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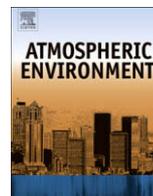
Estimating the contribution of point sources to atmospheric metals using single-particle mass spectrometry

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ABSTRACT

Single-particle mass spectra were collected using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) during December of 2003 and February of 2004 at an industrially impacted location in East St. Louis, IL. Hourly integrated peak areas for twenty ions were evaluated for their suitability in representing metals/metalloids, particularly those reported in the US EPA Toxic Release Inventory (TRI). Of the initial twenty ions examined, six (Al, As, Cu, Hg, Ti, and V) were found to be unsuitable due to strong isobaric interferences with commonly observed organic fragments, and one (Be) was found to have no significant signal. The usability of three ions (Co, Cr, and Mn) was limited due to suspected isobaric interferences based on temporal comparisons with commonly observed organic fragments. The identity of the remaining ions (Sb, Ba, Cd, Ca, Fe, Ni, Pb, K, Se, and Zn) was substantiated by comparing their signals with the integrated hourly signals of one or more isotope ions. When compared with one-in-six day integrated elemental data as determined by X-ray fluorescence spectroscopy (XRF), the daily integrated ATOFMS signal for several metal ions revealed a semi-quantitative relationship between ATOFMS peak area and XRF concentrations, although in some cases comparison of these measurements were poor at low elemental concentrations/ion signals due to isobaric interferences. A method of estimating the impact of local point sources was developed using hourly integrated ATOFMS peak areas, and this method attributed as much as 85% of the concentration of individual metals observed at the study site to local point sources. Hourly surface wind data were used in conjunction with TRI facility emissions data to reveal likely point sources impacting metal concentrations at the study site and to illustrate the utility of using single-particle mass spectral data to characterize atmospheric metals and identify point sources.

1. Introduction

Although a considerable fraction of metals observed in the atmosphere are of natural origin, from sources including wind blown dust, sea spray, and emissions from volcanoes and forest fires (Allen et al., 2001), emissions from industrial processes, mobile sources, and power generation can result in the release of large quantities of metals and metal containing compounds to the atmosphere, particularly in urban environments (Espinosa et al., 2001; Okuda et al., 2004; Ho et al., 2006; Morishita et al., 2006). The presence of metals in the atmosphere is of concern due to the health risks associated with exposure to toxic metals and metal containing compounds known to be carcinogens and neurotoxins. In addition, it is suspected that metals contained in ambient aerosols may be

a cause of adverse health impacts associated with exposure to elevated levels of fine particulate matter (Pritchard et al., 1996; Carter et al., 1997; Adamson et al., 2000; Prieditis and Adamson, 2002; Heal et al., 2005). The presence of metals can also impact atmospheric chemical processes; for example, laboratory studies have suggested that iron may be involved in the formation of humic-like substances in the atmosphere through Fenton reactions (Gelencser et al., 2003). Similarly, the introduction of metals into aquatic systems can have considerable impacts on the biogeochemistry of these systems (Jickells, 1995; Baker et al., 2003), and the deposition of atmospheric metals to surface waters has been shown to be a primary path by which some toxic metals are introduced into the food web (Hammerschmidt and Fitzgerald, 2006).

Traditional methods of observing metals in the atmosphere involve the collection of particulate matter onto substrates and subsequent sample analysis in the laboratory, which can be accomplished via a variety of methods including inductively-coupled plasma-mass spectroscopy (ICPMS), instrumental neutron

activation analysis (INAA), particle-induced X-ray emission (PIXE), and X-ray fluorescence spectroscopy (XRF). These methods have dramatically improved our understanding of the trace metal content of ambient aerosols; however, a substantial amount of mass must be collected in order to use these methods, often resulting in lengthy sample collection times. While 24-h filter-based observations have been routinely used in conjunction with statistical source apportionment methods, such as chemical mass balance (CMB) approaches and positive matrix factorization (PMF), it is difficult to integrate these models with meteorological data to identify the impact of individual point sources due to the low time-resolution of the input data. In addition, considerable uncertainty persists concerning the results of these models due to the sensitivity of CMB models to the types and composition of source profiles used (Lee and Russell, 2007) and the sensitivity of PMF models to measurement uncertainty (Christensen and Schauer, 2008).

In contrast with filter-based analytical techniques, the development of real-time aerosol mass spectrometry has resulted in the ability to obtain high time-resolved particle composition data. In particular, the laser-desorption/ionization method used by the Aerosol Time-of-Flight Mass Spectrometer (ATOFMS), in which a large amount of energy is directed into a single particle, is ideal for generating ions from a wide variety of chemical components, including metals, salts, elemental carbon/soot, and organic compounds (which might be fragmented). While the desorption/ionization method is complex and not fully understood, due to matrix effects which depend on the unique components of each particle, it is among the very few techniques that can be used to study a variety of metals/metalloids in particles in real time. Although other high time-resolved methods of studying metals in particles are currently in use or in development, e.g. Kidwell and Ondov (2001, 2004), Rastogi et al. (2009), these techniques are only able to identify the water-soluble or acid-leachable fraction of metals in aerosols whilst the ATOFMS is capable of identifying a wide of array of metals directly and without regard to their solubility or oxidation state.

The use of single-particle mass spectral data is complicated by the need to process a tremendous amount of data (instruments such as the ATOFMS are capable of producing hundreds of unique particle spectra each hour). Examination of these huge data sets is often aided by the use of statistical clustering techniques, such as k-means clustering (MacQueen, 1967; Lloyd, 1982) or the use of the ART-2a neural network algorithm (Carpenter et al., 1991). While it is generally recognized that such techniques work well to classify particles according to the major chemical components found in ambient aerosols, they perform poorly with regards to categorizing particles according to their metal content as metals often represent a minor fraction of the single-particle signal and tend to get incorporated into classes characterized by more abundant components (Tolocka et al., 2004).

