Electronic Supplementary Material (ESI) for Environmental Science: Atmospheres.

Supplemental Information

Evaluation of Airborne Particulates and Associated Metals Originating from Steel Slag Applied to Rural Unpaved Roads

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Filter Sample Analysis for Metals

Prior to analysis by ICP-MS, filter samples were dissolved by microwave-assisted digestion following EPA Method 3051A [1] using an Ethos UP microwave with SK-15 rotor (Milestone, Inc.,Via Fatebenefratelli 1/5 - 24010 Sorisole (BG) - Italy). Samples were immersed in 9 mL of concentrated trace-metals grade nitric acid (67%, Fisher Scientific) and 3 mL of trace metals grade hydrochloric acid (37%, Fisher Scientific) and sealed inside PTFE digestion vessels. The microwave temperature program followed the Milestone, Inc. supplied program for EPA 3051A on the Ethos UP. Microwave temperature was ramped linearly to 150 °C over ten minutes, followed by a second ramp to 180 °C over ten minutes, and was held isothermally at 180 °C for the remaining ten minutes. Total digestion time was 30 minutes. Finally, the samples were naturally cooled to room temperature prior to opening. After digestion samples were diluted to 50 mL with 18.2 MΩ deionized water. An aliquot of sample was filtered through a nylon filter (0.22 µm) and diluted again with deionized water (2 mL sample and 8 mL water). Each run contained at least one method blank consisting of acid in an empty digestion vessel carried through an identical procedure. Metals in the digested filter sample were analyzed on an Agilent 7900 ICP-MS using He collision cell mode to remove polyatomic interferences. ICP-MS and digestion performance was assessed using metals-spiked blanks carried through the digestion procedure and RM-8704, Buffalo River Sediment (U.S. National Institute of Standards and Technology). Spike recoveries were greater than 85% for all reported metals. Metal recoveries for the Buffalo River Sediment were 86% for manganese. Performance within a run was monitored using periodic analyses of a trace metals in drinking water standard diluted into the same matrix as samples (TMDW-A, High Purity Standards, Inc.). Repeatability was assessed by re-analysis of a duplicate sample every 15 samples. Element concentrations from ICP-MS were used to calculate µg of metal per filter and mg/kg of each element by using the gravimetric mass of material on each filter.

Tables

Table S1. Site locations, estimated traffic flows at each site, and instrumentation deployed. All counties in Iowa.

Site Name	Location/Slag Application Status	Traffic Flow[1], vehicles per day	Instruments Deployed
Background	920 220th Street, Scott County, no slag applied	45	Dichotomous sampler
Site A	3445 120th Street, Muscatine County, slag applied	100	Dichotomous sampler, ambient continuous metals monitor, beta attenuation monitor, meteorological station (all placed in a sample trailer)
Site B	1689 130th Street, Muscatine County, slag applied	100	Dichotomous sampler

[1]Traffic flow data were obtained from the Iowa Department of Transportation [2, 3]

Table S2A. Metals concentrations (mg/kg dust dry weight) from slag road dust samples taken at study sample site locations.

Sample	Background Site	Slag Site A	Slag Site B
Aluminum	3400	2200	7200
Antimony	32.7	82.5	55.1
Arsenic	1.1	5.4	6.2
Barium	NA	NA	NA
Beryllium	NA	NA	NA
Cadmium	5.7	33.3	82.7
Chromium	5.6	172.4	297.9
Cobalt	1.5	1.0	1.8
Copper	11.8	113.5	21.2
Iron	4390	9530	18120
Lead	0.0	0.1	0.2
Lithium	NA	NA	NA
Manganese	254.7	1391.5	2472
Mercury	NA	NA	NA
Molybdenum	NA	NA	NA
Nickel	2.7	2.7	9.4
Selenium	NA	NA	NA
Silver	NA	NA	NA
Strontium	NA	NA	NA
Thallium	NA	NA	NA
Tin	NA	NA	NA
Vanadium	8.0	19.7	34.1
Zinc	20.1	55.1	106.6

NA = not analyzed

Table S2B. Metals concentrations (mg/kg dust dry weight) from slag road dust samples taken at Iowa county roads* near study sample sites.

