Electronic Supplementary Information

Characterizing metals in particulate pollution in communities at the fenceline of heavy industry: Combining mobile monitoring and size-resolved filter measurements

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Description of contents:

- Accuracy and repeatability of ICP-MS elemental analysis methods
- MOUDI measurements compared to EPA AirToxScreen estimates for study domain
- Relevant toxicity values and comparison with HAP-MAP fixed-site MOUDI measurements
- Effect of MOUDI sampling integration time on percent detection for all analytes
- Temporal trends in elemental concentrations in southeastern PA reported by PA DEP
- Wind direction and speed throughout study period
- Hierarchical clustering of fixed-site MOUDI data; examples of concentration as a function of particle size fraction
- Plot of $Q/Q_{expected}$ parameter used in selection of PMF solution
- Spatial distributions of 11 additional metal/metalloids across study area based on mobile SP-AMS measurements
- Comparison of elemental concentrations in fine PM from HAP-MAP (fixed-site MOUDI) versus PA DEP

ESI Table S1: SRM 1648a and matrix-matched spike recoveries in ICP-MS analysis.* Repeatability calculated as the propagated standard deviation (all PM size fractions) for the two blank MOUDI runs.

	Run 1	Run 2	Run 3	Repeatability (ng/m³)	Notes
Na	93%	108%	112%	0.28	
Mg	85%	91%	90%	0.049	
Al	92%	92%	97%	0.23	
K	88%	109%	84%	0.37	
Ca	96%	87%	78%	0.82	
Ti	107%	113%	124%	0.033	Spikes data – low Ti recoveries in SRM as previously reported [1]
V	79%	69%	67%	0.00078	Spikes 83, 89, 83% (runs 1-3)
Cr	111%	115%	112%	0.0068	Spikes data – low Cr recoveries in SRM as previously reported [1]
Mn	92%	91%	96%	0.0019	
Fe	106%	96%	85%	0.078	
Co	77%	79%	84%	0.00053	
Ni	85%	82%	71%	0.028	
Cu	82%	85%	89%	0.0078	
Zn	90%	91%	97%	0.018	
As	92%	93%	78%	0.0044	
Se	75%	75%	67%	0.013	SRM reference value only; spikes 105, 176, 106% (runs 1-3)
Sr	94%	88%	102%	0.00075	
Mo	108%	110%	115%	0.0022	Spikes data – no SRM value
Ag	114%	113%	120%	0.00080	Spikes data – no SRM value
Cd	93%	99%	101%	0.00034	
Sn	115%	115%	134%	0.0031	Spikes data – no SRM value
Sb	88%	91%	76%	0.0014	
Ba	106%	109%	115%	0.0016	Spikes data – no SRM value
W	104%	108%	122%	0.0074	SRM reference value only; spikes 108, 112, 129% (runs 1-3)
Pb	97%	99%	112%	0.0016	
Th	No SRM or spike value			0.00013	
U	101%	107%	108%	0.00011	Spikes data – no SRM value

*Number of replicates: SRM 1648 (n=2, 1, 2 in Runs 1-3 respectively), matrix-matched spikes (n=3, 1, 2 in Runs 1-3 respectively)

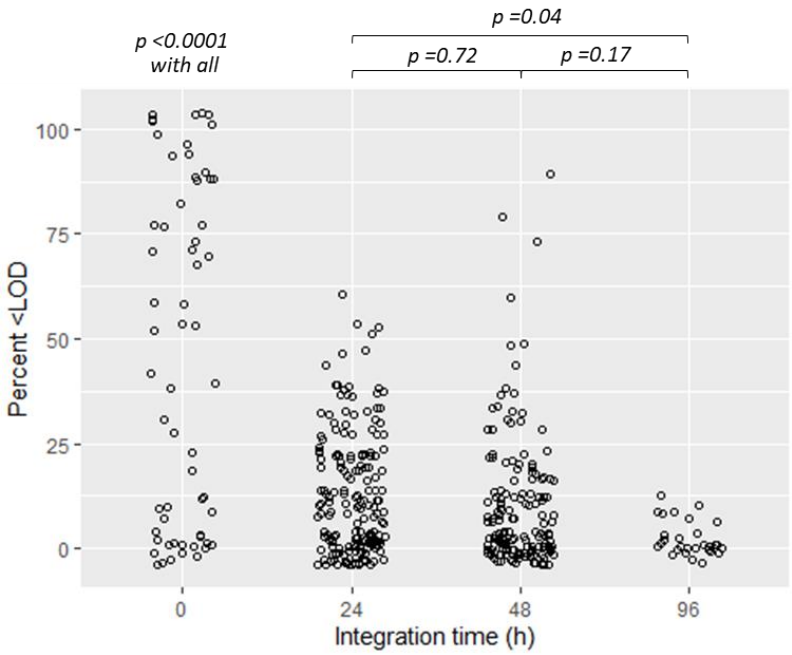
ESI Table S2: MOUDI measurements (mean and standard error of the mean (SEM) for all days of study campaign) for total suspended particles (TSP) and fine PM ($PM_{1.78}$), compared to TSP concentration estimates from EPA AirToxScreen for census tracts within the 6-mile area around the MOUDI fixed site (mean and range (min-max)).