In this work, we present a method for estimating the impact of local point sources on the concentrations of metals/metalloids observed in ambient particulate matter using single-particle measurements. Our objective is to present a straightforward and transparent source apportionment and source identification tool for ambient metals/metalloids that relies on direct examination of the ATOFMS signal and not the output of complex statistical models. While, as is demonstrated in this work, there are some uncertainties associated with the identification of specific elements due to isobaric interferences (organic or inorganic fragments that have the same mass-to-charge ratio as the elements of interest), direct examination of the data affords the opportunity to identify these interferences in order to avoid errors in species identification and examine time periods in which these interferences appear to be minimal. The methods presented here provide a framework for understanding the impact of local sources on metals concentrations in industrially impacted environments where differentiating between individual point sources, area sources, and regional sources is particularly challenging. Furthermore, the nature of the techniques employed lend themselves to broad use amongst regulators and investigators and the potential for inclusion in data processing software, which are currently challenges for more sophisticated analytical techniques.

2. Experimental

2.1. Study site

Atmospheric observations pertinent to this study occurred at the US Environmental Protection Agency (EPA) funded St. Louis-Midwest Fine-Particle Supersite during December of 2003 and February of 2004. The site is located in a residential/light commercial neighborhood of East St. Louis, IL approximately 3 km east of downtown St. Louis, MO and is impacted by emissions from numerous point sources located along an industrial corridor bordering the Mississippi River. Specific sources impacting the study site include manufacturing operations and both primary and secondary metals processing facilities.

2.2. Aerosol Time-of-Flight Mass Spectrometer

An Aerosol Time-of-Flight Mass Spectrometer (ATOFMS – TSI, Shoreview, MN, model 3800) was operated at the East St. Louis site in December 2003 and February 2004. The ATOFMS is a single-particle mass spectrometer that samples particles from ambient air through a converging nozzle inlet at 0.9 L min^{-1}. The instrument was housed in a heated trailer, and the inlet was connected to a 3/8 inch diameter copper tube that was run through the roof directly above the instrument. Although no specific tests were run to check for leaks or contamination from the use of a copper inlet, numerous published papers indicate that such problems are not typically observed. The copper sampling line that was within the trailer was surrounded by a 3 inch diameter flexible duct which was connected to a biscuit fan just above the connection to the instrument. The fan pulled ambient outside air as a sheath around the sampling line, thus maintaining the particles at near-ambient temperature until they were sampled into the ATOFMS.

Details of the operation of the ATOFMS are available elsewhere (Prather et al., 1994, 1996) and will only be described briefly here. The particles are introduced into the instrument through a converging nozzle where they are accelerated to a velocity that is inversely related to their vacuum aerodynamic diameter. Particles then are directed through two differentially pumped regions and into a particle sizing region where they are detected by two orthogonal (to each other and the particle beam) 50 mW continuous-wave diode-pumped Nd:YAG lasers (Crystalaser, Reno, NV). Scattered light is focused with ellipsoidal mirrors to photomultiplier tubes oriented orthogonally to the lasers. The difference in time between the two scatter-pulses is combined with the distance between the lasers to determine the particle velocity. The particle trajectory continues into the source of a bipolar Time-of-Flight Mass Spectrometer and the particles are desorbed and ionized by the fourth harmonic of a pulsed Nd:YAG laser (Quantel USA, Bozeman, MT, Ultra CFR). The positive and negative ions generated are directed into two Time-of-Flight Mass Spectrometers oriented orthogonal to the particle beam and 180° from each other. Ion signal is detected on two microchannel plate detectors, providing two mass spectra to accompany the measured particle velocity.

Size calibrations were generated twice within the study by running polystyrene latex spheres of known size through the instrument. The instrument samples particles in the $\sim$150 nm to 5 μm size range, and was calibrated from 200 nm to 5 μm. Mass calibrations were generated daily by sampling an atomized solution of mixed metal salts. Hourly summed peak areas for mass-to-charge ratios (m/z) pertinent to this study were determined using the Environmental Chemistry through Intelligent Data Analysis software package (ENCHILADA), a freeware program developed jointly by the University of Wisconsin–Madison and Carleton College for use with high time-resolved atmospheric data including the single-particle mass spectral data generated by the ATOFMS (Gross et al., submitted for publication).

2.3. XRF

24-h integrated (midnight-to-midnight CST) ambient fine particulate matter samples were collected every 6 days during the study period. PM$_{2.5}$ samples were collected onto Teflon filters using Harvard impactors (Air Diagnostics and Engineering Inc., Harrison, ME, USA) and the filters were subsequently shipped and stored at cold conditions. Samples were analyzed at the Desert Research Institute (Reno, Nevada) by energy dispersive X-ray fluorescence (EDXRF) for forty elements including the metals relevant to this paper.