Sample	No Slag Road	Slag Road 1	Slag Road 2	Slag Road 3	Slag Road 4	Slag Road 5	Slag Road 6
Aluminum	1,800	1,450	10,400	20,000	22,000	12,700	10,000
Antimony	ND	ND	ND	ND	ND	ND	ND
Arsenic	1.24	2.55	3.03	2.34	2.98	4.76	1.84
Barium	21.4	29.5	99.4	62.2	91.4	108	39.9
Beryllium	ND	ND	ND	ND	ND	ND	ND
Cadmium	ND	ND	ND	ND	ND	ND	ND
Chromium	3.59	44	329	316	444	148	162
Cobalt	1.2	1.89	3.75	2.07	2.96	3.92	1.56
Copper	2.39	10.3	22.1	38	50.7	26.4	17.5
Iron	3,859.30	7,537.54	29,175.05	30,700	39,600	16,900	19,100
Lead	6.11	9.98	10.1	29	30.5	27.2	15.2
Lithium	ND	ND	ND	ND	ND	ND	ND
Manganese	251	1,400	4,920	3,770	5,350	1,850	2,410
Mercury	ND	ND	ND	ND	ND	ND	ND
Molybdenum	ND	1.2	4.7	5.7	8.4	3.3	3
Nickel	3.08	7.27	13.1	16.5	30.9	15.4	10.5
Selenium	ND	ND	ND	1	ND	ND	ND
Silver	ND	ND	ND	1.39	1.53	0.91	0.93
Strontium	66.9	120	158	92.2	117	80.8	90.2
Thallium	ND	ND	ND	ND	ND	ND	ND
Tin	ND	ND	ND	8.8	7.2	ND	5.5
Vanadium	5.47	10.3	73.5	64.8	97.7	40.4	36.2
Zinc	15.6	57.1	125	370	533	244	191

ND = not detected

*No Slag Road = 210th St. + 1st Avenue, Scott County
Slag Road 1 = Yellow Avenue, Muscatine County
Slag Road 2 = 3727 120th St., Muscatine County
Slag Road 3 = 1072 260th St., Muscatine County
Slag Road 4 = 2051 Davis Ave., Muscatine County
Slag Road 5 = 2075 Trolley Ave., Muscatine County
Slag Road 6 = 2670 Independence Ave., Muscatine County

Table S3. Sieve Analysis of Crushed Limestone and Slag Applied to the Roads (Typical)

Sieve	Crushed Limestone % passing	Slag Batch 1 % passing	Slag Batch 2 % passing	Class A Specification % passing
1"	100	100	100	100
3/4"	92	97.2	97	95-100
1/2"	81.8	81	66	70-90
3/8"	72.6	72.5	52	
4	54,8	50	34	30-55
8	41.3	33.9	24	15-40
16	32.5	22.5		
30	26.9	14.4	14	
50	23.3	9	11	
100	19.2	5.5		
200	15.3	3.4	6.1	6-16

Results provided by the Muscatine County Engineer [4]

Table S4. Summary of XRD results for bulk samples collected from the road surface

	% Calcite	% Dolomite	% Quartz
No slag road (Scott County)	3	90.5	6.5
Background site (Scott County)	2.5	93.1	4.4
Slag sites (eight locations in Muscatine County)			
Mean	41.9	50.5	7.5
Minimum	24.3	21	2.4
Maximum	68	73.3	21
Std Dev	16.5	21.4	6.2

Table S5. Comparison of metals concentrations in PM at Site A as analyzed by the ACMM and by ICP-MS

Metal	ACMM, Average Concentration, ng/m^3, n = 709 (SD)	ACMM Detection Limit[1], ng/m^3	ACMM, Relative Abundance	ICP, Average Concentration, ng/m^3, n = 12 (SD)	t- test p values
Calcium	19000 (33000)	0.30	67%	30236 (22015)	0.24
Aluminum	2600 (4400)	100	9.2%	1886 (621)	0.57
Silicon	2300 (3300)	17.8	7.9%	NA	
Magnesium	NA		NA	11198 (725)	
Cadmium	1800 (9000)	2.5	6.4%	0.069 (0.036)	
Niobium[2]	1100 (1300)		3.8%	NA	
Iron	600 (910)	0.17	2.1%	978 (569)	0.15
Sulphur	390 (260)	3.16	1.3%	NA	
Potassium	230 (230)	1.17	0.80%	316 (195)	0.20
Lead	120 (590)	0.13	0.43%	1.6 (2.5)	0.49
Manganese	85 (140)	0.14	0.30%	156 (112)	0.081
Titanium	47 (66)		0.16%	NA	
Chromium	36 (140)	0.12	0.13%	30 (13)	0.88
Antimony	22 (97)	5.2	0.075%	0.57 (0.23)	0.44
Zinc	15 (23)	0.067	0.053%	169 (187)	<0.0001
Phosphorus	14 (27)	5.2	0.047%	NA	
Strontium	12 (21)		0.041%	NA	
Chlorine	8.3 (55)	1.73	0.029%	NA	
Palladium	3.7 (14)		0.013%	NA	
Tin	3.0 (20)	4.1	0.011%	NA	
Zirconium	2.9 (5.6)		0.010%	NA	
Vanadium	2.9 (5.6)	0.12	0.010%	3.2 (2.7)	0.88