	MOUDI				AirToxScreen	
	TSP (ng/m³)		$PM_{2.5}$ (ng/m³)		TSP (ng/m³)	
Analyte	**Mean**	**SEM**	**Mean**	**SEM**	**Mean**	**Range**
Na	403.2	139.5	153.4	41.2		
Mg	96.4	20.0	28.8	4.4		
Al	136.9	30.1	46.1	9.4		
K	110.8	15.4	61.7	8.0		
Ca	268.7	57.9	74.9	11.8		
Ti	12.49	2.10	5.37	0.78		
V	0.387	0.073	0.233	0.059		
Cr	1.58	0.24	0.86	0.11		
Mn	3.68	0.67	1.62	0.24	1.12	0.81-1.66
Fe	177.2	27.5	78.0	10.2		
Co	0.080	0.011	0.032	0.003	0.015	0.007-0.033
Ni	0.791	0.097	0.438	0.059	1.48	0.97-2.44
Cu	5.152	0.593	3.324	0.494		
Zn	9.091	1.218	6.318	0.923		
As	1.026	0.386	0.983	0.389	0.12	0.09-0.14
Se	0.580	0.127	0.512	0.120		
Sr	1.231	0.166	0.502	0.049		
Mo	0.369	0.036	0.279	0.029		
Ag	0.104	0.027	0.087	0.024		
Cd	0.238	0.069	0.084	0.015	0.086	0.067-0.152
Sn	1.133	0.184	0.841	0.168		
Sb	1.373	0.133	0.947	0.099	0.10	0.04-0.46
Ba	11.39	1.27	6.48	0.63		
W	0.054	0.008	0.031	0.005		
Pt	0.006	0.001	0.005	0.001		
Pb	2.02	0.34	1.58	0.30	0.74	0.48-3.50
Th	0.028	0.006	0.012	0.004		
U	0.009	0.002	0.004	0.001		

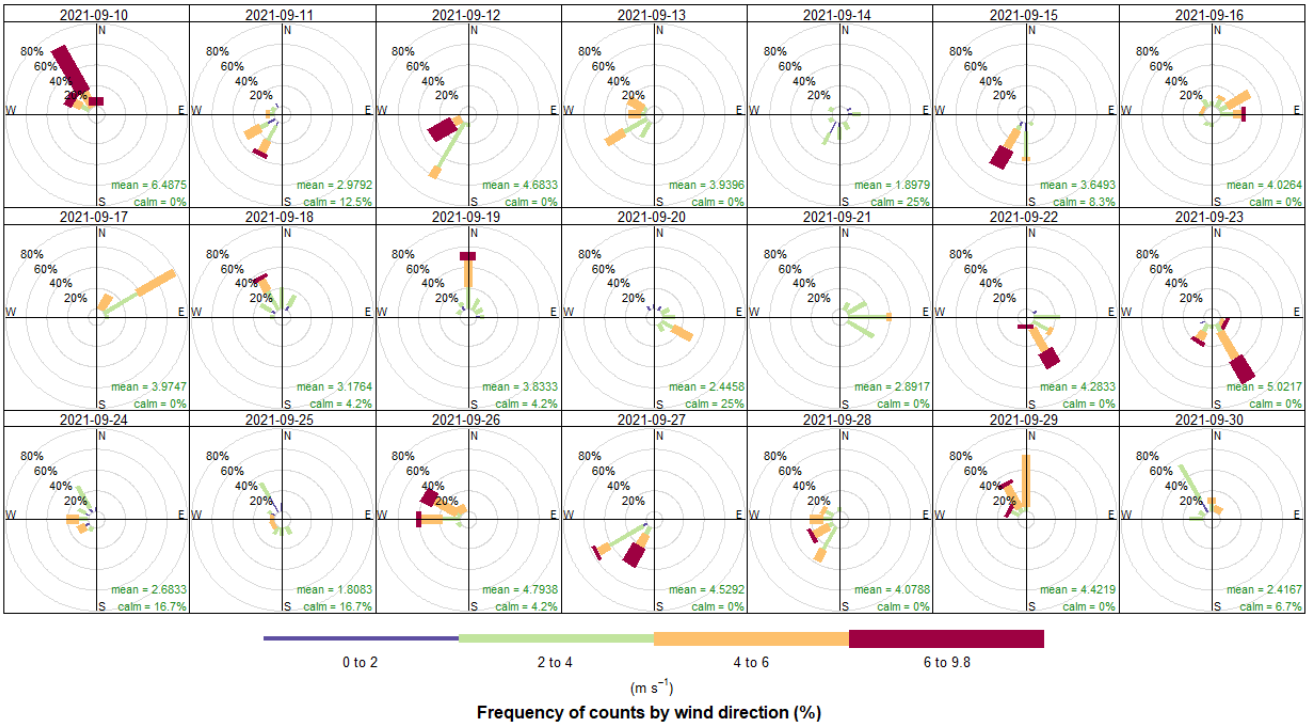
ESI Table S3: Toxicity values compared with total-element concentrations measured in this study in total suspended particles (TSP). All values in units of ng/m^3.