3. Results and discussion

An examination of the time series of several mass-to-charge ratios observed by the ATOFMS, as shown in Fig. 1, demonstrates that for many of the ions, short and intense episodes are dominant features of the time series, while for others, such episodes are less evident. Transient spikes in pollutant concentrations often indicate the impact of point source plumes (D'Alessandro et al., 2003; Rutter et al., 2008) and have been previously observed at this study site with regards to atmospheric mercury (Manolopoulos et al., 2007). The absence of sharp peaks in an ion time series, however, does not necessarily preclude the impact of local point sources, particularly
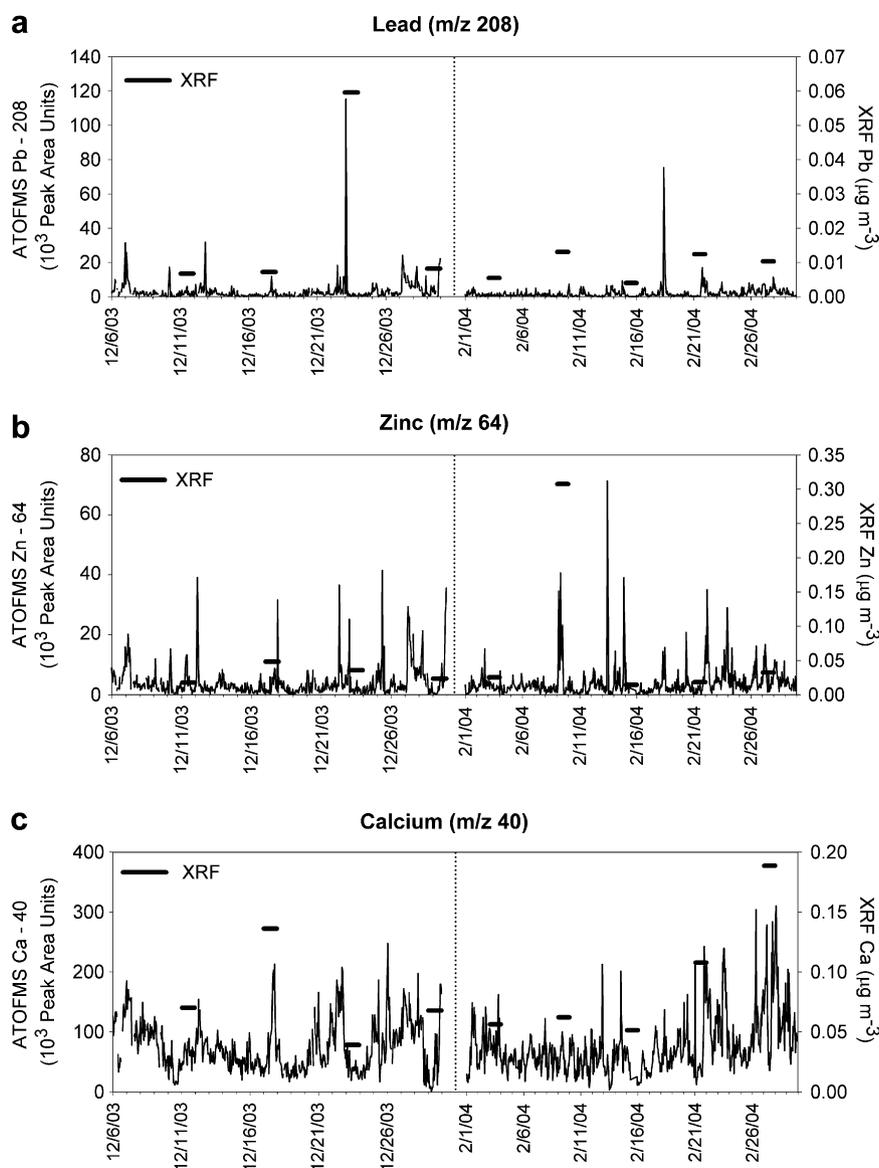
Fig. 1. Time series of selected ions (ATOFMS integrated peak areas) revealing short-term lead (a) and zinc (b) events consistent with the impact of local point sources. Also shown is the time series corresponding to calcium (c), which reveals fewer short-term events and broader peaks consistent with area source and non-local point source impacts.

in industrial environments where the influence of multiple sources may temporally overlap at a given receptor site. Accordingly, a more systematic evaluation of the data is necessary in order to identify and evaluate the impact of local point sources on the metals/metalloids concentrations observed during the current study.

3.1. Ion identification

In order to understand the impact of point sources of metals/metalloids on the East St. Louis, IL study site, hourly integrated ATOFMS peak areas for twenty mass-to-charge ratios (m/z) were examined. These m/z values correspond to the most abundant isotopes of eleven elements whose compounds are listed by the US EPA as hazardous air pollutants (HAPs) (Sb, As, Be, Cd, Cr, Co, Pb, Mn, Hg, and Ni) as well as nine other metals of interest (Al, Ba, Ca, Cu, Fe, K, Ti, V, and Zn), some of which are listed in the EPA's Toxic Release Inventory (TRI).

Confirmation of the identity of elements of interest was accomplished by first looking at the correlation between the mass-to-charge ratio for a given element and the m/z value of one or more ions previously observed to represent common organic fragments in the ATOFMS spectra. Common organic fragments used included m/z 63 and m/z 50 (aromatic fragments) and m/z 27 ($C_2H_3^+$) (Silva and Prather, 2000; Gross et al., 2005; Denkenberger et al., 2007). If a given mass-to-charge ratio was well correlated ($R^2 > 0.50$) with one or more of the organic fragments, the ion was deemed to be unsuitable for use in the study as there was a high likelihood that the metal/metalloid signal could not be easily distinguished from that of an organic fragment having the same mass-to-charge ratio (known as an isobaric interference). In this manner, five elements were eliminated from consideration (Al, As, Cu, Hg, and V). One metal, Ti (m/z 48), was eliminated due to isobaric interference with elemental carbon (EC), which commonly ionizes to fragments with mass-to-charge ratios that are multiples of 12. An additional three metals, Co, Cr, and Mn, were found to be generally well correlated with organic fragments; however, an examination of the time series of these metals demonstrated that there were several time periods in which distinct differences between the organic signal and the metal signal were observed. These elements were deemed to have limited suitability for the purposes of this study and selected data were utilized for source identification purposes only. The m/z value corresponding to one element, beryllium, was found to have no significant ion signal.