Metals constituting less than 0.01% relative abundance were not included in this table.

[1]60-minute sampling period, 68% confidence interval [5], DLs not provided for every analyte .

[2]Niobium not analyzed as part of the sample, used for QA/QC only. Not included in Figure S1.

NA = not analyzed

Table S6. Comparison of mean (Std. Dev.) Mn concentrations at Site A as analyzed by the ACMM and by ICP-MS for the same 12 sample dates.

ICP Mn, PM10, ng/m^3	ACMM Mn, PM10, ng/m^3
156.0 (112.0)	87.4 (65.3)

Table S7. Mean (Std. Dev.) PM_{10} and Mn concentrations at Site A for 73 hours of coincidental ACMM and BAM data.

	Site A PM_{10} (µg/m^3)	Site A Mn (ng/m^3)	Traffic Count (vehicles per hour)
Average	175 (145)	182 (154)	6.65 (5.22)

Table S8. ACMM HAP Metals Correlations[1] with BAM PM_{10} results (n = 177).

	Cr	Mn	Ni	As	Se
Spearman r	0.852	0.855	0.835	0.506	-0.053
p value	<0.001	<0.001	<0.001	<0.001	0.481

[1]HAP metals with over 48% non-detects were not included in the correlation calculations.

Table S9. Summary of HAP metals measured with the ACMM at Site A (n = 710).

HAP metal	ACMM Median[1] Concentration, ng/m^3	ACMM Detection Limit (60 min), ng/m^3 [5]
Cr	1.04	0.12
Mn	15.1	0.14
Co	0	0.14
Ni	0.09	0.10
As	1.22	0.063
Se	0.15	0.081
Cd	0	2.5
Sb	0	5.2
Hg	0	0.12
Pb	0	0.13
Be	Not analyzed[2]	

[1] The ACMM metal concentration distributions are neither normal nor lognormal.
[2] The ACMM cannot measure some of the lighter elements, including Be.

Table S10. Mean proportions (Std. Dev.) of coarse PM manganese mass to coarse PM total mass at Sites A and B and ratio of the Site A mean Mn proportion relative to the Site B Mn mean proportion (n = 8).

Site A Mn mass/PM mass (μg/mg)	Site B Mn mass/PM mass (μg/mg)	Ratio
1.24 (0.34)	1.44 (0.34)	0.85

Table S11. Pairwise Spearman Correlations of Metals Results (Bulk Road Samples and Airborne PM Samples)

Sample 1	Sample 2	n	Correlation	p-Value
log ACMM (air)	log ICP-MS (road)	13	0.75	0.007
log ICP-MS (air)	log ICP-MS (road)	13	0.92	<0.001
log ICP-MS (air)	log ACMM (air)	13	0.87	<0.001