Metal/ metalloid	Regulated forms/ compounds by inhalation	Toxicity value	Source	Most Sensitive Target Organ/System*	Fixed-site MOUDI measurements, median (range)	Hazard Quotient
Antimony	Antimony and compounds	300	ATSDR MRL chronic	Respiratory	1.40 (0.552-2.25)	0.005
	Antimony trioxide	200	IRIS Inhalation RfC	Respiratory		0.007
Arsenic	Inorganic	15	OEHHA chronic REL	Developmental, cardiovascular, neurological, respiratory, dermal	0.577 (0.231-5.10)	0.038
	Arsine	0.5	IRIS Inhalation RfC	Immune/ hematological		
Cadmium	Cadmium and compounds	10	ATSDR MRL chronic	Respiratory, renal	0.145 (0.0397-0.796)	0.015
Chromium	Soluble hexavalent compounds	10	IRIS Inhalation RfC[2]	Respiratory, renal, gastrointestinal	1.41 (0.505-3.62)	0.141
Cobalt	Metal	100	ATSDR MRL chronic	Respiratory	0.0685 (0.0352-0.153)	0.001
Lead	Lead and compounds	150	NAAQS rolling 3-mo. avg. primary/ secondary standard	Neurological	1.58 (0.617-4.15)	0.011
Manganese	Metal	50	IRIS Inhalation RfC	Neurological	3.14 (1.23-8.72)	0.063
Molybdenum	Dust and insoluble compounds	2,000	ATSDR MRL chronic	Respiratory	0.335 (0.239-0.711)	0.0002
Nickel	Nickel and compounds	90	ATSDR MRL chronic	Respiratory, renal	0.812 (0.346-1.44)	0.009
Selenium	Selenium and compounds	20,000	OEHHA chronic REL	Hepatic, cardiovascular, neurological	0.396 (0.133-1.68)	0.00002
Titanium	Titanium tetrachloride	100	ATSDR MRL chronic	Respiratory	10.6 (2.68-24.7)	0.106
Uranium	Soluble salts	40	ATSDR MRL chronic	Respiratory, renal	0.00793 (0.00173-0.0192)	0.0002
Vanadium	Vanadium and compounds; vanadium pentoxide	100	ATSDR MRL chronic	Respiratory	0.307 (0.0653-0.797)	0.003