It should be noted that a strong correlation between a metal/metalloid ion and a common organic fragment does not necessarily imply that an isobaric interference is being observed. Several metals, including vanadium, are emitted by combustion sources that also emit organic compounds, and this co-emission may explain the observed correlation. A more detailed analysis of the data, including an examination of isotopes and metal oxides ions, might be useful in finding proxies for species which exhibit strong temporal correlations with organic fragments; however, such an analysis is beyond the scope of the present work.

It was found that the mass-to-charge ratios corresponding to the remaining ten elements (Sb, Ba, Cd, Ca, Fe, Ni, Pb, K, Se, and Zn) were poorly correlated with common organic fragments. These ion signals were then compared with the signals of one or more naturally occurring isotopes of each element in order to confirm their identity (examples of these correlations are shown in Fig. 2a–c). Table 1 lists all twenty elements examined, the m/z value of the most common isotope and the confirmatory isotope, and the emissions rate, where reported, for each metal/metalloid taken from the 2002 TRI (US EPA, 2002). Coefficients of determination for metal vs. organics and isotope comparisons are provided in the supplemental materials accompanying this paper (Table S2).

Lead Isotopes

Iron Isotopes

Antimony Isotopes
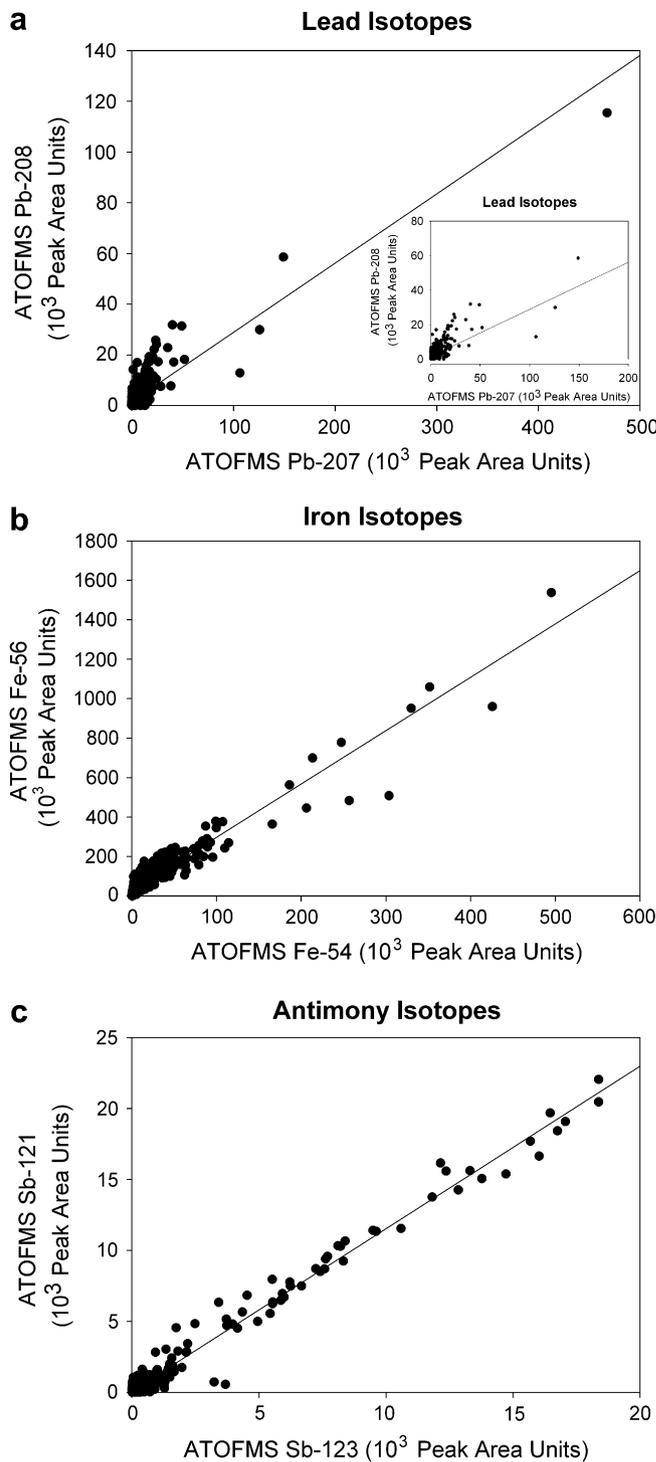
Fig. 2. (a–c) The identity of metal ions was supported by comparing the ATOFMS m/z ratio representing the most abundant isotope with one or more m/z values representing less abundant isotopes.

3.2. Quantification

While it is clear that for many reasons (matrix effects during ionization, transmission efficiency, and instrument busy-time, among others) it is challenging to quantify ATOFMS data, there is a great deal of work demonstrating the relationship between atmospheric aerosol concentrations and ATOFMS peak area/particle counts (Liu et al., 2000; Fergenson et al., 2001; Bhave et al.,

Table 1
Summary of ATOFMS ions evaluated and TRI data for elements of interest.

