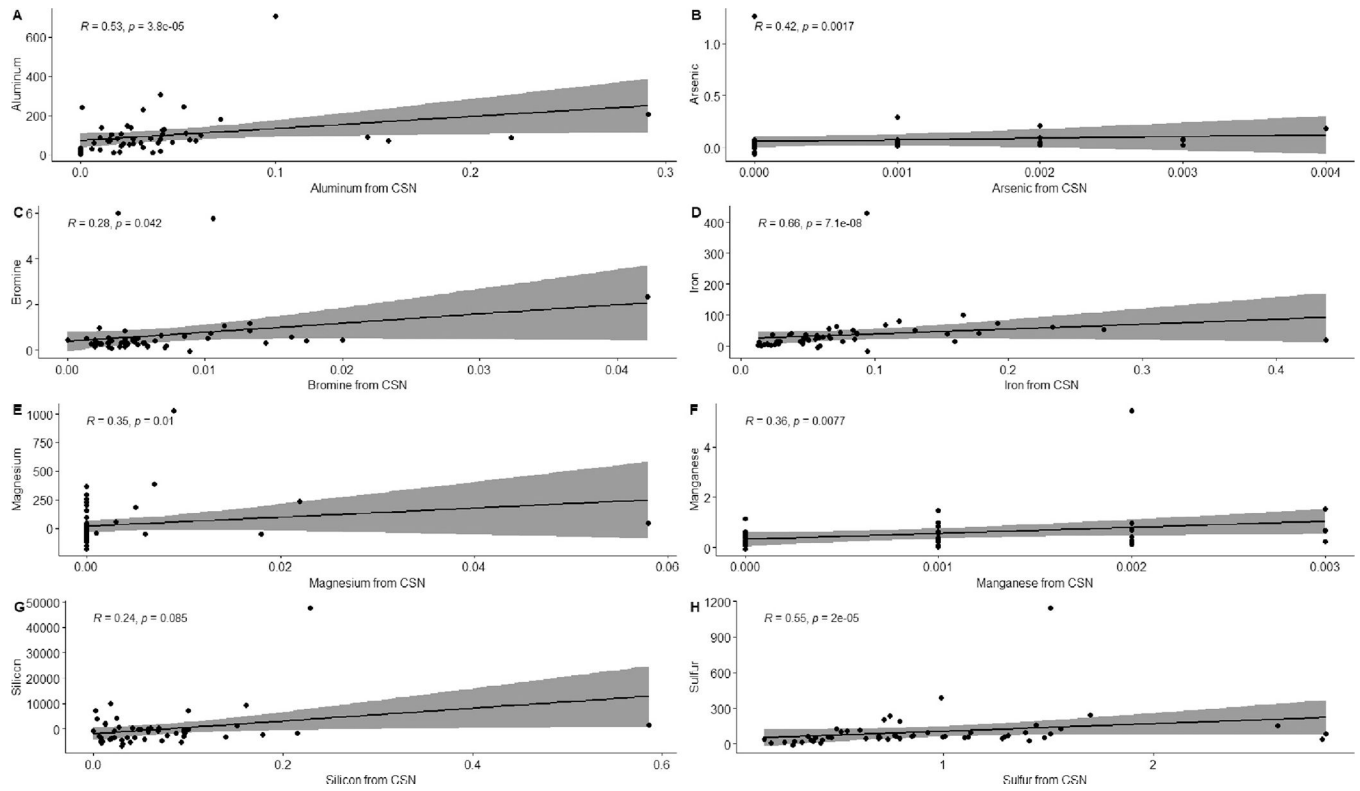


Fig. 2. Spearman ranked correlations between Chemical Speciation Network (CSN) elements with elements assessed in the current study. LA-ICP-MS data are on the y axis and CSN data are on the x axis.