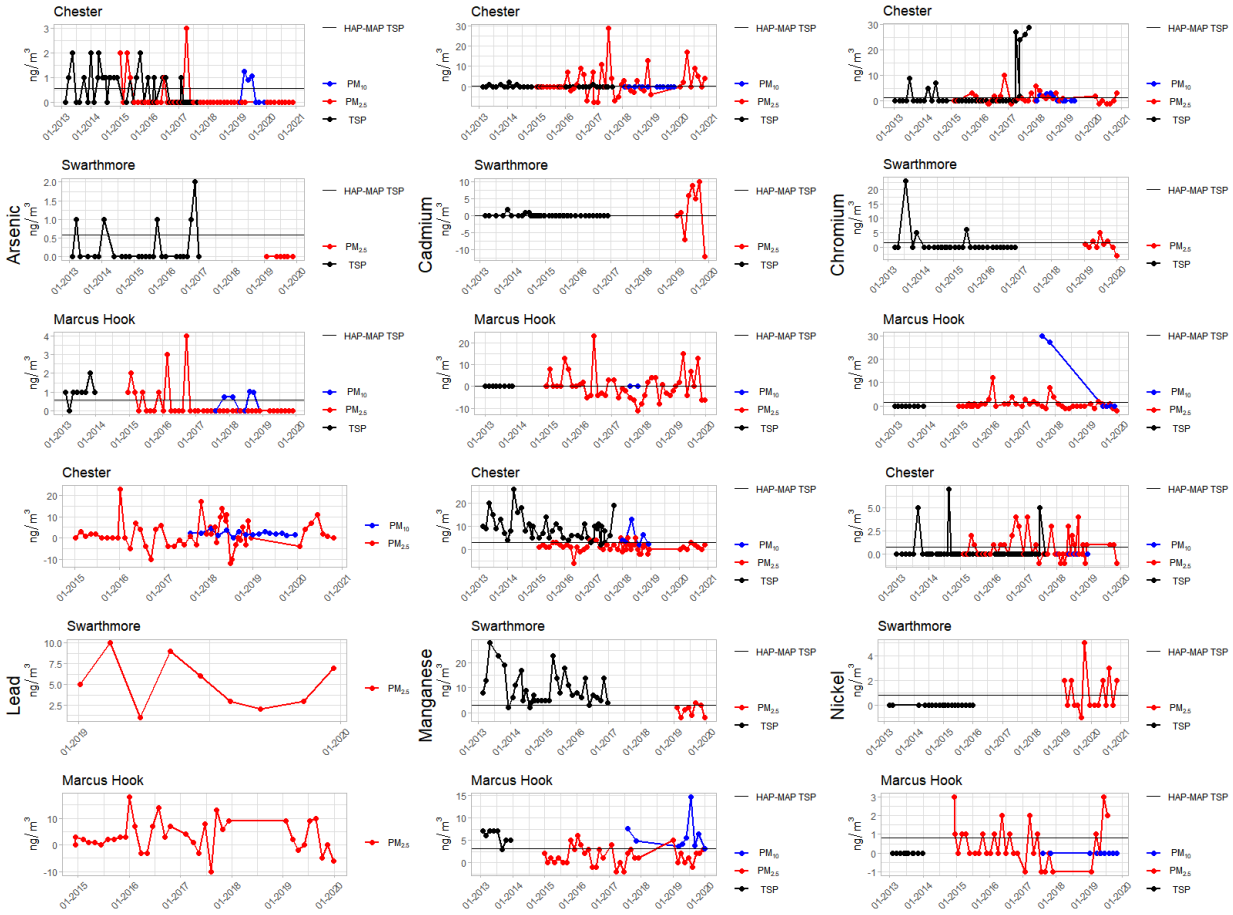
Abbreviations: REL, Reference Exposure Level; MRL, Minimum Risk Level; RfC, Reference Concentration; OEHHA, California Office of Environmental Health Hazard Assessment; NAAQS, National Ambient Air Quality Standard. *In the cases where multiple organ systems are listed, the same study dose elicited statistically significant impacts in all listed organ systems.



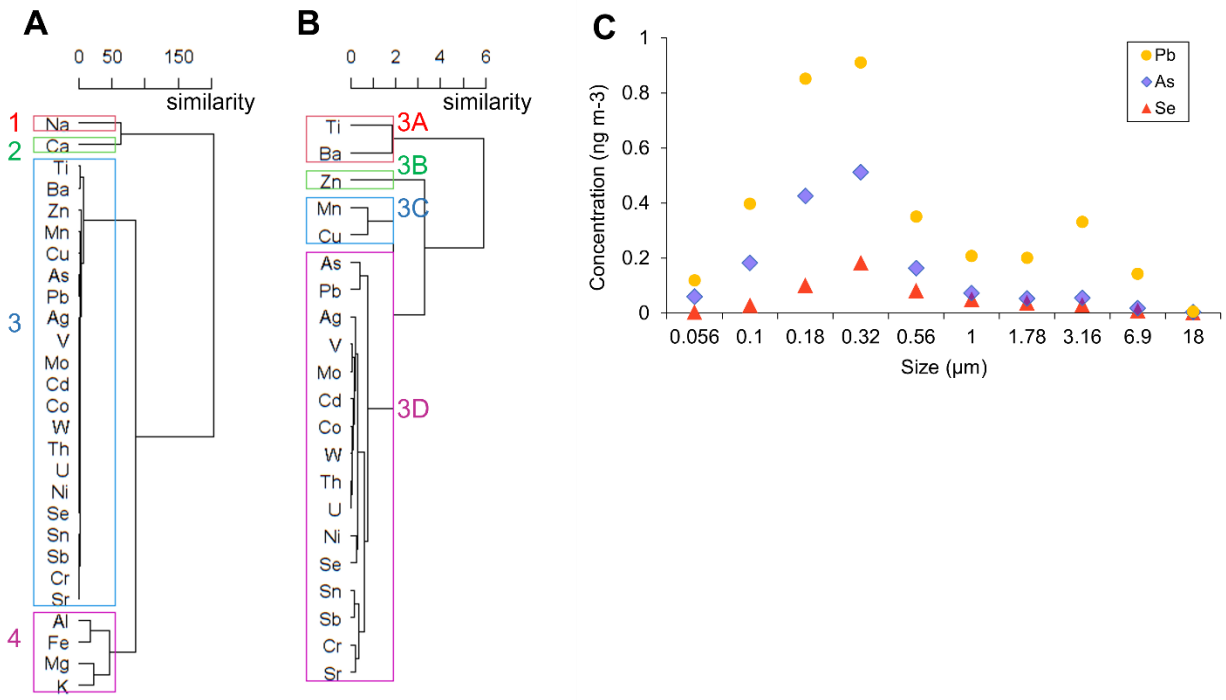
ESI Figure S1: Comparison of percent below limit of detection (LOD) measurements for all analytes between filter samples of varying integration times: 0 h (i.e., field blanks), 24 h, 48 h and 96 h. For each integration time, each symbol represents an individual analyte. Detectable levels of the 30 metals/metalloids included in the study were found in more than 60% of MOUDI filter samples. The percentage of measurements for all analytes <LOD was significantly lower in sample filters than the field blanks, and the 96-hour integration time had significantly lower levels of <LOD measurements than the shorter integration times.