Element	Identifying ion (m/z)	Confirmatory ion (m/z)	Suitable for use in this study?	TRI emissions (lbs. yr.$^{-1}$)[a]
Aluminum	27	None	No	22,500
Antimony	121	123	Yes	900
Arsenic	75	None	No	5230
Barium	138	136	Yes	65,200
Beryllium	9	None	No	100
Cadmium	114	112	Yes	3000
Calcium	40	44	Yes	NR
Chromium	52	53	Limited	11,300
Cobalt	59	None	Limited	1600
Copper	63	65	No	56,200
Iron	56	54	Yes	NR
Lead	208	207	Yes	134,900
Manganese	55	None	Limited	24,900
Mercury	202	199	No	3000
Nickel	58	62	Yes	12,800
Potassium	39	41	Yes	NR
Selenium	80	78	Yes	29,400
Titanium	48	47	No	NR
Vanadium	51	50	No	10,100
Zinc	64	66	Yes	279,200

NR: Not reported.

[a] Includes stack and fugitive emissions of both metals and metal containing compounds within 100 km of the study site according to the 2002 US EPA Toxic Release Inventory (TRI).

2002; Bein et al., 2006; Qin et al., 2006; Spencer and Prather, 2006). It should be noted that previous studies have principally focused on scaling/normalizing ATOFMS data in order to obtain quantitative agreement with measurements of major constituents of ambient aerosols, such as organic carbon, elemental carbon, and nitrate, and little work has been done to explore the relationship between ambient concentrations of trace species and ATOFMS peak areas/ particle counts.

In order to evaluate the relationship between ATOFMS integrated peak area and atmospheric concentrations observed during this study, 24-h integrated peak areas for metal ions of interest were compared with 24-h integrated elemental concentrations as determined by X-ray fluorescence spectroscopy (XRF). In some cases, as shown in Fig. 3a–c, a good correlation between ATOFMS peak area and XRF concentrations is observed. In others, however, a poorer correlation is seen. Further examination of the data indicates that for some elements, isobaric interference may be problematic for such comparisons, especially when metal concentrations/ion signals are low. In the case of lead, for example, the mass-to-charge ratio used (m/z 208) is generally well correlated with common organic fragments (m/z 63 and m/z 50) during periods of lower ATOFMS signal (see Supplemental Figure S1a), but poorly correlated with these fragments during hours in which sharp spikes in the signal at m/z 208 were observed. This results in the appearance of outliers in the XRF/ATOFMS comparison as is shown in Fig. 3a. However, in the case of XRF metals for which concentrations are above detection limits, these comparisons support a semi-quantitative relationship between ambient concentrations and integrated ATOFMS signal at least to the extent that increased peak area is analogous to increased atmospheric concentrations.

3.3. Point source identification

Hourly integrated peak areas were plotted against wind direction by first grouping data into 10-degree wind direction bins, as determined by the average wind direction for each hour. The average hourly peak area was then determined for each 10-degree wind direction bin, and these data were used to identify likely point
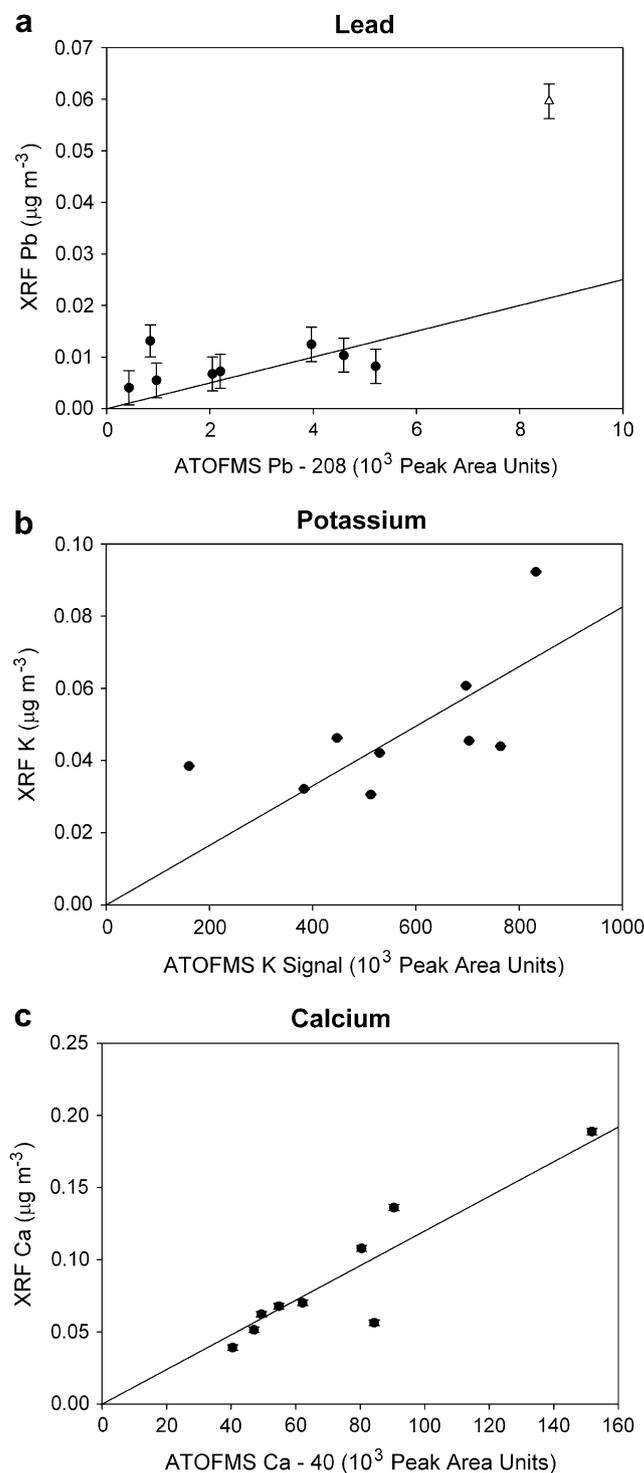
Fig. 3. Comparison of daily ATOFMS integrated peak area with daily integrated XRF data revealing that a poor relationship with respect to lead (a) and strong relationships with respect to potassium (b) and calcium (c).