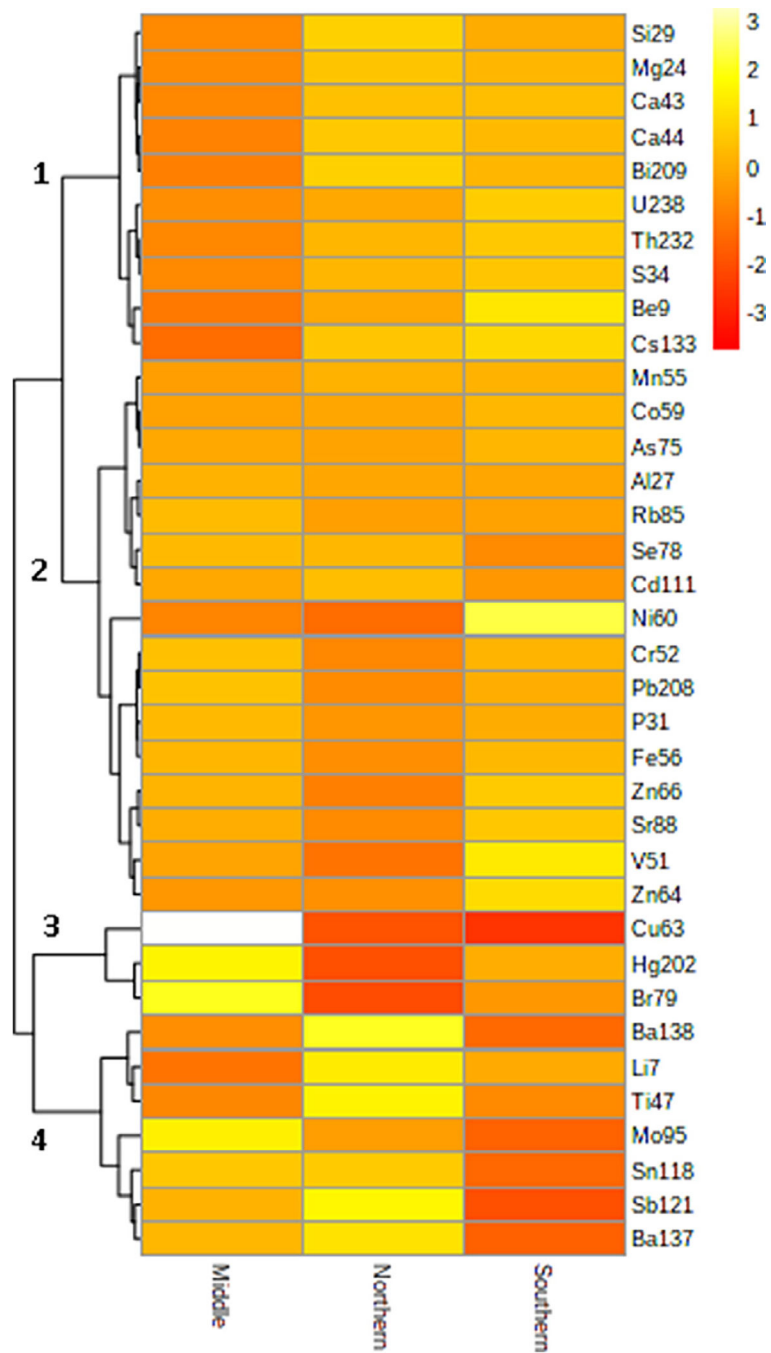