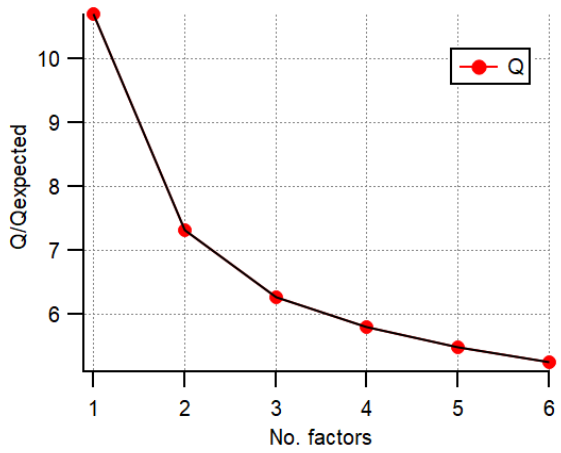
ESI Figure S2: Wind roses showing wind direction and wind speed on each day of fixed-site MOUDI sampling.



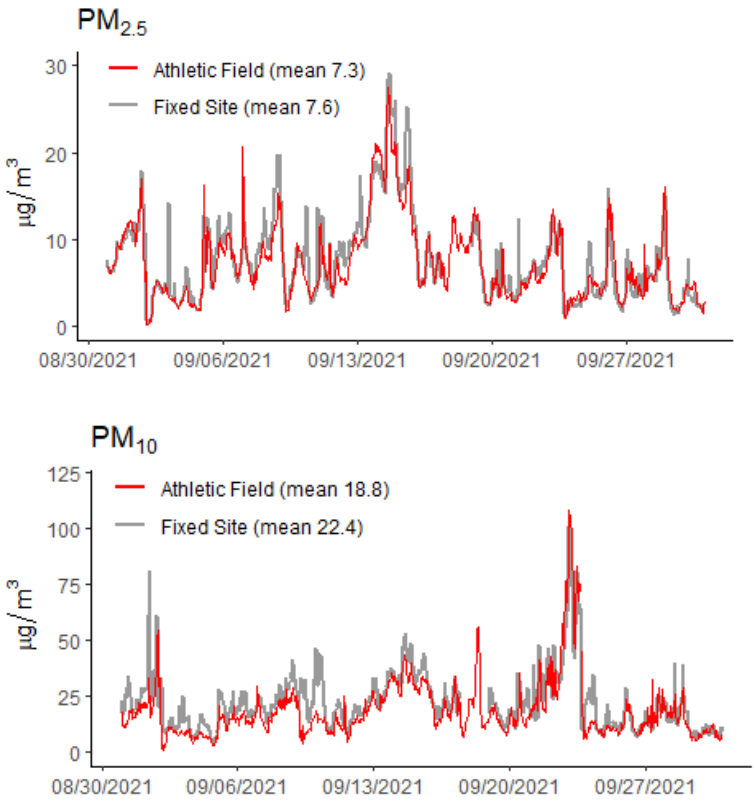
ESI Figure S3: Temporal trends of concentrations reported by PA DEP from monitors at three sites within the HAP-MAP study area over up to ten years for six elements.