sources impacting the study site. Hours in which winds were calm (wind speeds of less than 0.5 m per second) were eliminated from consideration, and wind direction bins for which less than 20 h of ATOFMS data were available were not considered for point source identification. The depth of the mixed layer was examined during this study using the National Oceanic and Atmospheric Administration's (NOAA) Hybrid Single-Particle Lagrangian Transport

Model (HySPLIT) (Draxler and Rolph, 2003; Rolph, 2003) in order to address potential problems that might arise from the use of wind direction for source identification purposes. These data did not indicate the presence of severe inversions or abrupt changes in the boundary layer that might contribute to the spikes in metals concentrations observed during the study.

As shown in Fig. 4a–d, the distribution of metals signal with wind direction supports the contention that the concentration of several metals, including lead, nickel, iron and zinc, observed at the study site are strongly influenced by local point sources. Other metals, including calcium and potassium, show a broad distribution of concentration with wind direction that is consistent with the influence of area sources or non-local point sources. For the three metals determined to have limited use in this study, Cr, Mn, and Co, individual hours in which isobaric interferences were observed to be low (determined by inspection of the time series of the metal ion vs. a common organic fragment as shown for Cr in Supplemental Figure S1c) were plotted against wind direction. These plots (shown in Supplemental Figure S2a–c) also suggest the influence of point sources.

For four elements, cadmium, antimony, barium, and selenium, significant ion signals were only observed during a brief period from December 27th through December 30th, 2003. When plotted against wind direction, as shown in Fig. 5a–d, these data strongly suggest the impact of local point sources on the study site during these days. Inspection of the time series for other ions indicated that elevated levels of zinc, lead, and chromium were also observed during this same episode.

Individual point sources of metals/metalloids within 100 km of the study site were identified from the TRI, and their locations relative to the site were determined. A complete listing of these sources, their bearing and distance from the study site, and their emissions rates are available in Supplemental Table S1. As shown in Supplemental Figure S3a–c, point sources of metals/metalloids are numerous and widely scattered throughout the greater St. Louis area. Sources along the most significant wind directions (±5°) as indicated by pollution wind-roses, were identified and are listed in Tables 2 and 3. As can be seen in Table 2, the primary wind directions for many of the elements correlate well with known point sources, although in the case of cobalt, there are few or no identified point sources in the directions indicated by this analysis.

Good agreement between the direction from which metals signals were observed and the locations of point sources of metals identified by the TRI suggests that observed spikes in ATOFMS peak area for these metals are good indicators of the impact of point sources at the study site. Sources of lead along bearings indicated by this analysis include lead and zinc smelting operations and a steel foundry. Sources of nickel identified included a metal fabrication facility and a variety of zinc sources, including zinc smelting operations, a steel mill, and a primary metal industry were identified. Indications of a source of iron were also observed, but at present, the identity of this source remains unknown.