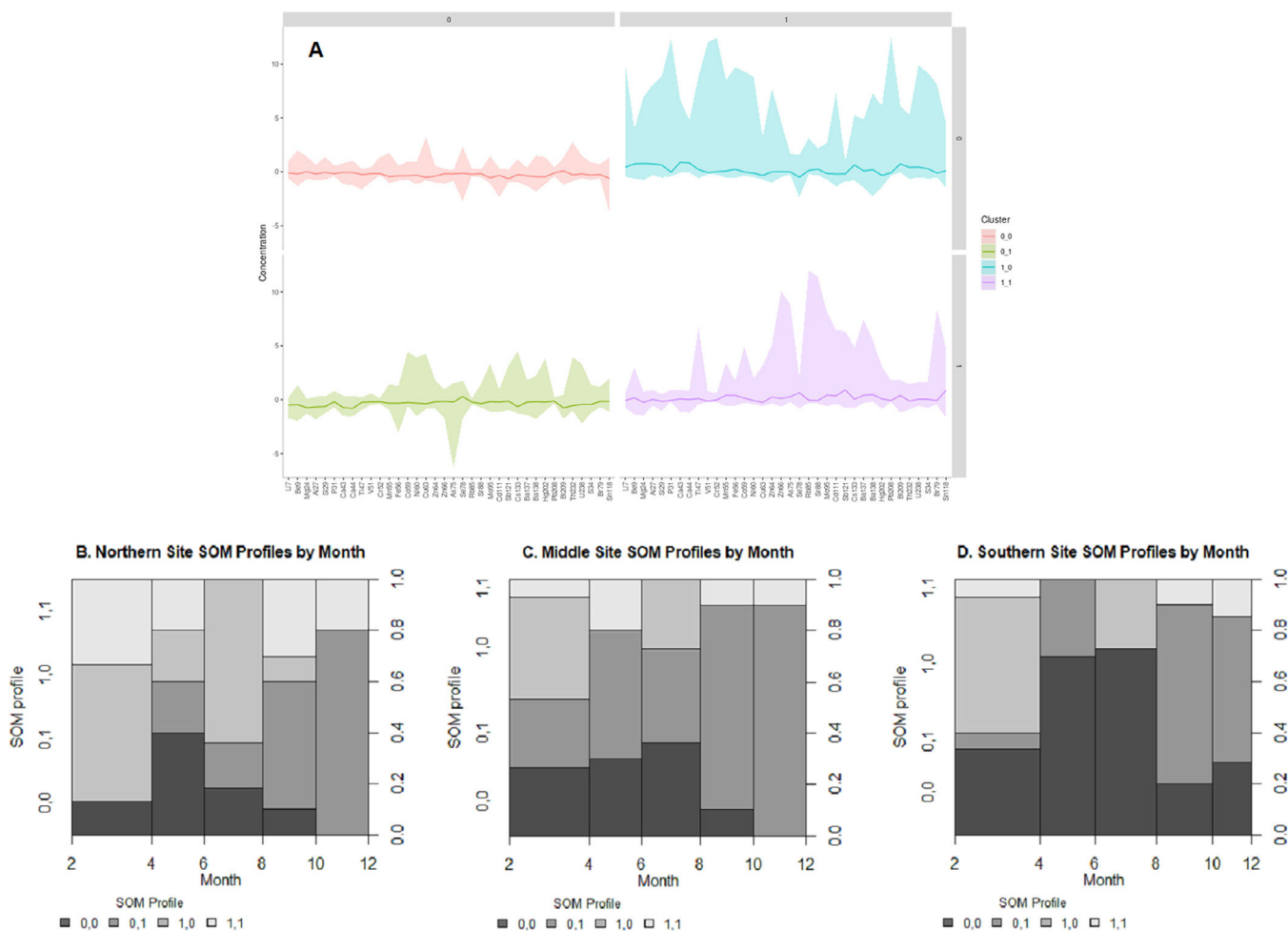