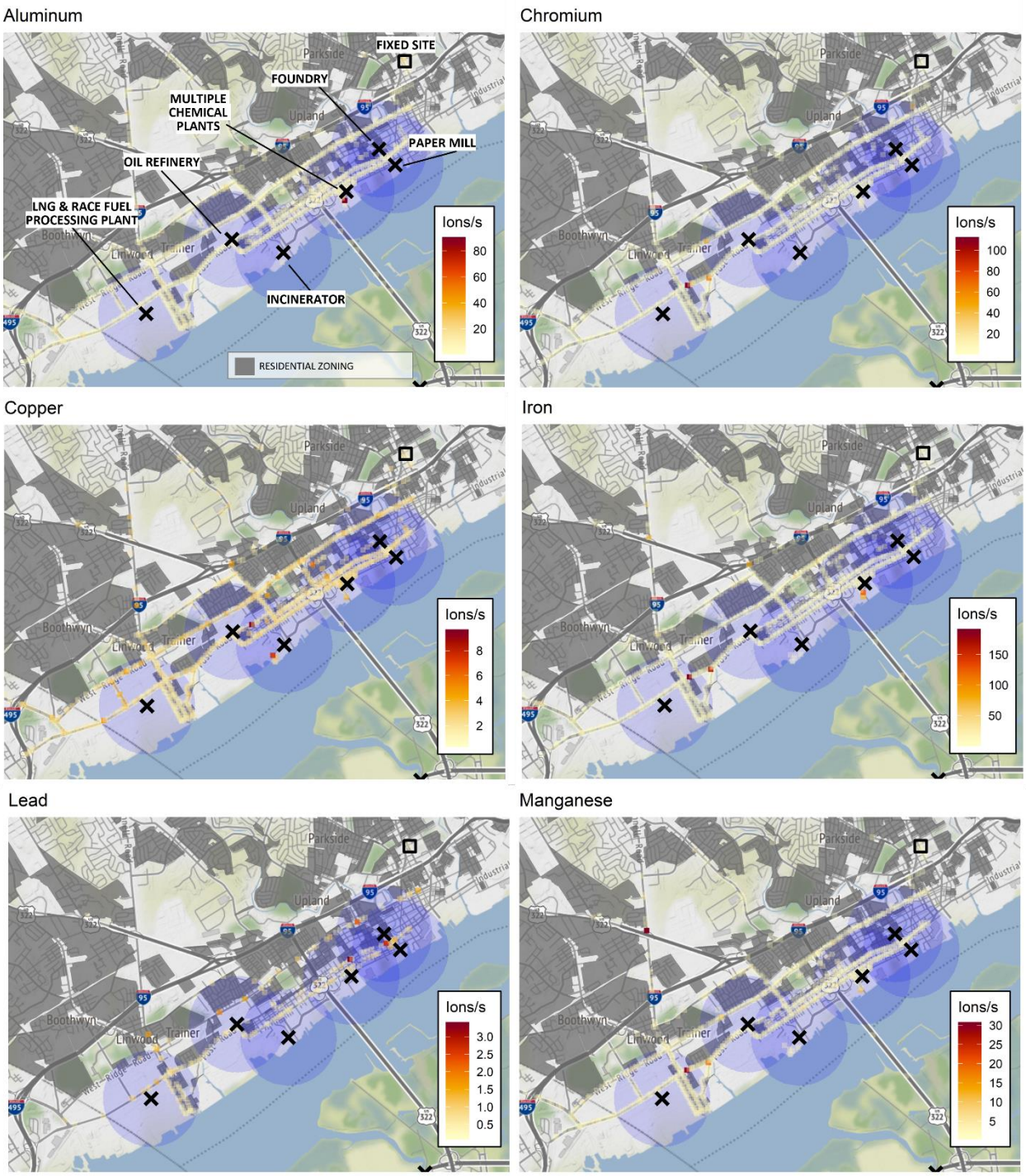
ESI Figure S4: Dendrograms showing clusters of fixed-site MOUDI data: A) Four major clusters of all elements measured; B) four minor clusters within cluster 3; C) example of size-resolved concentrations of trace elements lead, arsenic and selenium.