Although coal-fired power plants are located in directions from which several metals were observed, a previous study in East St. Louis concluded that it is unlikely that plumes from these highly elevated point sources can significantly impact metals concentrations at
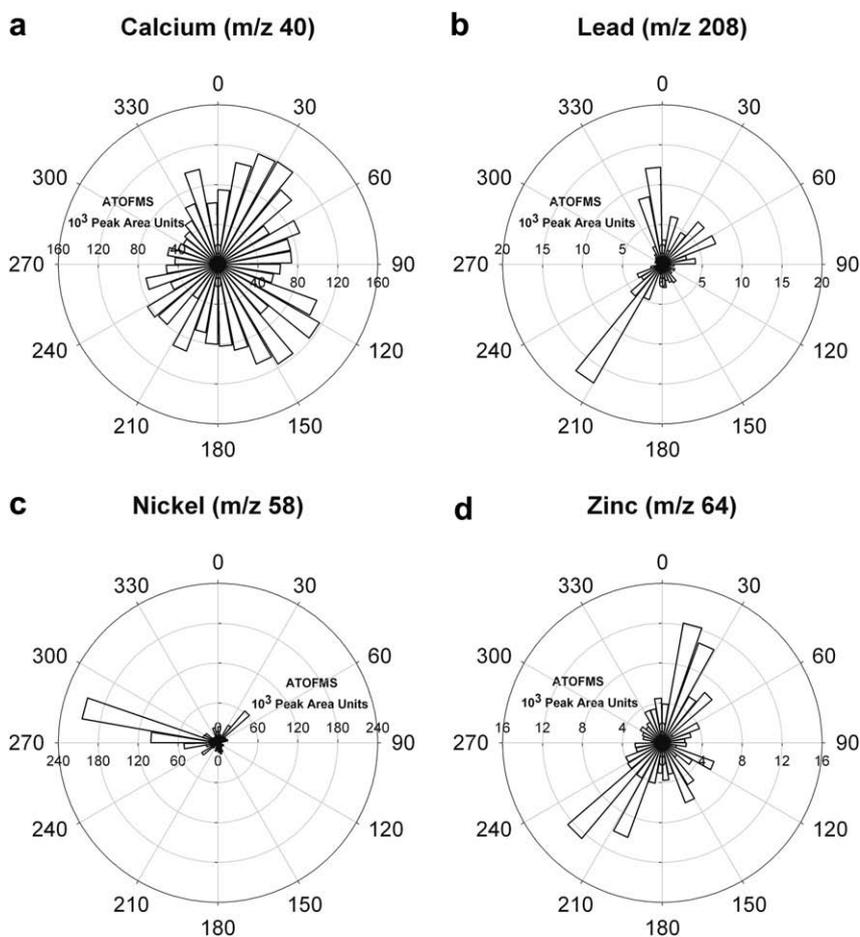
Fig. 4. (a–d) Pollution roses of selected metals observed at the study site.
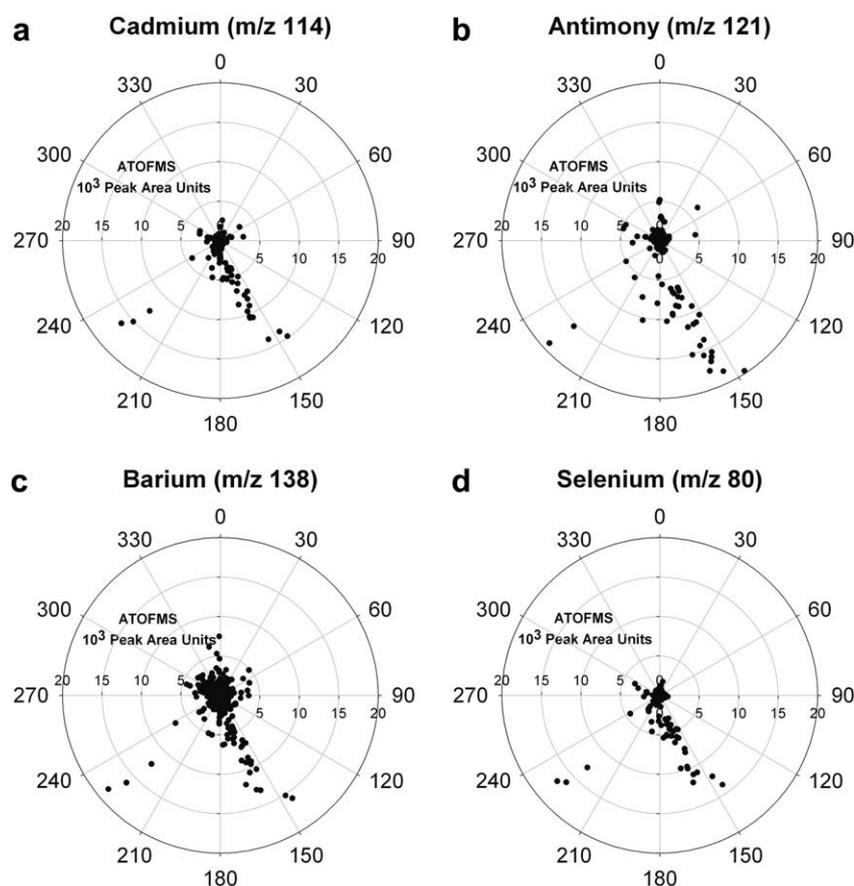
Fig. 5. (a–d) Wind-roses demonstrating that increased concentrations of Cd, Sb, Ba and are predominantly observed when the winds are from the SSE. Because these metals were only observed for a few hours during the study, the wind-roses shown in here feature hourly data plotted against hourly averaged wind direction instead of being presented in 10-degree bins.

the Midwest Supersite (Manolopoulos et al., 2007). However, as shown in Table 3, a coal-fired power station is the only identified point source SSE of this location – the direction from which elevated levels of Sb, Ba, Cd, and Se were observed. The observation of selenium, a recognized tracer for coal combustion (Laden et al., 2000), during this event increases the likelihood that the sources of metals observed during this episode included a power station.

3.4. Estimation of point source impacts

A method for apportioning metals concentrations at the East St. Louis study site was developed based on the evidence that sharp increases in the ATOFMS signal for metal ions such as those seen in Fig. 1a–b, appear to indicate the impact of point sources and that increased ATOFMS peak area is roughly analogous to increased metals concentration. The percentage of metals concentration attributable to point sources was calculated as follows. Background signal levels were established as the geometric mean of the hourly summed peak areas for each metal ion. The fraction apportioned to point sources was calculated as the sum of all peak areas above the 99% CI of the geometric mean divided by the total summed peak area for a given ion. Uncertainties for these estimations were determined as plus or minus three times the 99% confidence interval (CI) of the geometric mean. As the geometric mean represents the anti-log of the mean of the common log of the measurements, the confidence intervals are not symmetric. Accordingly, the uncertainty for each result was taken from the greater of the two confidence intervals. The sensitivity of the

analysis to the choice of confidence interval was investigated by calculating source contributions using a range of CIs. It was found that the model was relatively insensitive to the choice of CI, as point source contributions varied by 1% or less for all elements regardless of whether the 95, 97.5, or 99% confidence intervals was used.

An alternate calculation was also used for comparison against the method outlined above. In this method, the background signal was determined by removing all hours in which peak area exceeded the 99% CI of the arithmetic mean of the measurements. The arithmetic mean of the remaining hours was used as the threshold value for point source impacts, and the sum of all peak areas above this threshold was then divided by the total summed peak area for a given ion. The method that utilized the geometric mean as the background level proved to be the more conservative approach in nearly all cases but differed by less than 10% from the arithmetic mean method. It should be noted that the methods outlined here are applicable only in estimating the contribution of point sources to metals in aerosols and not the contributions of these sources to total aerosol mass. Additionally, it should be noted that the results presented here are derived from semi-quantitative data and as such do not represent a definitive source apportionment of trace-metals concentration, and the uncertainties presented in this analysis represent the confidence intervals for the mathematical averaging of the data and are not necessarily representative of the combined analytical and data analysis uncertainty.