Figures

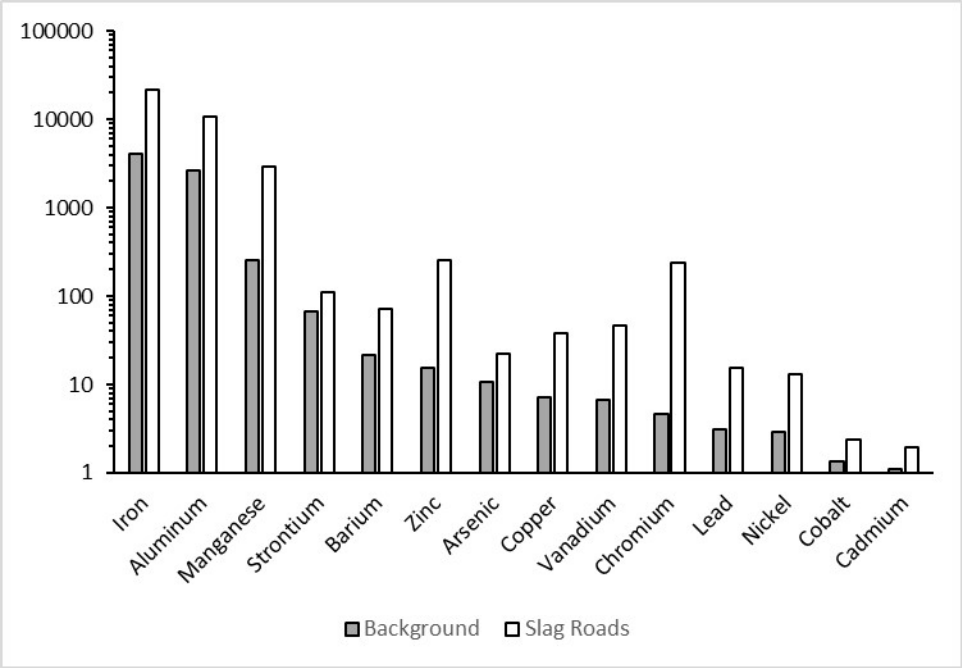

Figure S1. Average metals concentrations for 2 background sites relative to 8 sites near slag road.

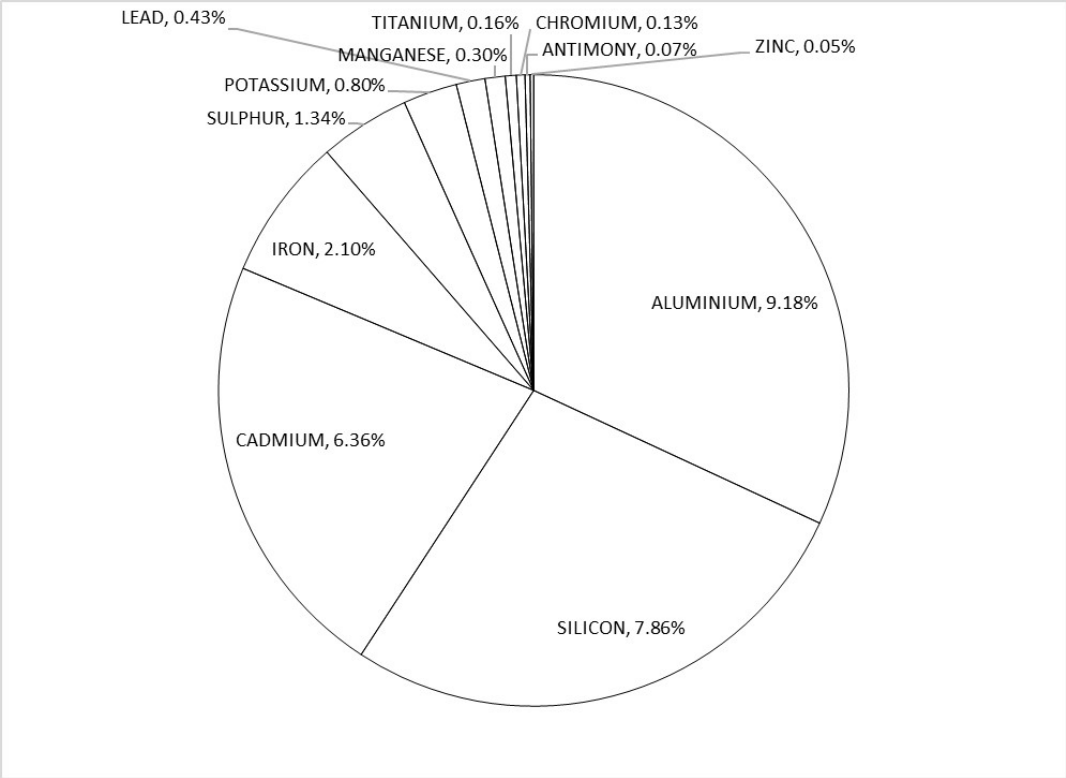

Figure S2. Distribution of average metal concentrations from the ACMM analyses in the PM_{10} fraction of the PM from Site A (n = 709). Calcium, contributing 67% of the total, was excluded from this figure.

References

1. EPA, *Method 3051A, Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils*, U.S.E.P. Agency, Editor. 2007.
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4. White, K., *Personal Communication*, J. Kacer, Editor. March 3, 2022.
5. Cooper Environmental, *Xact® 625i Multi-Metals Monitoring System Specification Sheet*. 2016, Cooper Environmental.