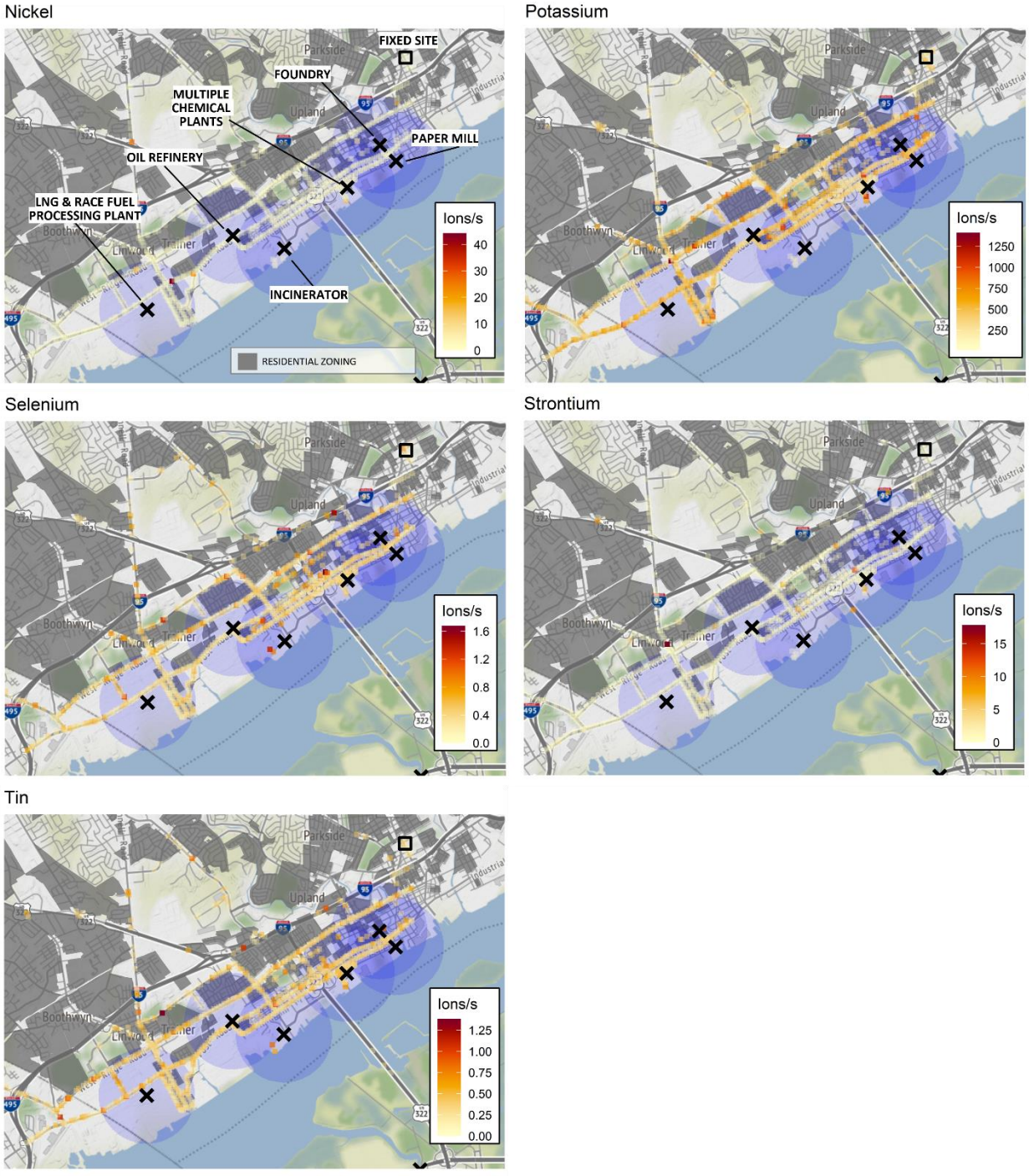
ESI Figure S5: Plot of the ratio of the sum of the weighed squared residuals of the fit (Q) to expected Q as a function of the number of factors in the PMF solution.