The results of the geometric mean method are shown in Table 2 for all confirmed metals/metalloids with the exception of three metals (Co, Cr, and Mn), which were used for source identification

Table 2
Point source contributions & identification of likely point sources impacting the study site during January 2003 and February 2004.

Metal	% Apportioned to point sources[a]	Notable wind directions (deg)	Potential sources	Distance (km)	Bearing (deg)	Emissions (lbs. yr.$^{-1}$)
Calcium	30 ± 3	None	NR			
Chromium	ND	140–160	Power plant	53	149	800
Cobalt	ND	20–50	Petroleum refinery	26	17	300
		140–170	Power plant	82	53	200
		270–300	Not identified			
Iron	49 ± 9	40–50	NR			
Lead	65 ± 9	210–220	Primary metals	43	206	117,600
		350–360	Glass products	41	210	400
			Power plant	28	213	800
			Primary metals	2	219	1000
			Fabricated metals	26	220	10
			Primary metals	10	360	800
Manganese	ND	00–70	Power plant	30	4	700
		180–190	Primary metals	31	8	100
			Primary metals	29	8	200
			Primary metals	9	10	8000
			Power plant	82	53	1400
			Power plant	59	189	900
Nickel	80 ± 6	270–290	Power plant	59	265	400
			Fabricated metals	8	285	800
Potassium	35 ± 6	None	NR			
Zinc	54 ± 9	10–20	Primary metals	29	8	77,800
		220–230	Fabricated metals	15	9	26
			Primary metals	9	10	35,000
			Petroleum refinery	26	17	3200
			Cement kiln	51	199	1000
			Primary metals	2	219	80,000
			Waste incineration	2	233	<10

ND: Not determined.
NR: Not reported in the US EPA Toxic Release Inventory (TRI).
[a] Uncertainties represent 3 times the 99% CI of the geometric mean of the data and do not necessarily represent the underlying analytical and data analysis uncertainties.

purposes only. In general, point source contributions to metals whose pollution wind-roses showed a broad distribution of signal with wind direction, such as calcium and potassium, were low while a much greater percentage of the signals corresponding to metal ions whose wind-roses demonstrated clear directionality, including lead and nickel, were attributed to point sources. In some cases greater than 85% of the signal, and by analogy concentration, of specific metals was attributed to local point sources via this method. While this apportionment is taken from a limited time period and should not be viewed to represent the annual contribution of point sources, it clearly shows the extent to which industrial activity can contribute to metal concentrations in East St. Louis.

3.5. Discussion

As demonstrated in this work, the use of ATOFMS data represents an exceptional opportunity to understand the sources of atmospheric metals impacting a given receptor site through the integration of meteorological data and high time-resolved single-particle data. Information derived from wind direction and particle composition can potentially be used to validate emissions inventories or locate unidentified sources impacting a given location. The challenges presented in conducting such an analysis clearly include ion identification, which can be complicated by isobaric interferences from non-metal species effectively ionized by this instrument. Organic species, which can comprise between 10 and 70 percent of the total fine aerosols in many locations (Andrews et al., 2000), pose a particular challenge in this respect. It is expected that such interferences may vary considerably from location to location, and the application of the methods outlined in this paper must be accompanied by rigorous scrutiny of individual ions in order to confirm their identity. Isobaric interferences remain a fundamental challenge, and it is clear that this analysis, and the study of aerosols at large, would greatly benefit from the development of higher-resolution single-particle mass spectrometric techniques.

While not definitively quantitative, the use of ion peak area to estimate the contribution of point sources to individual metals

Table 3
Point source contributions for selected metals and identification of likely point sources impacting the study site during the period December 27th–30th, 2003.

Metal	% Apportioned to point sources[a]	Notable wind directions (deg)	Potential sources	Distance (km)	Bearing (deg)	Emissions (lbs. yr.$^{-1}$)
Antimony	85 ± 3	150–160	Power Plant	53	149	NR
Barium	70 ± 6	150–160	Power plant	53	149	18,000
Cadmium	86 ± 3	150–160	Power plant	53	149	NR
Selenium	86 ± 3	150–160	Power plant	53	149	4400

NR: Not reported in the US EPA Toxic Release Inventory (TRI).
[a] Uncertainties represent 3 times the 99% CI of the geometric mean of the data and do not necessarily represent the underlying analytical and data analysis uncertainties.

concentrations clearly has some advantages over more complex statistical source apportionment analyses. These advantages include eliminating the need for *a priori* knowledge concerning sources and the ability to provide a straightforward analysis largely free from subjective interpretation. The methods outlined in this paper, while not designed as a replacement for commonly used techniques such as CMB approaches or PMF analyses, provide additional/complementary tools for understanding the extent to which metal concentrations are impacted by local point sources and for identifying sources directly impacting a given receptor site. The potential ability to identify the influence of specific point sources is also inherent in these methods, although the capacity to conduct such an analysis is limited by the veracity of emissions inventory data and by the location of sources relative to one another and relative to a given receptor site. It is hoped that the straightforward nature of the techniques outlined in this work will help to make a powerful tool for understanding aerosol composition, single-particle mass spectral data, more useable by a broader array of investigators and regulatory agencies.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.atmosenv.2009.05.011.

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