Fig. 3. Heat map with cluster analysis of particulate matter species at three locations in South Carolina. Lighter colors in heatmap represents high relative mass fractions while darker colors are lower relative mass fractions.

**Fig. 4.**

Panel A is a 2×2 self-organizing maps (SOM) depicting element mass fraction profiles observed for the state of South Carolina in 2011. For each profile type, the plots reflect the standardized elemental mass fraction on a percentage scale with zero reflecting the median on the y-axis. Darker lines represent median intensities of each cluster. The SOM coordinates are in brackets [x,y]. Panels B, C and D show when the SOM profiles, identified in panel A, occur throughout the year and by location. Profile 0,0 for instance occurred more at the Southern site throughout the year (particularly between the months of October [10] and December [12], compared to the Northern or Middle sites).

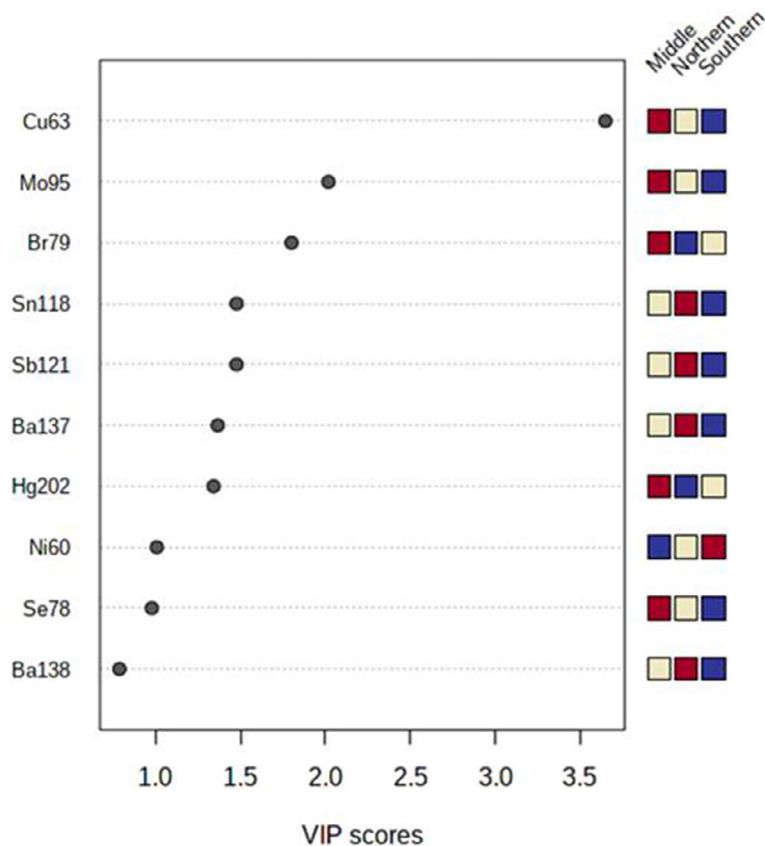


Fig. 5.

Results of partial least squares discriminate analysis (PLS-DA). PLS-DA uses the mass fraction information from all elements to discriminate between the three sites. The variable importance in projection (VIP) scores provide information about which elements contribute most to discriminating between sites. The figure shows important classifier elements, and site differences. The squares denote each of the three sites. The red, yellow and blue colors in the boxes denote highest, average and lowest mass fractions respectively at a particular site for that element. Cu, Mo, Br, Hg and Se emerge as important classifier elements, and point to a unique ‘fingerprint’ for the Middle site due to their relatively high mass fractions compared to the Northern or Southern sites. Only the first 10 isotopes from the analysis are displayed.

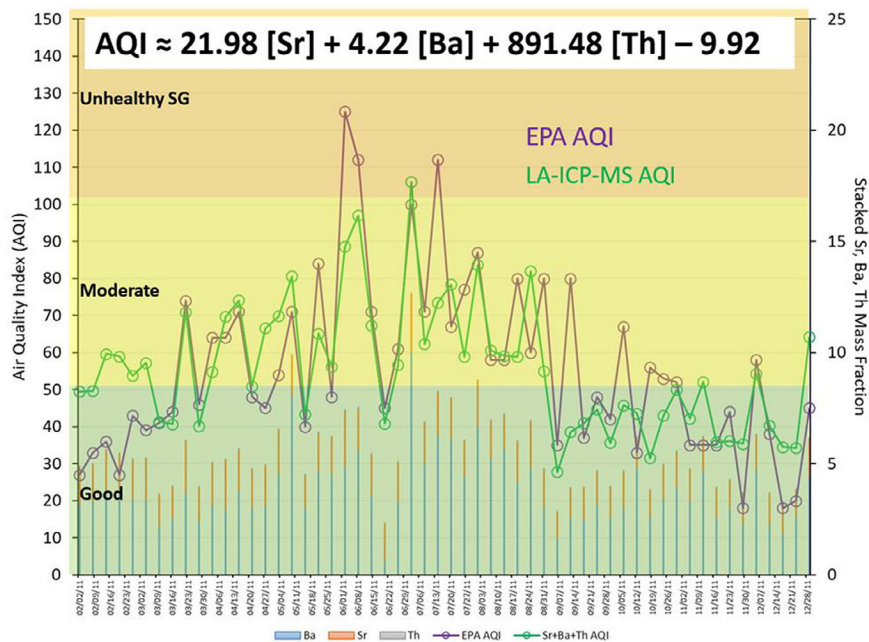


Fig. 6. One potential way to translate these data into publicly understandable measures include using LA-ICP-MS data to construct an Air Quality Index (AQI). Green = linear model LA-ICP-MS AQI with Sr, Ba and Th and purple = federally reported EPA AQI for the Northern part of South Carolina in 2011.