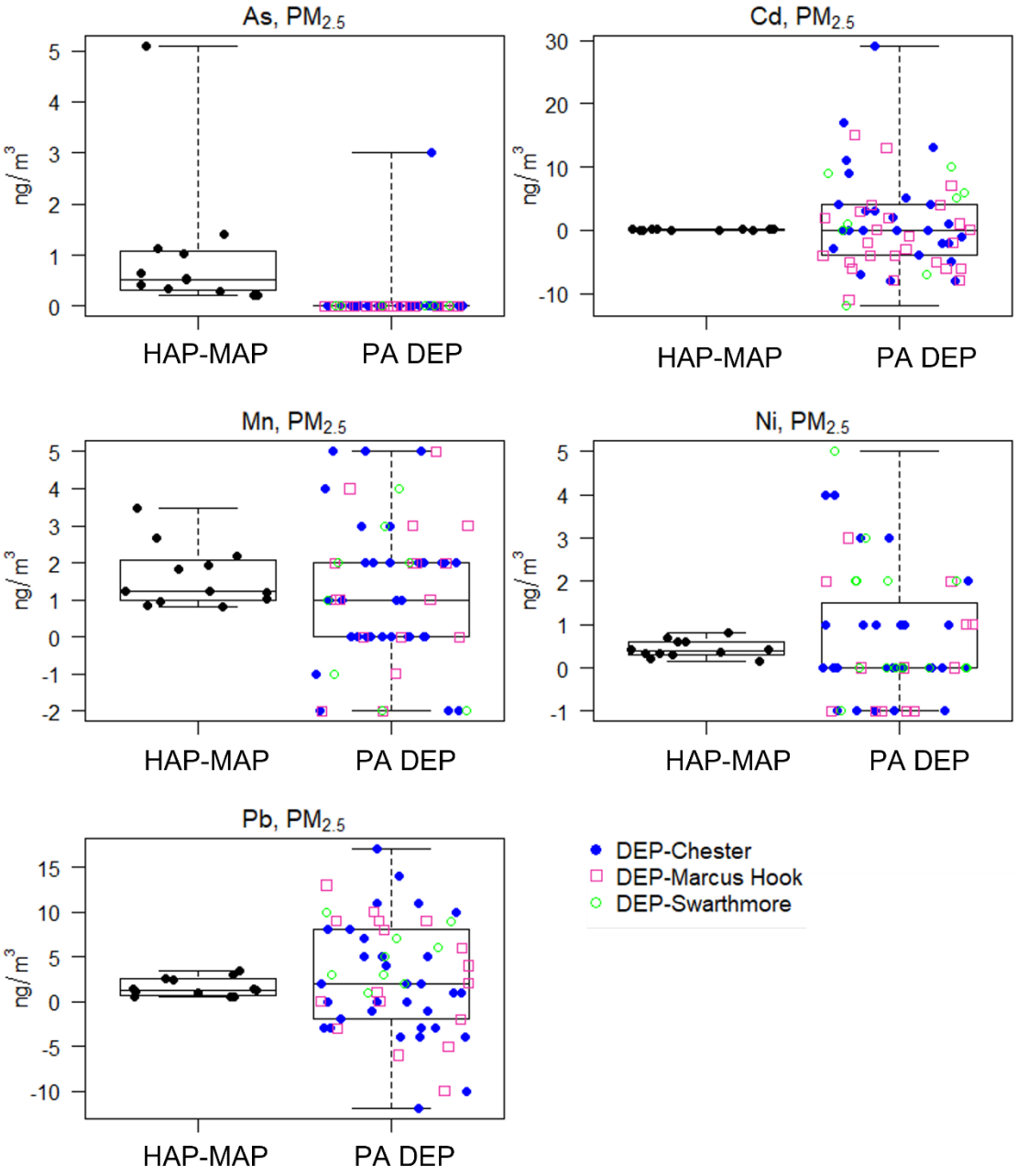
ESI Figure S6: Comparison of MODULAIR-PM sensor PM measurements at two sites within study domain: athletic field used for SP-AMS stationary measurements (885 m from fixed site) and MOUDI fixed site.



ESI Figure S7: Spatial distribution of metal/metalloids across study area, throughout the 1-month campaign, based on mobile SP-AMS measurements. Means of 3 measurements per 50m x 50m grid cell are shown. Residential zoning is shown by gray fill; light blue circles represent 1000-m buffers around TRI facilities (x). Symbol colors represent ions/s. The Pb-206 isotope was used to avoid major organic interferences. Additionally, Pb data were only included where above the detection limit (3*standard deviation) and greater than the signal of $C_{16}H_{14}^{+}$, a potential organic interference.



ESI Figure S7, cont.: Spatial distribution of metal/metalloids across study area, throughout the 1-month campaign, based on mobile SP-AMS measurements. Means of 3 measurements per 50m x 50m grid cell are shown. Residential zoning is shown by gray fill; light blue circles represent 1000-m buffers around TRI facilities (x). Symbol colors represent ions/s.



ESI Figure S8: Comparisons of fixed-site MOUDI measurements from the HAP-MAP study with PA DEP measurements (2017-2020) for 5 elements in $PM_{2.5}$.

References:

(1) Celo, V.; Dabek-Zlotorzynska, E. Validation of a Simple Microwave-Assisted Acid Digestion Method Using Microvessels for Analysis of Trace Elements in Atmospheric PM2.5 in Monitoring and Fingerprinting Studies. *Open Chem. Biomed. Methods J.* **2010**, *3* (1), 143–152. https://doi.org/10.2174/1875038901003010143.

(2) US EPA. *IRIS Toxicological Review of Hexavalent Chromium [Cr(VI)]: External Review Draft*; 2022.